

UNIVERSIDAD POLITÉCNICA DE MADRID
Escuela Técnica Superior de Ingenieros Industriales



**Sustainable hydrothermal processing of
hybrid cellulose nanomaterials for
electrochemical and environmental
applications**

DOCTORAL THESIS

Submitted for the degree of Doctor by:

Manuel Prieto Lobato

M. Sc. in Energy Engineering

Madrid, 2025



UNIVERSIDAD POLITÉCNICA DE MADRID
Escuela Técnica Superior de Ingenieros Industriales

**Doctoral Degree in Environmental, Chemical and Materials
Engineering**

**Sustainable hydrothermal processing of
hybrid cellulose nanomaterials for
electrochemical and environmental
applications**

DOCTORAL THESIS

Submitted for the degree of Doctor by:

Manuel Prieto Lobato

M. Sc. in Energy Engineering

Under the supervision of:

Dr. Peter S. Shuttleworth

Dr. Mohammed Naffakh Cherradi-Hadi

Madrid, 2025

Title: Sustainable hydrothermal processing of hybrid cellulose nanomaterials for electrochemical and environmental applications

Author: Manuel Prieto Lobato

Doctoral Programme: Environmental, Chemical and Materials Engineering

Thesis Supervision:

Dr. Peter S. Shuttleworth, Tenured Scientist, Instituto de Ciencia y Tecnología de Polímeros, Consejo Superior de Investigaciones Científicas (Director)

Dr. Mohammed Naffakh Cherradi-Hadi, Full Professor, Escuela Técnica Superior de Ingenieros Industriales, Universidad Politécnica de Madrid (Director)

External Reviewers:

Thesis Defence Committee:

Thesis Defence Date:

This thesis has been partially funded by: NextGeneration EU via SusPlast; CSIC (IMOVE 23076); FEDER/Ministerio de Ciencia, Innovación y Universidades-Agencia Estatal de Investigación (MAT2017-84691-P & Project SPoNaFun/PID2020-117573GB-I00); Subprograma Estatal de Incorporación (IED2019-001134-I); Consejería de Educación e Investigación de la Comunidad de Madrid y del Fondo Social Europeo (PEJD-2019-PRE/IND-16080).

This thesis was undertaken at the **Department of Polymer Physics, Elastomers and Energy Applications (FISPOL)** of the **Institute of Polymer Science and Technology** of the **Spanish National Research Council (ICTP-CSIC)**.



*“Knowledge, like air, is vital to life.
Like air, no one should be denied it”*

Alan Moore

Acknowledgements

This thesis is the culmination of several years of hard work. However, this journey did not begin with my PhD, but a few years earlier, when I first joined the Polymer Physics group during my undergraduate internship. For that opportunity, I am grateful to my supervisor, Dr. Peter Shuttleworth, for taking in an unexperienced student and showing the patience and enthusiasm to introduce me to research, laboratory work, and experimental science. Thank you for trusting me, for allowing me to carry my own work, make mistakes and learn from them—and for all the nights and weekends spent reviewing this thesis.

I would also like to thank Dr. Mohammed Naffakh, co-Director of this thesis, for giving me the opportunity to pursue this PhD. Thank you for always being available to support me throughout the process, and for providing the calm and perspective I needed to complete this work.

I gratefully acknowledge the institutions that provided the funding necessary to carry out this research. I thank the *Consejería de Educación e Investigación de la Comunidad de Madrid y del Fondo Social Europeo* (PEJD-2019-PRE/IND-16080) for a predoctoral contract at ETSII-UPM. I also acknowledge the *Ministerio de Ciencia, Innovación y Universidades-Agencia Estatal de Investigación* for national projects funding (MAT2017-84691-P & PID2020-117573GB-I00) and CSIC-SUSPlast for supporting my predoctoral contract. Additionally, I am grateful to the French Embassy in Spain and CSIC-IMOVE grants (IMOVE 23076) for funding my research stays in Montpellier, France.

During these years at the Institute of Polymer Science and Technology in the Spanish National Research Council (ICTP-CSIC), I have had the privilege of working alongside wonderful people, without whom this thesis wouldn't have been possible. First, I would like to thank the senior researchers in our group—Gary, Marian, Horacio and Araceli—for welcoming me from day one and selflessly sharing your time and expertise. Special thanks to Gary for all the time you spent teaching me about FTIR and for all your effort in seeking funding opportunities.

A heartfelt thank you to all the students and researchers with whom I had the chance to share time in our office. First, thanks to Susana, you were the first to believe I would pursue a PhD—even before I did. Thank you very much for showing me the kind of researcher I aspire to be. Paula, you had to deal with my worries

more than anyone else and always found a way to cheer me up, thank you very much. Minghao, thank you very much for celebrating every success with me and encouraging me after every setback. You truly understand the struggles of research better than anyone else and you have become a real friend. María, your motivation, discipline and care in science is inspiring, thank you for always lifting the mood, even in the most difficult times. And Vitaliy, thank you for being an endless source of knowledge and good energy. It's always enlightening to share time with you. All of you made ICTP not only a workplace, but a safe and welcoming space.

Beyond the FISPOL group, I would also like to thank many others at CSIC. Special thanks to Isa for all the dedication you put in work, for all the knowledge you shared with me and all our refreshing conversations. Also, I want to thank Alberto and Manuel, you have been incredibly kind to me and it's a pleasure to speak to you, thank you for always offering a creative solution—and a smile. I'm also grateful to the people in the characterisation service team that have been incredibly helpful—especially Laura, David, Patricia, Esperanza and Pedro.

I extend my thanks to Dr. Enrique Morales, my Master's supervisor and guide through my thesis. I can't explain how much I learned from you, and I truly admire your dedication to work. Special thanks to Dr. Leoncio Garrido for allowing me to use—and teaching me to operate—the electrospinning equipment and Dr. Carmen del Río for her support using the electrochemical station.

During my PhD, I had the opportunity to go on two international research stays at the Institut Charles Gerhard Montpellier, in the Centre National de la Recherche Scientifique (ICGM-CNRS). I am especially grateful to Dr. Nicolas Brun, my supervisor in France, for welcoming me into the Porous and Hybrid Materials group, for your time and dedication in teaching me how to use equipments and analyse data, and for your tireless efforts to resolve any inconvenience that could come up during the research. Thank you very much for your constant support.

I also want to thank all the students, researchers and personnel that made my stay in Montpellier so enjoyable—Léa, Ali, Lilia, Shilpa, Soha, Inderdip, Anu, Rafa, Christophe and Rodrigo—thank you for reminding me that research stays are about more than science.

Outside the research world, I've been incredibly lucky to be surrounded by people who genuinely care for me and have supported me through every stage of my life. First, to my childhood friends—Kike, Victor, Miguel, Nava, Dani, Luis, Pedro—I

couldn't have asked for a better group to grow up with, to share so many memories with, and to continue growing alongside every day. Even in the most stressful times you have always been there to make me crack a smile and forget about my worries—and for that, I'll always be grateful.

Then, to those who came into my life and never left: Andrea, Jordi, Sara, Natalia, Mario and Alex, all of you became a meaningful part of my life and I couldn't have completed this journey with your help. To all of you, thank you for being such an amazing support and make this path not only possible, but lighter and brighter.

Finally, the most important thank you goes to my family. To my sister, Ali, you've always set the standards for everything I aspire to accomplish. Like any older sister, you've been both my role model and, at times, my worst enemy, but I know I would have come this far without your support, understanding and inspiration. Thank you for always challenging me to grow and be the best version of myself.

And of course, to my parents: everything I am today is because of you. All your dedication, sacrifices and love shaped not only my education but also the person I have become. Thank you for your unconditional support, for always believing in me and for encouraging me to pursue my dreams no matter the obstacles.

Abstract

As technological advances raise living standards around the globe, the world's population continues to grow—driving energy demand to levels that conventional power sources can no longer satisfy. These sources are not only limited, but also environmentally harmful, making renewable power the only sustainable solution to cover this demand. However, to fully harness the potential of renewable energy, it is crucial to develop reliable, high-performing energy storage technologies that effectively address the intermittent nature of these energy sources.

Furthermore, increased industrial production has intensified environmental pollution. In particular, synthetic dyes, when released into water courses, are responsible for the persistent contamination of millions of litres of water. Unfortunately, conventional water treatment methods are unable to effectively remove these pollutants completely, resulting in severe environmental damage that presents a serious threat to wildlife, ecosystems and human health.

This doctoral thesis aims to effectively tackle these global challenges through the development of sustainable, multifunctional biopolymeric materials. Specifically, biomass-derived activated carbons (ACs) were synthesised via hydrothermal carbonisation (HTC), an environmentally friendly, energy-efficient alternative to conventional carbonisation. These materials were further modified through the addition of layered transition metal dichalcogenides (TMDCs)—specifically, 2D-WS₂ nanosheets, to add functionality and improve conductivity.

For energy storage applications, these sustainable ACs (and their WS₂-doped counterparts) were assessed as electrodes for electrochemical capacitors, measuring their capacitance, power density and energy density. Remarkably, these materials yielded capacitance values exceeding 270 F/g and power densities close to 5000 W/kg—performance levels that, to date, few biomass-based materials have achieved.

Moreover, their applicability as electrocatalysts for the Oxygen Reduction Reaction (ORR)—a crucial reaction in fuel cell energy storage was explored. Parameters such as the number of transferred electrons and the concentration of byproducts (specifically, the harmful HO₂⁻ ion) were evaluated. Overall, the synthesised ACs displayed competitive results compared to commercial platinum-based catalysts, highlighting the electrocatalytic potential of these materials.

Simultaneously, a polymeric scaffold was developed by electrospinning a poly-L-lactic acid (PLLA) solution, which was further reinforced with WS₂ nanosheets to enhance mechanical properties. Subsequently, AC was integrated into the polymeric matrix, yielding a hybrid material with excellent surface area, mechanical properties and adsorption capacity.

This hybrid adsorbent was further tested for wastewater remediation, specifically for the adsorption of four dyes: two cationic (Methylene Blue, MB, and Rhodamine B, RB) and two anionic dyes (Methyl Orange, MO, and Congo Red, CR). The adsorption mechanism was studied through kinetic modelling and adsorption isotherms. Notably, the hybrid PLLA-WS₂-AC adsorbent exhibited excellent adsorption performance with near-complete removal of the dyes, some of which were fully adsorbed in less than 15 minutes.

Overall, the sustainably derived materials developed in this thesis exhibit impressive potential to tackle the energy and environmental challenges that will shape our future. Their exceptional performance underscores the importance of innovative, green solutions that pave the way for future advancements in sustainable development and green technology.

Resumen

A medida que los avances tecnológicos mejoran la calidad de vida, la población mundial continúa creciendo, conllevando unos niveles de demanda energética que las fuentes convencionales ya no pueden satisfacer. Estas fuentes no solo son limitadas, sino que resultan perjudiciales para el medio ambiente, lo que convierte a la energía renovable en la única solución sostenible para cubrir esta demanda. Sin embargo, para aprovechar plenamente el potencial de la energía renovable, es fundamental desarrollar tecnologías de almacenamiento energético eficientes y seguras que permitan abordar los problemas derivados de la naturaleza intermitente de estas fuentes.

Al mismo tiempo, el incremento en la producción industrial ha intensificado la contaminación ambiental. En particular, las tintas sintéticas, al ser vertidas en las masas de agua, contribuyen a la contaminación persistente de toneladas de agua. Por desgracia, los métodos convencionales de tratamiento de aguas no son capaces de eliminar eficazmente la totalidad de estos contaminantes, lo que conlleva graves daños medioambientales que presentan una seria amenaza a la fauna, los ecosistemas y la salud humana.

Esta tesis tiene como objetivo abordar de forma efectiva estos desafíos globales mediante el desarrollo de materiales biopoliméricos multifuncionales y sostenibles. Concretamente, se sintetizaron carbones activados (ACs) derivados de biomasa mediante carbonización hidrotermal (HTC), una alternativa sostenible más eficiente energéticamente que la carbonización convencional. Estos materiales se modificaron posteriormente con la adición de dicalcogenuros de metales de transición (TMDCs), específicamente nanoláminas de 2D-WS₂, para añadir funcionalidad y mejorar su conductividad.

Para las aplicaciones de almacenamiento de energía, estos ACs sostenibles (y sus versiones dopadas con WS₂) se utilizaron como electrodos en condensadores electroquímicos, evaluando su capacitancia, densidad de potencia y densidad energética. Estos materiales alcanzaron valores de capacitancia superiores a 270 F/g y densidades de potencia cercanas a 5000 W/kg—niveles de rendimiento que, hasta la fecha, pocos materiales basados en biomasa han alcanzado.

Además, se exploró su aplicabilidad como electrocatalizadores para la reacción de reducción de oxígeno (ORR), una reacción crucial en las células de combustible. Se

evaluaron parámetros como el número de electrones transferidos y la concentración de subproductos (en concreto el pernicioso ion $\text{HO}_2^\cdot$). En general, los ACs sintetizados exhibieron resultados competitivos comparados con catalizadores comerciales basados en platino, lo que pone en valor el potencial electrocatalítico de estos materiales.

Paralelamente, se desarrolló una matriz polimérica mediante el electrohilado de una disolución de ácido poli-L-láctico (PLLA), que fue reforzado con nanoláminas de WS_2 para mejorar sus propiedades mecánicas. Posteriormente, se añadió AC a la matriz polimérica, dando lugar a un material híbrido con excelente área superficial, propiedades mecánicas y capacidad de adsorción.

Este adsorbente híbrido se utilizó para la descontaminación de aguas, específicamente para la adsorción de cuatro tintas: dos catiónicas (Azul de Metileno, y Rodamina B) y dos aniónicas (Naranja de Metilo y Rojo Congo). El mecanismo de adsorción se estudió mediante modelos cinéticos e isotermas de adsorción. Cabe destacar que el adsorbente híbrido PLLA- WS_2 -AC mostró una excelente capacidad de adsorción, con una eliminación casi completa de las tintas, algunas de las cuales se eliminaron completamente en menos de 15 minutos.

En conjunto, los materiales de origen sostenible desarrollados en esta tesis muestran un excelente potencial para abordar los desafíos energéticos y medioambientales que marcarán nuestro futuro. Su rendimiento sobresaliente recalca la importancia de soluciones innovadoras y ecológicas que marquen el camino hacia futuros avances en desarrollo sostenible y tecnología verde.

Table of contents

<i>Acknowledgements</i>	v
<i>Abstract</i>	ix
<i>Resumen</i>	xi
<i>List of Figures</i>	xvii
<i>List of Tables</i>	xxii
<i>List of QRs</i>	xxiv
1. Introduction	1
1.1. Global energy picture: Current situation, challenges and opportunities	1
1.1.1. General energy outlook	1
1.1.2. Energy storage technologies	4
1.1.2.1. Supercapacitors	6
1.1.2.2. Fuel cells	10
1.2. Environmental pollution. Dyes: risks, treatments and novel solutions	15
1.2.1. Environmental impact of dyes	15
1.2.2. Current remediation methods	16
1.2.2.1. Dye remediation through adsorption	18
1.3. Advanced materials for energy and environmental applications	22
1.3.1. Sustainable carbons from biomass	22
1.3.1.1. Cellulose	22
1.3.1.2. Hydrothermal carbonisation	23
1.3.2. Biopolymers	32
1.3.2.1. Poly-L-lactic Acid	34
1.3.2.2. Electrospinning	36
1.3.3. Transition metal dichalcogenides (TMDCs)	38
1.3.3.1. Tungsten disulphide	41
1.3.4. TMDC-Polymer nanocomposites strategies	42
2. Objectives	43
3. Materials and experimental techniques	45
3.1. Materials	45
3.1.1. Cellulose	45
3.1.2. Albumin	45

3.1.3.	Poly-L-lactic Acid	45
3.1.4.	Tungsten disulphide	45
3.2.	Characterisation techniques.....	46
3.2.1.	Gas sorption porosimetry.....	46
3.2.2.	Scanning electron microscopy (SEM).....	48
3.2.3.	Transmission electron microscopy (TEM)	48
3.2.4.	Fourier-transform infrared spectroscopy (FTIR)	49
3.2.5.	Raman spectroscopy	50
3.2.6.	Elemental analysis.....	51
3.2.7.	Energy dispersive X-Ray spectroscopy (EDX)	52
3.2.8.	X-Ray photoelectron spectroscopy (XPS)	52
3.2.9.	Thermogravimetric analysis (TGA)	53
3.2.10.	Differential scanning calorimetry (DSC)	54
3.2.11.	Tensile tests.....	54
3.2.12.	Electrical conductivity	55
3.2.13.	Electrochemical characterisation.....	56
3.2.13.1.	Cyclic voltammetry (supercapacitors).....	56
3.2.13.2.	Galvanostatic cycling	57
3.2.13.3.	Electrical impedance spectroscopy (EIS)	58
3.2.14.	Fuel cell characterisation	59
3.2.14.1.	Cyclic voltammetry (Rotating Ring Disk Electrode).....	59
3.2.15.	Ultraviolet-visible spectroscopy (UV-Vis).....	62
4.	Activated carbon from cellulose	65
4.1.	Introduction	65
4.2.	Aim of this chapter	66
4.3.	Synthesis procedure	67
4.3.1.	Albumin addition	68
4.3.2.	Tungsten disulphide addition.....	69
4.3.3.	Assembly of the supercapacitor electrochemical cells	71
4.3.4.	Preparation of inks for the ORR electrocatalytic application	71
4.4.	Results and discussion.....	73
4.4.1.	Carbon properties and morphology.....	73
4.4.1.1.	Structural and morphological properties.....	73
4.4.1.2.	Elemental and atomic composition	89
4.4.1.3.	Thermal and electrical properties	93
4.4.2.	Supercapacitor application	99
4.4.2.1.	Cyclic voltammetry	99

4.4.2.2. Galvanostatic cycling	103
4.4.2.3. Electrical impedance spectroscopy	107
4.4.2.4. Post-mortem analysis.....	108
4.4.3. Electrocatalytic application for ORR	113
4.4.3.1. Rotating Ring Disk Electrode (RRDE).....	113
4.5. Conclusions	117
5. Poly-L-lactic acid hybrid materials.....	119
5.1. Introduction	119
5.2. Aim of this chapter	120
5.3. Experimental procedure	121
5.3.1. Preparation of poly-L-lactic acid scaffold	121
5.3.1.1. PLLA films.....	121
5.3.1.2. PLLA beads	122
5.3.1.3. PLLA pills	123
5.3.1.4. PLLA fibres.....	124
5.3.2. Development of the electrospinning method	124
5.3.2.1. Optimisation of electrospinning parameters through testing.....	124
5.3.2.2. Optimisation of electrospinning parameters using SEM	128
5.4. Results and discussion	130
5.4.1. Fibre characterisation.....	130
5.4.1.1. Scanning electron microscopy	130
5.4.1.2. Thermogravimetric analysis.....	133
5.4.1.3. Differential scanning calorimetry	136
5.4.1.4. Tensile tests.....	142
5.4.2. Fibre application for dye adsorption	143
5.4.2.1. Adsorption kinetics	144
5.4.2.2. Adsorption isotherms.....	149
5.5. Conclusions	152
6. General conclusions and future work	153
6.1. General conclusions of the thesis	153
6.2. Limitations of the work and future research	155
References.....	157
Annexes.....	199
Annex 1: Enthalpy calculations	199
Annex 2: SEM and TEM micrographs of the remaining carbons	201

Annex 3: Electrical conductivity calculations	202
Annex 4: Cyclic voltammetry results of the prepared ACs	204
Annex 5: Determination of specific capacitance through cyclic voltammetry experiments.....	205
Annex 6: Determination of electrochemical parameters through galvanostatic cycling.....	207
Annex 7: Determination of ring's collection efficiency	211
Annex 8: Calculation example of RRDE parameters.....	213
Annex 9: SEM micrographs of the prepared fibres.....	214
Annex 10: Calculation of AC & WS ₂ concentrations via TGA.....	216
Annex 11: Determination of the nucleating activity using the Dobрева model.....	218
Annex 12: Calculation of the crystallisation activation energy using Kissinger model.....	220
Annex 13: Calibration curves of dyes	221
Annex 14: Determination of adsorption kinetics	224
Annex 15: Determination of adsorption isotherms	229
Publications	235
Articles published in indexed journals	235
Presentations at national and international congresses	236
Oral communications.....	236
Poster communications.....	237

List of Figures

Figure 1.1: Climate projections for the next 75 years according to each RCP [8].	2
Figure 1.2: Projected annual investment in clean energy and fossil fuels according to the STEPS and NZE scenarios [1].	2
Figure 1.3: International Energy Agency's summary of world energy investment flows over the last decade for a) clean energy and b) fossil fuels (data obtained from [9]).	3
Figure 1.4: Projected CO ₂ emissions according to different scenarios through the 2010-2050 period [1].	4
Figure 1.5: Ragone plot containing the main electrochemical energy storage systems compared with a combustion engine [21].	6
Figure 1.6: Summary of the construction of different types of capacitors [22].	7
Figure 1.7: Electrical double layer schematic [30].	9
Figure 1.8: Schematic of a typical fuel cell with its main architecture and chemicals [46].	11
Figure 1.9: Schematic of HTC precursors, primary products and main applications of the produced hydrochar [172].	24
Figure 1.10: A mechanistic overview of cellulose and hemicellulose breakdown, and the formation of humin and hydrochar during HTC [172].	27
Figure 1.11: Global bioplastic production for the year 2024, divided into biodegradable and non-biodegradable polymers [254].	34
Figure 1.12: Electrospinning products as a function of viscosity and polymer concentration [298].	37
Figure 2.1: Schematic of the proposed objectives for the thesis.	44
Figure 3.1: Classification of adsorption isotherms according to IUPAC [383].	46
Figure 3.2: In-house manufactured 4-probe conductivity sample holder used to test the prepared samples.	56
Figure 3.3: Types of voltammograms according to the energy storage mechanism (modified from [396]).	56
Figure 3.4: Charge-discharge curves of a carbon-based symmetrical supercapacitor [307].	57
Figure 3.5: Schematic of a typical Nyquist plot for a supercapacitor material [398].	58
Figure 3.6: Schematic representation of typical RRDE and RDE electrodes [404].	60
Figure 4.1: Obtained cellulose hydrochar (C200) before and after drying.	67
Figure 4.2: Residue after activation without (left) and with (right) pre-carbonisation step.	67
Figure 4.3: Image of the resulting activated carbon derived from cellulose.	68

Figure 4.4: Flow diagram representing the synthesis methodology, with the nomenclature for each sample.	69
Figure 4.5: Components and assembly of the EDLC electrochemical cell.	71
Figure 4.6: Detail of the electrodes used for the ORR tests.	72
Figure 4.7: Nitrogen sorption isotherms for different C300-to-KOH ratios.....	73
Figure 4.8: Changes in the precursor structure during the different stages of the AC (adapted from [419-421]).....	74
Figure 4.9: Nitrogen sorption isotherms of the final carbons.	76
Figure 4.10: Porous structures according to the hysteresis loop type associated to Type IV a) isotherms (from [422]).....	76
Figure 4.11: Total pore volume of the final ACs, highlighting the contribution of micropore volume, and volume of pore with a diameter >2nm.	78
Figure 4.12: CO ₂ sorption isotherms of the final ACs at temperatures of 273 K, 298 K and 323 K.	79
Figure 4.13: Results of the NLDFT method to obtain a) the PSD of the final ACs and b) cumulative pore volume of the ACs.	80
Figure 4.14: Enthalpy of adsorption of the prepared ACs versus Q _e (CO ₂).	81
Figure 4.15: SEM micrographs of a) Cellulose; b) C300; c) C 1-1.5; d) C 1-4; e) CA 1-4 and f) C 1-4 W. The main images are at a resolution of x1k, and the insert images at x20k or x40k.	83
Figure 4.16: FTIR spectra of cellulose, C200 and C300.	84
Figure 4.17: FTIR spectra of albumin, CA200 and CA300.....	85
Figure 4.18: Raman spectra of the C 1-1.5 set of samples.	86
Figure 4.19: Raman spectra of the C 1-4 set of samples.	86
Figure 4.20: Example of deconvolution of the AC Raman spectrum (C 1-4 W), with peak identification labels presented.	87
Figure 4.21: Carbon structure and changes with temperature increase (for soft carbons) [438]. ..	88
Figure 4.22: D/G ratios of all the analysed samples, a) calculated from the ratio of area and b) from height.	89
Figure 4.23: Example of EDX spectrum of the developed AC (CA 1-4 W).	91
Figure 4.24: XPS deconvolution of a) the N 1s spectrum of CA 1-4 and b) the S 2p spectrum of C 1-4 W.	92
Figure 4.25: a) TGA of C300 (red) and C300-HTC (black) under N ₂ atmosphere and b) DTG of the same samples.	94
Figure 4.26: TGA and DTG of the C 1-1.5 (a,c) and C 1-4 (b,d) set of samples under N ₂ atmosphere.	95

Figure 4.27: TGA and DTG of the C 1-1.5 (a,c) and C 1-4 (b,d) set of samples under oxidative atmosphere.	97
Figure 4.28: Conductivity of the prepared ACs and their derivatives.	98
Figure 4.29: a) Cyclic voltammograms, and; b) Specific capacitance vs voltage of the C 1-4 electrode.....	100
Figure 4.30: Capacitance variation of the prepared ACs and their derivatives with increasing scan rate from 1 to 100 mV/s.....	101
Figure 4.31: a) Galvanostatic charge-discharge cycles for the C 1-4 electrode sample at constant currents of 5 mA (black) and 30 mA (red); b) Galvanostatic curves at different currents of one full cycle taken from the 2 nd charge-discharge cycle.....	103
Figure 4.32: a) Specific capacitances of all ACs, calculated from galvanostatic tests; b) Maximum specific capacitances (measured at 1 mA) of all samples.	104
Figure 4.33: Ragone plot showing the energy density versus power density of the prepared ACs supercapacitors electrodes.....	106
Figure 4.34: ESI Nyquist plots of the samples with highest capacitances (C 1-1.5, CA 1-1.5, C 1-4 and CA 1-4).....	107
Figure 4.35: SEM micrographs of a) C 1-4, b) CA 1-4, c) C 1-4 W and d) CA 1-4 W after electrochemical testing.	109
Figure 4.36: a) Nitrogen adsorption isotherms and b) micropore and total pore volume comparison of the C 1-4 set of samples before and after electrochemical treatment.	109
Figure 4.37: PSD of the C 1-4 set of samples before and after electrochemical treatment.....	110
Figure 4.38: Cumulative pore volume of the C 1-4 set of samples before and after electrochemical treatment.....	110
Figure 4.39: Variation of the D/G area ratio for the C 1-4 set of samples before and after electrochemical testing.	113
Figure 4.40: Number of electrons transferred by each catalyst in the oxygen reduction reaction.	114
Figure 4.41: Amount of HO ₂ [•] produced in presence of each catalyst during the oxygen reduction reaction.	114
Figure 5.1: a) Pressed PLLA-AC (10% w/w) film, and b) SEM micrograph showing the cross-section of the cryofractured end of the same film.	122
Figure 5.2: Molecular structure of Methylene Blue made using ChemDraw software.	122
Figure 5.3: Prepared PLLA (left) and PLLA-AC (25% w/w) beads (right).	123
Figure 5.4: Final PLLA-AC (20% w/w) pills prepared at 10 tonnes.	124
Figure 5.5: Electrospun PLLA-W fibre mat after 30 minutes.....	126
Figure 5.6: PLLA-AC electrospun material with an AC content of a) 2% w/w and b) 5% w/w.	127

Figure 5.7: Final PLLA-W-AC fibrous structure.	128
Figure 5.8: SEM micrographs of the a) PLLA; b) PLLA-W; c) PLLA-AC and d) PLLA-W-AC prepared electrospun fibres.	130
Figure 5.9: Breath figure mechanism of pore formation on the fibre surface [510].	132
Figure 5.10: SEM micrographs of WS ₂ nanosheets dispersed in ethanol at x20k (inserted image) and x60k resolution.	133
Figure 5.11: a) TGA and b) DTG curves of hybrid PLLA composites under N ₂ atmosphere.	134
Figure 5.12: a) TGA and b) DTG curves of hybrid PLLA composites under air atmosphere.	135
Figure 5.13: An example of DSC for the PLLA-AC-W composite fibre. The sample was heated and cooled according to the following program: heating (10°C/min for all runs), 5-minute isothermal, cooling (2°C/min for this run) and heating again (10°C/min, for all runs).	136
Figure 5.14: DSC cooling thermograms of a) PLLA, b) PLLA-W and c) PLLA-W-AC fibres.	138
Figure 5.15: Variation of a,c) crystallisation temperature and b,d) crystallinity with cooling rate and particle loading, respectively.	139
Figure 5.16: DSC heating thermograms of a) PLLA, b) PLLA-W and c) PLLA-W-AC hybrid composites after cooling from the melt at the indicated cooling rates.	141
Figure 5.17: Young's modulus of the fibres produces with different parameters.	142
Figure 5.18: Molecular structure of a) Rhodamine B, b) Methyl Orange and c) Congo Red made using ChemDraw software.	144
Figure 5.19: Dye removal at different times using PLLA-W-AC.	145
Figure 5.20: Removal kinetics of a) Congo Red; b) Methyl Orange; c) Methylene Blue and d) Rhodamine B at 298 K, 308 K and 318 K.	148

Annexed Figures

Figure A1: Comparison between actual isotherms and polynomial fit for C 1-4.	200
Figure A2: SEM images of a) CA 1-1.5; b) C 1-1.5 W; c) CA 1-1.5 W and d) CA 1-4 W.	201
Figure A3: Resistance of C 1-4 derived samples.	202
Figure A4: Voltammograms of the C 1-4 set of samples at a scan speed of 2 mV/s.	204
Figure A5: Voltammograms of the C 1-4 set of samples at a scan speed of 40 mV/s.	204
Figure A6: Integration of the discharge curve of C 1-4 at 40 mV/s.	205
Figure A7: Capacitances of C 1-4 at different scan rates.	206
Figure A8: Parts of a voltage vs. time graph representing charge and discharge cycles.	207
Figure A9: Experimental galvanostatic curve of C 1-4 at 40 mA.	208
Figure A10: Geometrical RRDE electrode values.	211
Figure A11: Ring and disk currents at different rotation speeds.	212

Figure A12: Ring and disk currents of the Pt/C electrode.....	213
Figure A13: SEM micrographs of PLLA 4%, 8% and 12% w/v and at at needle-to-collector distances of 12 and 16 cm are shown.....	214
Figure A14: SEM micrographs of PLLA and PLLA-W fibres produced at electrospinning times of 15 and 120 minutes.....	215
Figure A15: TGA and DTG of WS ₂ nanosheets under N ₂ atmosphere.....	216
Figure A16: Dobrev-Gutzow linear fit of the PLLA-W-AC crystallisation process carried out at different cooling rates.....	218
Figure A17: Kissinger plot for PLLA-W-AC crystallisation.....	220
Figure A18: UV-Vis spectra of Congo Red at different aqueous solution concentrations.....	221
Figure A19: UV-Vis spectra of Methyl Orange at different aqueous solution concentrations.....	222
Figure A20: Linear fitting for the different Methyl Orange concentrations.....	222
Figure A21: UV-Vis spectra of a) Methylene Blue and B) Rhodamine B at different aqueous solution concentrations.....	223
Figure A22: Pseudo 1 st order kinetic fit for Methyl Orange adsorption.....	225
Figure A23: Pseudo 2 nd order kinetic fit for Methyl Orange adsorption.....	226
Figure A24: Intra particle diffusion kinetic fit for Methyl Orange adsorption.....	227
Figure A25: Elovich kinetic fit for Methyl Orange adsorption.....	227
Figure A26: Langmuir isotherm fit for Methyl Orange adsorption.....	230
Figure A27: Freundlich isotherm fit for Methyl Orange adsorption.....	231
Figure A28: Temkin isotherm fit for Methyl Orange adsorption.....	231
Figure A29: Dubinin-Radushkevich isotherm fit for Methyl Orange adsorption.....	232

List of Tables

Table 1.1: Established thresholds for dye effluents discharge into waters [77].	18
Table 1.2: Main adsorption parameters [77].	20
Table 1.3: Examples of TMDC+HTC prepared carbon combinations for batteries.	40
Table 1.4: Examples of TMDC+HTC prepared carbon combinations for batteries and supercapacitor electrodes.	40
Table 4.1: Product yields and nitrogen content at different cellulose to albumin ratios.	69
Table 4.2: Yields for the total carbon preparation process.	71
Table 4.3: Textural properties of carbons with different KOH dosages.	75
Table 4.4: Textural properties of the final carbons calculated from their N ₂ sorption isotherms.	77
Table 4.5: Raman deconvolution results for the C 1-1.5 and C1-4 series of samples.	87
Table 4.6: Atomic composition from elemental analysis and EDX testing.	90
Table 4.7: Details of functional group contribution from XPS fitting of the N 1s spectrum and S 2p spectrum of CA 1-4 and C 1-4 W, respectively.	92
Table 4.8: TGA results of the HTC pre-treated and untreated cellulose after preliminary heating to 300 °C under inert atmosphere.	94
Table 4.9: TGA results of the final activated carbons under inert atmosphere.	95
Table 4.10: TGA results of the final ACs under oxidative atmospheric conditions.	97
Table 4.11: Specific capacitance retention (stability) of the prepared ACs at different currents.	105
Table 4.12: Comparison of different biomass-derived, HTC processed ACs for use as electrodes for symmetrical supercapacitors.	106
Table 4.13: Charge transfer resistance values for all developed carbons.	108
Table 4.14: Textural properties of the C 1-4 set of ACs after electrochemical testing.	110
Table 4.15: Raman deconvolution results.	112
Table 4.16: Summary of electrocatalytic parameters of the developed ACs compared with the commercial Pt/C catalyst and glassy carbon pristine electrode.	116
Table 5.1: Thermal and electrical properties of the selected electrospinning solvents.	125
Table 5.2: Experimental electrospinning parameters.	128
Table 5.3: Final optimised electrospinning parameters.	129
Table 5.4: DSC results from the cooling and second heating processes of PLLA, PLLA-W and PLLA-W-AC.	137

Table 5.5: Kinetic parameters for Congo Red adsorption using the PLLA-W-AC prepared samples.	146
Table 5.6: Kinetic parameters for Methyl Orange adsorption using the PLLA-W-AC prepared samples.	146
Table 5.7: Kinetic parameters for Methylene Blue adsorption using the PLLA-W-AC prepared samples.	146
Table 5.8: Kinetic parameters for Rhodamine B adsorption using the PLLA-W-AC prepared samples.	146
Table 5.9: Isotherm fitting parameters for Congo Red adsorption using the prepared PLLA-W-AC samples.	149
Table 5.10: Isotherm fitting parameters for Methyl Orange adsorption using the prepared PLLA-W-AC samples.	149
Table 5.11: Isotherm fitting parameters for Methylene Blue adsorption using the prepared PLLA-W-AC samples.	149
Table 5.12: Isotherm fitting parameters for Rhodamine B adsorption using the prepared PLLA-W-AC samples.	150
Table 5.13: Biomass-derived adsorbents and their performance compared to the developed materials presented.	151

Annexed Tables

Table A1: Enthalpy determination for C 1-4 at 0.4 mmol/g.	199
Table A2: Different enthalpies for C 1-4.	200
Table A3: Voltage and current measurements for C 1-4.	202
Table A4: Electrochemical parameters of C 1-4.	210
Table A5: Geometrical parameters for the determination of collection efficiency.	211
Table A6: Collection efficiency at different rotation speeds.	212
Table A7: Thermal stability of PLLA fibres and its individual components.	216
Table A8: Linear fitting equations for all the studied dyes.	223
Table A9: Kinetic data for Methyl Orange adsorption.	224
Table A10: Isotherm data at different starting concentrations for each dye.	229

List of QRs

QR 1: Rotovapor use for sample drying.	67
QR 2: Electrospinning process.	124
QR 3: Spray coating.	128

Annexed QRs

QR A1: TEM analysis of C 1-4 W rotation.....	201
--	-----

Abbreviations and Acronyms

2-Me-THF	2-Methyltetrahydrofuran
AC	Activated Carbon
CAGR	Compound Annual Growth Rate
CR	Congo Red
CV	Cyclic voltammetry
DCM	Dichloromethane
DHH	2,5-Dioxo-6-hydroxy hexanal
DMF	Dimethylformamide
DSC	Differential Scanning Calorimetry
DTG	Differential Thermogravimetric Analysis
EDLC	Electrical Double Layer Capacitance
EDX	Energy Dispersive X-ray Spectroscopy
EIS	Electrical Impedance Spectroscopy
ESD	Energy Storage Device
FTIR	Fourier-Transform Infrared Spectroscopy
GHG	Greenhouse Gases
HHV	High Heating Value
HMF	5-Hydroxymethyl furfural
HTC	Hydrothermal Carbonisation
IPCC	Intergovernmental Panel on Climate Change
LA	Lactic acid
MB	Methylene Blue
MO	Methyl Orange
NMP	N-methyl-2-pyrrolidone
NZE	Net Zero Emissions
ORR	Oxygen Reduction Reaction

PEM	Polymer Electrolyte Membrane/Proton Exchange Membrane
PEMFC	Polymer Electrolyte Membrane Fuel Cell
PLA	Poly Lactic Acid
PLLA	Poly-L-lactic Acid
PSD	Pore Size Distribution
PP	Polypropylene
PU	Polyurethane
PVA	Poly-vinyl alcohol
RB	Rhodamine B
RCP	Representative Concentration Pathways
R_{CT}	Charge transfer resistance
RDE	Rotating Disk Electrode
RRDE	Rotating Ring Disk Electrode
SC	Supercapacitor
SDG	Sustainable Development Goals
SEM	Scanning Electron Microscopy
STEPS	Stated Policies Scenario
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
TMDC	Transition Metal Dichalcogenides
UV-Vis	Ultraviolet-visible spectroscopy
XPS	X-Ray Photoelectron Spectroscopy

1. Introduction

1.1. Global energy picture: Current situation, challenges and opportunities

1.1.1. General energy outlook

To gain a comprehensive overview of the current world energy situation, economic, political, and environmental factors must also be considered. According to the International Energy Agency's *World Energy Outlook 2023*, the prospect remains challenging, driven by tough macroeconomic factors [1]. The main reasons for this are growing inflation, high debt levels and increasing borrowing costs, all aggravated by an ever-increasing energy demand [2, 3] and fuel price instability [4], to which geopolitical conflicts are a major contributor [5]. From an environmental perspective, global temperatures have risen on average by 1.2°C compared to pre-industrial levels, resulting in heatwaves, aggravated by greenhouse gas (GHG) emissions that haven't yet peaked, entering in direct conflict with the main goals of the COP 21 Paris agreement, which aims to limit global warming to 1.5°C and reduce GHG emissions by 43% before 2030 [6]. Furthermore, it is estimated that the energy sector contributes to about 90% of global GHG emissions, which causes more than 6 million deaths each year [1].

To quantitatively assess these issues, the Intergovernmental Panel on Climate Change (IPCC) has modelled various Representative Concentration Pathway (RCP) scenarios (see Figure 1.1). Each of these considers different climate change drivers (GHG emissions, atmospheric concentrations of air pollutants and land use), and uses them to predict four different pollution scenarios. The first is a scenario where a tight mitigation of these climate change drivers is applied (RCP 2.6), followed by two intermediate pathways (RCP 4.5 and 6.0) and a final representation of high pollution levels (RCP 8.5). All of these RCPs present climate projections for the forthcoming years (see Figure 1.1) based on environmental consequences, such as global temperature increase, rise in atmospheric CO₂ levels, ocean acidity (and its effect on aquatic ecosystems), and climatic impact factors like flooding, storms, cyclones, heatwaves and drying trends [7].

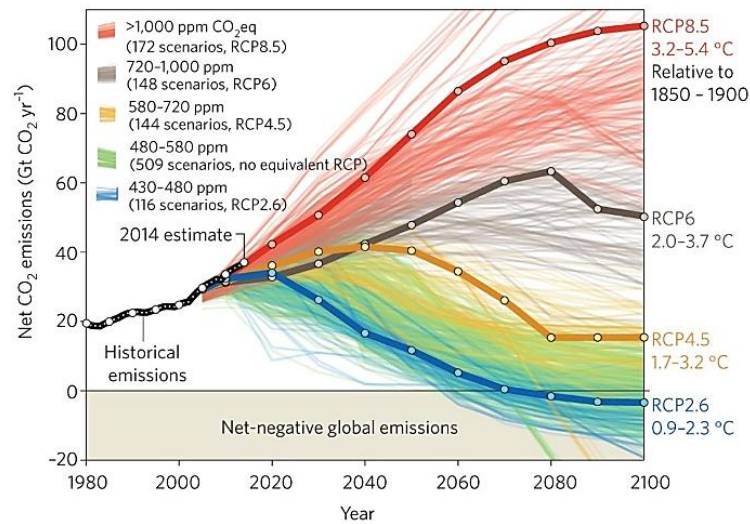


Figure 1.1: Climate projections for the next 75 years according to each RCP [8].

Despite the aforementioned data, there are still some indicators that point to a sustainable future. Only in the 2018-2023 time frame, investment in clean energy has risen by over 40% and is projected to continue this upward trend (see Figure 1.2 & Figure 1.3), with renewable energy generation expected to increase by an additional 500 GW before 2030. In addition, the share of electric vehicles sold worldwide has increased from 4% in 2020 to 20% in 2023. This tendency is a step in the right direction towards the objective of keeping global temperatures below the critical 1.5°C increase, following the COP 21 climate goals, apart from helping reduce fossil fuel use.

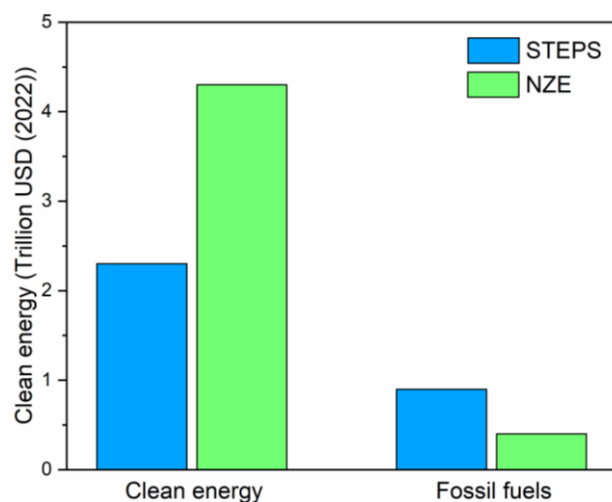


Figure 1.2: Projected annual investment in clean energy and fossil fuels according to the STEPS and NZE scenarios [1].

Furthermore, the International Energy Agency (IEA) has explored three different forecasts (STEPS, NZE and APS), each based on how successfully current and proposed environmental policies are implemented.

The Stated Policies Scenario (STEPS) includes the most recent energy, climate and industrial legislations. In this scenario, fossil fuel (coal, oil and gas) presence in the energy mix is projected to decrease to 73%, an improvement from the previously stagnated 80% level that lasted for various decades. However, despite this improvement, it is still not sufficient, with STEPS predictions anticipating that if fossil fuel presence persists at high levels, the required climate goals will not be achieved. Moreover, the current investment in oil and gas is approximately twice the amount that the Net Zero Emissions (NZE) scenario for 2030 considers appropriate, which means a high dependency on fossil sources and contrary to the 1.5°C temperature increase limit climate goal.

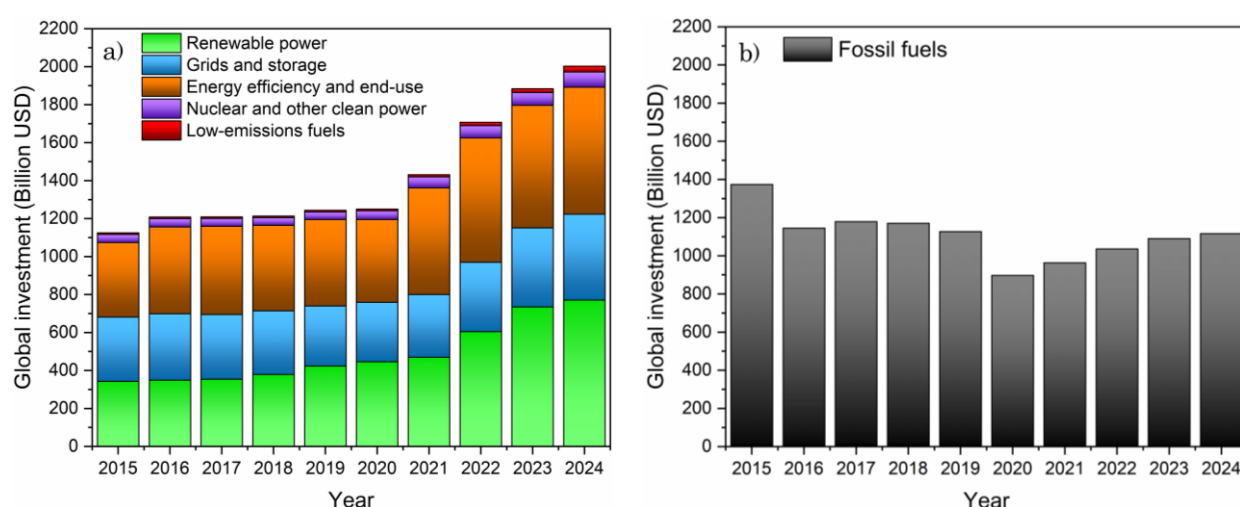


Figure 1.3: International Energy Agency's summary of world energy investment flows over the last decade for a) clean energy and b) fossil fuels (data obtained from [9]).

STEPS predicts renewable sources to account for 80% of the newly installed electricity generation infrastructure, with solar photovoltaics accounting for more than half. Before 2030, the manufacturing capacity for solar modules could reach 1200 GW per year, but only 500 GW are expected to be installed. If 70% of this capacity were installed, it would be enough to reach the deployment levels expected in the NZE scenario, strongly reducing the dependency on fossil fuels and CO₂ emissions. According to STEPS projections (further confirmed by IEA's World Energy Outlook 2024 [10]), these emissions are expected to peak before 2030 and unfortunately remain at high enough levels to cause a 2.4°C rise in global temperatures by 2050 (Figure 1.4).

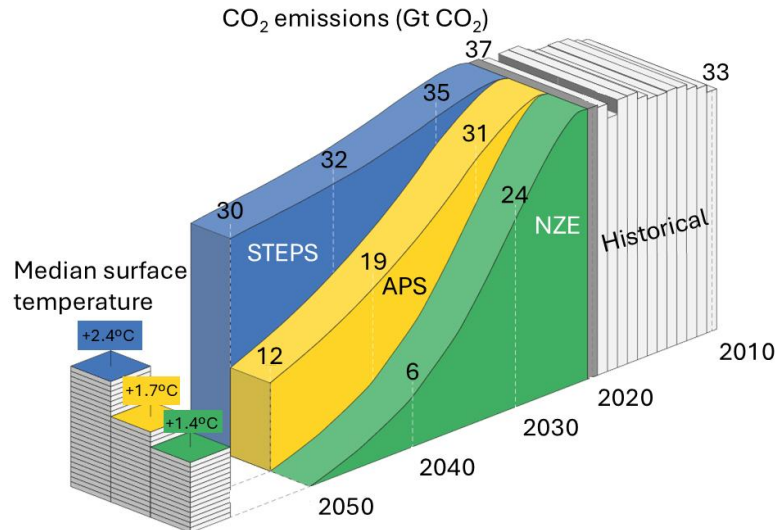


Figure 1.4: Projected CO₂ emissions according to different scenarios¹ through the 2010-2050 period [1].

To help emerging economies and developing countries meet their climate targets, several policies must be implemented, including a transition to clean electrification, improvements in energy efficiency and a gradual integration of low-emission fuels. As the global energy system evolves towards an electrified and renewable model, it becomes critical to ensure the security and sustainability of electricity supply. To achieve this goal, there is a critical need for investment in robust, digitised grid infrastructures, which can be substantially aided by the implementation of batteries and supercapacitors. There is also a high demand for devices that can tackle short-term flexibility and seasonal fluctuations, for which energy storage devices represent a promising solution.

1.1.2. Energy storage technologies

Currently, renewable energy generation is no longer the limiting factor for its use, but rather the means to store this renewable energy. Energy storage devices (ESDs) are becoming increasingly popular for the energy grid, as they are able to effectively address the intermittency challenges posed by renewable energy generation. In short, renewable energy sources can only generate energy when certain conditions are met (sun, wind, water flow...). This energy is delivered at the moment of generation, but cannot be stored when the energy demand is covered, resulting in large amounts of energy being wasted. However, if unused

¹ APS means Announced Pledges Scenario, implying a middle point between STEPS and NZE, exploring a timely implementation of energy and climate goals.

energy is efficiently stored, it can be further supplied when renewable generation is not possible.

Energy storage technologies can be divided into five categories according to their storage mechanism:

- Thermal energy storage refers to the storage of heat by cooling, heating, melting, condensing and vaporisation processes. Hot water energy storage, latent heat storage and thermochemical energy storage are the main representatives of this process [11-14].
- Mechanical energy storage involves the use of kinetic energy to generate electricity (flywheel energy storage), as well as the use of turbines to generate electrical energy using compressed air, or through pumped water (pumped hydro storage) [12-14].
- Chemical energy storage is based on the use of chemical reactions to generate electrical energy. Examples of fuels that store chemical energy include petrol, diesel, propane, butane, bio-oil, biodiesel and hydrogen [12, 14].
- Electrical energy storage is related to the utilisation of electric and magnetic fields to store energy. Electrostatic capacitors and superconducting magnets are the main examples of this technology [11-14].
- Electrochemical energy storage relies on electrostatic and chemical processes. Batteries and fuel cells operate on redox (chemical) reactions, while electrolytic capacitors present an electrostatic mechanism. Electrochemical capacitors (or supercapacitors, SCs) can present two different mechanisms, electrostatic energy storage (double layer capacitance) and chemical energy storage (pseudocapacitance) [14-16]. Both mechanisms can take place simultaneously.

For a deeper understanding of energy storage technologies and mechanisms, the following articles and reviews are recommended [11-16].

Since the beginning of this century, pumped hydro storage has held the largest share of renewable energy storage [17]. However, this share has been declining in recent years, with a compound annual growth rate (CAGR) of only 8.75% for the 2023-2033 period [18], compared to supercapacitors and fuel cells, which present CAGRs of 17.5% and 26.2%, respectively [19, 20]. These values underline the great influence that electrochemical ESDs have on the present and short-to medium-

term future of energy storage and renewable energy generation. This is particularly relevant for supercapacitors and fuel cells, which are portable, practical devices that can be integrated into new technologies, and will be the focus of the energy-related section of the thesis.

A summary of the main electrochemical energy storage devices is shown in a Ragone plot in Figure 1.5, where the advantages of fuel cells (high energy density) and supercapacitors (high power density) are observed. Nevertheless, further work is needed in order to compete with standard non-renewable and established technologies, like combustion engines, which present both excellent energy and power densities (defined as the amount of energy that a device can store and the rate at which this energy can be delivered, respectively, per unit mass).

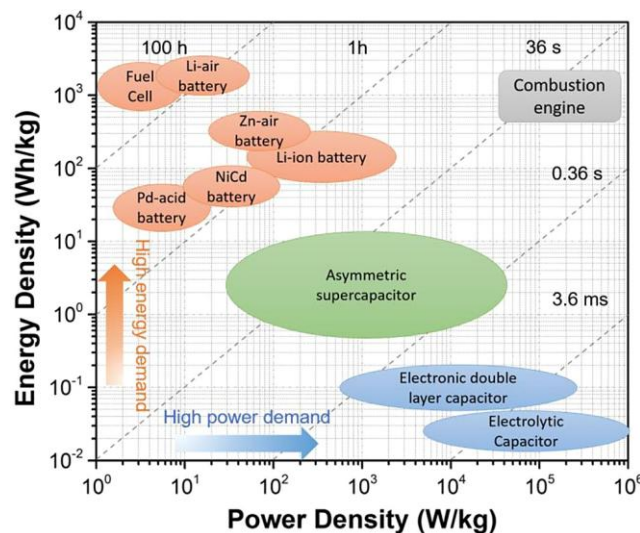


Figure 1.5: Ragone plot containing the main electrochemical energy storage systems compared with a combustion engine [21].

1.1.2.1. Supercapacitors

History and types of capacitors:

Although the earliest capacitors can be traced back to the end of the 18th century with Volta's work, it was not until the late 1950s that the initial electrochemical capacitors were developed. These devices were the first to use a liquid electrolyte instead of a solid dielectric, which marks a clear difference between electrostatic and electrochemical capacitors. Briefly, capacitors can be divided into three categories:

- **Electrostatic capacitors:** These devices operate on the generation of an electric field when a potential difference is applied between the two metal

plates that make up the device, separated by an insulating material. When this voltage is applied, one of the metal plates becomes positively charged, while the other becomes negatively charged [14]. These devices display large power densities, but with low energy densities.

- Electrolytic capacitors have the same architecture as the electrostatic capacitors, but they incorporate an electrolyte in direct contact with the electrodes. The presence of the electrolyte gives the process an electrochemical aspect, as opposed to the electrical character of the previous capacitors. These devices exhibit higher energy density than their electrostatic counterparts (approximately an order of magnitude greater) [15].
- Electrochemical capacitors, or SCs, have no dielectric (insulating) material. Instead, they consist of highly porous electrodes and a separator that prevents short circuits. These devices can be stacked due to their low mass and volume, and display capacitances about 100 times higher than electrolytic capacitors [15]. SCs also exhibit higher efficiency, durability and power density compared to batteries [16]. Figure 1.6 provides an overview of the different types of capacitors:

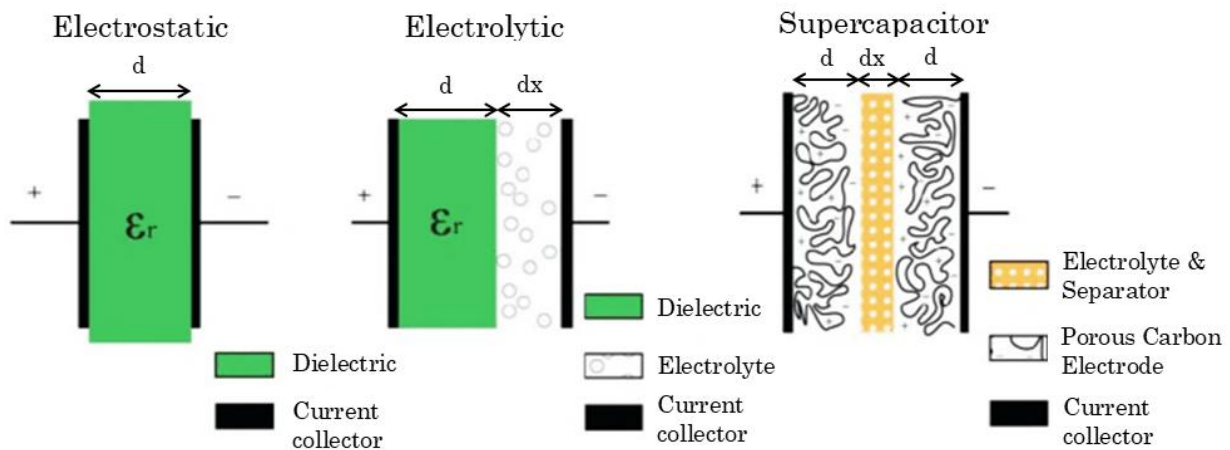


Figure 1.6: Summary of the construction of different types of capacitors [22].

The first electrochemical supercapacitors (dating from 1957) consisted of two carbonaceous electrodes impregnated with an aqueous solution of H_2SO_4 working as an electrolyte [23]. During the following decade, the performance of these devices was improved using other materials, such as polyaniline [24, 25].

For example, in the 1970s, advances were made with the development of novel alkaline solution electrolytes, or non-aqueous solutions (notably quaternary

ammonium salts or propylene carbonate) that allowed higher potential windows to be used. Nevertheless, low energy densities persisted, setting the impulse for extensive research to be carried out on ruthenium oxide electrodes during the second half of that decade, despite their costs [26].

During the 1980s and 1990s, SCs emerged as a commercial product, initially for use in low energy applications such as back-up energy sources in computers [27]. In the following years, SCs experienced rapid commercial growth, due to improvements in energy density, reaching values of 2 W·h/kg, and exhibiting capacitances of 5000 F in less than a decade [25]. Ongoing progress in the performance of SCs have now led to their integration into everyday life, supporting diverse applications in areas such as automation, aviation and renewable energy generation grids [28, 29].

Energy storage mechanisms:

Electrochemical capacitors use two different energy storage mechanisms. The first is electrical double layer capacitance (EDLC), which is an electrostatic process based on charge accumulation at the electrode's surface. This process takes place at the interface between the electrode and the electrolyte, similar to an electrostatic plate capacitor with a nanometre scale thickness, known as the Helmholtz layer. This theory was first proposed by Helmholtz in his electrostatic model in the 19th century. He defined the double layer capacitance as a phenomenon that occurs whenever two regions with different charge densities enter in contact, such as when the electrolyte contacts the electrode surface.

According to the Helmholtz model, electrons accumulate at the surface of the electrode, providing a negative charge, leaving the electrode surface positively charged and surrounded by the oppositely charged ions of the electrolyte. In this case, the electrode and the electrolyte achieve different potentials, which leads to a potential difference also known as Galvani voltage (φ_0), or the electrode potential. Knowing the Galvani voltage leads to the determination of the charge of the electrons in the contact area, Q , and also to the quantification of the charge density, σ , if the area is known. The calculation of these parameters leads to the determination of the double layer capacitance (C_H) using the Equation 1.1 and Equation 1.2:

$$\varphi_0 = \varphi_{Electrode} - \varphi_{Electrolyte} \quad \text{Equation 1.1}$$

$$C_H = \frac{Q}{\varphi_0} = A \frac{\sigma}{\varphi_0} \quad \text{Equation 1.2}$$

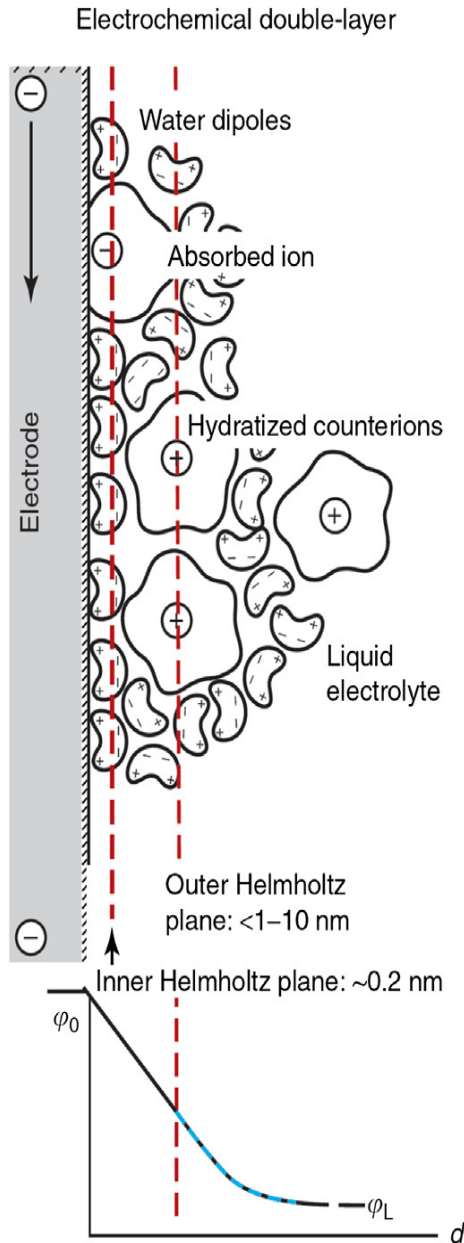


Figure 1.7: Electrical double layer schematic [30].

The dielectric part in supercapacitors is actually formed by the layer of adsorbed ions on the electrode surface, surrounded by solvent molecules that form the Helmholtz double layer. However, this layer can be divided into two different planes: the inner Helmholtz plane, formed by the adsorbed particles on the electrode surface, and the outer plane, which contains a second layer of adsorbed particles plus the solvated electrolyte ions [30]. Finally, beyond these planes there is a diffuse layer of electrolyte. Figure 1.7 provides a summary of this mechanism.

While double layer capacitance is purely an electrostatic mechanism, the second, pseudocapacitance, relies on faradaic processes based on redox reactions. Pseudocapacitance is a mechanism that works similarly to battery energy storage, but with a lower activation overpotential [25]. In this process, electrolyte ions migrate to the electrode of opposite charge when a voltage is applied. Anions undergo an oxidation process, supplying electrons to the circuit, and cations undergo reduction reactions.

Electrodes are a critical part of the energy storage process as they provide the surface for the polarisation of ions and the formation of the

double layer, for which high conductivity is required. In the pseudocapacitive process, electrodes are usually made of transition metal oxides [31], as well as conductive polymers [32], while carbonaceous materials are often used in the double layer process.

The use of activated carbons as electrodes has been favoured primarily due to their low cost (depending on the feedstock), ease of processing and high surface areas (which can easily exceed 1000 m²/g upon activation). Furthermore, recent work has shown that activated carbons used as electrodes in supercapacitors can reach capacitances ranging from 100 to 300 F/g [33-40], although this value is highly dependent on parameters such as the type of feedstock, surface area, pore size and distribution. Typically, a hierarchical combination of micro and mesopores is preferred for improved performance to overcome ion diffusion limitations.

In addition to the aforementioned properties, other features that make activated carbons ideal for supercapacitor applications are their chemical and thermal stability, polarisability, conductivity and the ability to be doped with heteroatoms. Carbonaceous gels have shown potential in this last aspect, due to the pseudocapacitive contribution of their heteroatoms, mainly oxygen, nitrogen and sulphur [41, 42].

1.1.2.2. Fuel cells

Fuel cells are electrochemical energy storage devices that convert chemical energy into electrical energy, provided there is a continuous supply of fuel and an oxidizing agent. Fuel cells offer several advantages over conventional combustion systems, including higher efficiency, lower emissions or an energy conversion $\geq 60\%$. Furthermore, in the case of hydrogen fuel cells, water is the only resulting by-product of the process, eliminating CO₂ emissions, as well as other air pollutants. The acoustic impact of these devices is also minimal, due to the reduced number of moving parts. Fuel cells are used in applications with low-to-moderate power requirements (such as residential energy grids, electronics, vehicles, emergency systems or backup supply sources) [43]. These devices can also be employed for mid-power generation grids and electricity generation in areas where power plants can't be installed due to geographical limitations [44].

Fuel cell systems are made up of three separate parts. The first consists of an electrolyser, which draws unused energy from the grid to produce hydrogen from water. The second, a tank that stores the hydrogen and delivers it on demand. And finally, a fuel cell that receives the hydrogen from the tanks, as well as an oxidising agent, typically oxygen (from air), and generates electricity from them through a redox process that takes place inside an electrochemical cell. This cell consists of two electrodes separated by an electrolyte that determines the type of fuel cell. At the anode, hydrogen undergoes an oxidation reaction, releasing protons that

migrate to the cathode through the electrolyte, while electrons move through the external circuit [45]. On the other hand, an oxygen reduction reaction (ORR) takes place at the cathode, converting the oxygen into water, which is subsequently withdrawn. Figure 1.8 shows a schematic of this mechanism.

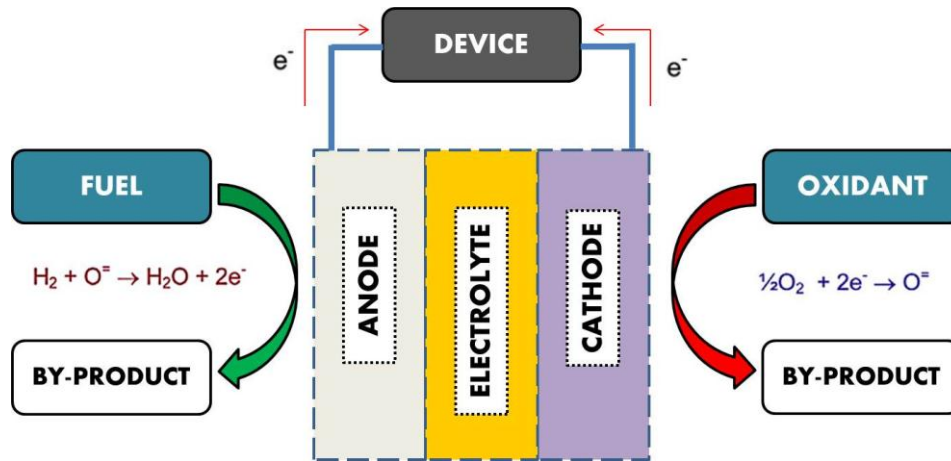


Figure 1.8: Schematic of a typical fuel cell with its main architecture and chemicals [46].

Depending on the type of electrolyte used, the main types of fuel cells are alkaline fuel cells, proton exchange membrane fuel cells (PEMFCs), phosphoric acid fuel cells, molten carbonate fuel cells, and solid oxide fuel cells [47].

Electrolysis:

The first electrolytic process dates back to 1789 [48], with alkaline electrolysis being the primary process for hydrogen production [49]. The mechanism of this technology is based on the immersion of two electrodes in a 20-30% KOH electrolytic solution. Both electrodes are separated by a diaphragm, which separates the generated gases in order to increase efficiency and ensure safe conditions, preventing gas cross-contamination, while allowing OH^- ions to migrate from one electrode to the other. However, this process has several disadvantages:

- i) The diaphragm does not completely prevent the diffusion of gas products, resulting in oxygen entering the cathode chamber. This leads to a reduction in the electrolyser's efficiency as oxygen is converted back to water in the presence of hydrogen. It can also result in dangerous levels of hydrogen exceeding the established explosion limit of 4 mol% H_2 [50].
- ii) Significant ohmic losses across the liquid electrolyte and diaphragm limit the maximum current density, thereby restricting hydrogen generation.

- iii) The characteristics of the liquid electrolyte limit the pressure range in which the electrolyte can operate, resulting in a bulky design if a stack configuration is desired [51].

To overcome these limitations, the first water electrolysis process using a solid polymer electrolyte was developed in the 1960s [52], using a solid sulfonated polystyrene membrane as the electrolyte [53]. This technology is known by the acronym PEM, standing for both Polymer Electrolyte Membrane or Proton Exchange Membrane.

In this technology, the polymer electrolyte membrane (mainly Nafion®) must ensure a high proton diffusion, prevent cross-contamination of gases, be compact for stack configuration and work under high pressure. PEM electrolyzers, with membrane thicknesses between 20-300 μm , permit much higher current densities, exceeding 2 A/cm^2 due to their high conductivity of around 0.1 S/cm . Additionally, the membranes significantly reduce gas crossover, allowing the electrolyser to obtain high purity hydrogen while operating over a wide range of power inputs, due to the rapid response of protons across the membrane (whereas in the liquid electrolyte proton diffusion is delayed by inertia). Another advantage of this method is that the production of hydrogen and oxygen remains stable, resulting in a more efficient process and safer working conditions [54].

However, this technology still presents some drawbacks:

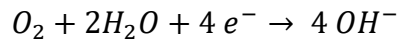
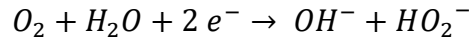
- i) Ohmic losses and challenges linked to higher cross-permeation as pressure increases [55]. Thicker, more durable membranes are needed at pressures above 100 bar, but these require the addition of internal gas recombiners to ensure that gas concentrations remain under safe thresholds [56].
- ii) The highly corrosive environment (pH 2) and high current densities (applied overvoltage $\approx 2 \text{ V}$) require very resistant materials. This also includes the catalysts, current collectors and separator plates. As such, typical catalysts are based on platinum group metals (Pt, Ir, Ru), and current collectors are made of titanium, significantly elevating the cost of the process.

In the 1980s, the first experiments with a supported tubular electrolyte were reported, leading to the use of solid oxide electrolysis cells (SOECs) [57]. Since then, SOECs have attracted interest due to their ability to produce hydrogen with high efficiency at low voltages and current densities [58]. Current research focuses on the development of low-cost, durable and efficient materials for these devices. In addition, the versatility of SOECs, combined with their ability to operate at

elevated temperatures makes them an attractive alternative for the electrolysis of CO₂ to CO, as well as for the co-electrolysis of H₂O and CO₂ to produce H₂ and CO (syngas). However, before this technology can be applied for hydrogen production, some challenges related to the durability of current SOEC materials at high temperatures must be first rectified.

Catalysts for Oxygen Reduction Reactions (ORR):

Although the Hydrogen Oxidation Reaction is a straightforward process, the ORR display sluggish kinetics that require the presence of a catalyst to accelerate the process. Furthermore, ORR can take place through two different pathways: the 2-electron pathway, or the 4-electron pathway, as displayed below.



The second pathway is preferred over the 2-electron reaction as it can generate HO₂⁻, a corrosive by-product that can damage the electrodes [59]. In order to promote the 4-electron reaction, a catalyst is needed, and therefore play a critical role in the efficiency of PEM fuel cells. Platinum is the most commonly used catalyst due to its excellent performance and high chemical stability. However, since initial studies [52] on PEM electrolyzers, concerns have persisted regarding the high costs associated with catalyst production (first catalysts were based on pure Pt and Ir). To reduce costs, efforts are underway to either reduce catalyst loading or find more affordable alternatives, but up to date, Pt still remains essential to ensure high PEM efficiency [60]. The catalysts used in PEMFCs can be divided into three categories: Pt-based catalysts, modified Pt-based catalysts (incorporating other metals such as Cr, Cu or Co) and non-Pt-based catalysts, which include non-precious metal or organometallic compounds [61].

As mentioned, Pt-based catalysts remain the most widely used option, and extensive research has been carried out in order to improve their morphology and find more cost effective synthesis methods [62]. The main efforts are directed towards the development of modified carbon-based or alternative non-carbon-based materials as supports for catalysts, in order to improve platinum's efficiency [63]. Furthermore, the use of platinum alloys offers positive catalytic results, but their durability is yet to be proven. A recent study used Pt₃Sc/PECNT as catalyst and achieved a power density of 760 mW/cm² at 60 °C during single-cell tests for oxygen reduction reaction (ORR) [64], whilst a Pt-Ni/C alloy reached power densities of 1022 mW/cm² [65], surpassing the 900 mW/cm² displayed by

commercial Pt/C based PEMFCs [66]. From this, it is evident that the correct addition of certain metals to Pt-based catalysts can result in impressive power densities. More examples of this can be found in Pt-Co catalysts, with power densities of 880 mW/cm² [67], or a notable value of 1618 mW/cm² achieved by a SnO₂-coated carbon nanotube catalyst decorated with Pt nanoparticles [68].

The current research direction focuses on the development of catalysts free from platinum group metals (especially iron), in order to reduce cost and increase PEMFCs lifespan. For this purpose, high-temperature pyrolysed FeN_(x)/C is emerging as a promising alternative. For example, a catalyst [69] made from poly-m-phenylenediamine (PmPDA-FeN_(x)/C) showed excellent current densities (11.5 A g⁻¹ at 0.8 V vs RHE) in ORR with minimal H₂O₂ production rate (<1%), and power densities of approximately 350 mW/cm². Recent studies have also reported on the synthesis of these catalysts using peptone as a precursor and NaCl as a template, providing a more environmentally friendly and cost effective approach [70].

Within PGM free catalysts, the incorporation of metallic nanoparticles is gaining interest in recent years. In particular, transition metal dichalcogenides (TMDCs) are being used for ORR catalysis due to their conductivity and increase in catalytic active sites. Recent studies have been carried out on the use of chalcogenides (S, Se and Te) with transition metals (Rh, Ru and Ir) for their use in ORR [71]. Other examples of TMDC-based catalysts include MoS₂ [72], MnSe [73], WS₂ [74], ReSe₂, RuTe₂ and IrS₂ [71]. The application of these materials, however, is still more focused on the ORR itself than the final fuel cell application, providing only values of the number of electrons transferred (from 3.5 to 3.9), but not about the power density of the fuel cells.

With this evidence, it is clear that non platinum and modified Pt-based catalysts are solid alternatives to Pt-based catalysts. However, there are still some significant performance challenges to be addressed before their practical implementation. Nevertheless, innovative materials are being tested, such as sludge biochar-based (SBC) catalysts, which can act as electrodes in microbial fuel cells. In this case, the abundant carbon and metal content in SBCs makes them particularly effective as catalysts, due to their combined adsorptive and catalytic properties [75]. However, their transferability to PEMFCS is still under review.

1.2. Environmental pollution. Dyes: risks, treatments and novel solutions

Synthetic textile dyes have become increasingly popular since their first use in the mid-20th century, with an estimated current production of 1 million tonnes per annum [76]. Of this, the textile industry accounts for about 80% of their total production, which results in more than 70 million tonnes of contaminated water [77]. Typically, these dyes do not adhere strongly to the textiles (less than 80% of the dye binds to the fabric), and are often released into rivers, oceans and lakes [78], where they persist for long periods of time, posing a serious threat to the ecosystem and human life [79].

It is estimated that approximately 85% of dye effluent is discharged into watercourses after the dyeing process. This effluent contains a significant number of toxic substances, like heavy metals (mercury, chromium, lead, arsenic...), dissolved solids and/or salts. This is specially concerning in developing countries, where access to water is limited, and water toxicity due to pollution represents a serious threat to human health. This situation enters in clear conflict with several Sustainable Development Goals (SDG), including SDG 3 (health and well-being) and SDG 6 (clean water and sanitation) [76].

Current methodologies for dye removal can be divided into three categories: chemical, physical and biological processes. These methods include approaches such as oxidation, microbial degradation, and membrane filtration, which can remove dyes to a high degree, but not completely [76]. For this reason, water remediation is becoming one of the most important issues to be addressed in the current era.

1.2.1. Environmental impact of dyes

Aquatic environments:

The release of these dye molecules into water effluents results in changes in water colour, which in turn reduces light penetration, and limits or inhibits the synthesis of chlorophyll, reducing photosynthetic activity [80]. Adverse effects in fish have also been reported, including reduced growth rates, decreased levels of proteins, and kidney damage [81]. Other effects of dye presence in water include reduced water quality, taste, and bacterial proliferation [82, 83].

Terrestrial environment:

The presence of dyes can cause a decrease in bacterial and fungal populations, reducing soil fertility [84]. Phytotoxic effects on plant germination and genotoxic effects on crops have also been observed [85]. Similar to aquatic ecosystems, dyes also hinder plant photosynthesis by limiting light penetration to the chlorophyll and restricting CO₂ assimilation [86]. Low oxygen levels due to solid presence in water can also lead to cell death [87].

Risks to human health:

Prolonged dye exposure can cause dermatitis, irritation, organ dysfunction, and even cancer [76]. These risks are particularly evident in people with chronic exposure, which is more common in developing countries. Dye contact by inhalation has been associated with respiratory problems, conjunctivitis, rhinitis, allergic reactions, and asthma [79]. In addition, exposure to heavy metals can cause severe damage to the central nervous system and organ failure in the liver, lungs, kidneys, stomach, and other organs [88]. Consumption of contaminated fish can also cause fever, hypertension, and muscle cramps in humans [89, 90]. The genotoxic and mutagenic potential of dyes has also been demonstrated [76, 91-94]. It is estimated that about 100 of the 4000 (2.5%) tested dyes for their potential toxicity still remain on the market, despite their inherent risks [95]. This clearly poses a threat to both humans and ecosystems, which highlights once again the need for better dye removal.

1.2.2. Current remediation methods

Chemical remediation

These methodologies are based on the use of chemical or electrochemical processes to remove dyes. They typically exhibit high removal rates, but generate hazardous by-products and require significant investment, making their industrial implementation less appealing than other remediation methods [76].

The most commonly used chemical processes are oxidation and advanced oxidation processes (using oxidising agents to break down molecules into CO₂ and water); electrochemical processes (based on non-soluble anodes to break down molecules); Fenton reaction (eliminating dye molecules through a mixture of catalyst and H₂O₂); ozonation (removal of dye particles by using ozone derived from oxygen); ultraviolet radiation (based on the use of UV light to break down dissolved dye

molecules) and photochemical methods (combination of ozonation and UV radiation) [76, 77, 96-98].

Although chemical processes offer good results, their industrial implementation is limited by the significant economic investment needed, the high energy costs and the amount of residues produced [79]. Other factors such as the demand for catalysts and the reduced lifespan of several materials also contribute to its unappealing character [77].

Biological remediation

This approach relies on aerobic and anaerobic processes to remove the dyes before the effluent is discharged into water streams [99].

The main biological processes are microbial biosorption (using different microorganisms with high affinity for dyes); algal degradation (based on the algae consuming the dye molecules for their own growth); aerobic-anaerobic combination (production of a sludge that breaks down dye molecules); enzymatic degradation (using enzymes to break down the dye molecules) and microbial culture (combination of bacteria and other chemical reagents to remove dyes) [77, 100-102].

The main advantages of these biological approaches are their low cost, sustainability and simplicity. However, challenges in controlling the growth of these organisms, and their low efficiency and inability to remove these dyes completely are a serious limitation that needs to be taken into account [76, 103].

Physical remediation

Among the most commonly employed remediation processes, physical remediation treatments (based on mass transfer mechanisms) are favoured due to their low requirement of chemical reagents, ease of operation, simplicity and not needing to use living organisms [104].

The main physical processes are adsorption (based on the use of porous adsorbents to remove a wide variety of dyes); coagulation/flocculation (relying on the agglomeration of dye molecules to remove them by filtration); ion exchange methods (using a resin bed in which ions are exchanged with the dye molecules); irradiation (removing dye particles by using of radiation); membrane filtration (passing a contaminated water stream through a porous membrane that can retain dye molecules) and reverse osmosis (using high pressure to separate dye molecules from water through a thin membrane) [77, 105-110].

Overall, these processes present significant advantages over biological and chemical approaches due to their low cost, simple design, and reduced sludge generation [111]. However, it should be noted that these techniques also present important drawbacks in some cases, like limited dye affinity, significant oxygen demand and strong dependence on process parameters such as temperature, pressure, pH or dye concentration [112]. However, considering these issues, adsorption is a process that can be adapted to overcome them, since dye affinity can be tuned through the development of different adsorbents, oxygen demand is not relevant in adsorptive processes, and environmental parameters (temperature, pressure, pH, concentration) can be tightly controlled. For these reasons, adsorption has been chosen as the preferred methodology for dye removal within the framework of this thesis.

1.2.2.1. Dye remediation through adsorption

In recent years, several environmental policies have been established in order to regulate the presence of polluted wastewater in the environment [113]. This legislation ensures that the dye industry complies with the International Dye Industry Wastewater Discharge Quality Standards, which are derived from the Zero Discharge of Hazardous Chemicals Programme. Dyeing effluents contain a number of pollutants, including hazardous chemicals, and dissolved salts that increase biological oxygen demand, chemical oxygen demand and can alter water colour. The established limits for these parameters are listed in Table 1.1:

Table 1.1: Established thresholds for dye effluents discharge into waters [77].

Factor	Limit allowed
Biological Oxygen Demand	30 ppm
Chemical Oxygen Demand	50 ppm
Colour	1 ppm
pH	6-9
Suspended solids	20 ppm
Temperature	42°C

It is common, especially in developing countries, for dyeing industries to store effluents as industrial waste after use, and then to release them into the environment without prior treatment, thereby polluting water [114]. It is crucial to abolish this practice and treat dye effluents before discharge, as these residues

often contain high dye concentrations, which can alter pH levels and water temperatures, resulting in the aforementioned environmental issues.

Adsorption basics:

Adsorption is recognised as one of the most cost effective and straightforward processes for dye removal. It is a highly efficient technology with the potential advantage of adsorbent regeneration. This process depends on several factors, such as dye concentration, pH of the solution, temperature, contact time, and adsorbent dosage. The removal of dyes from water and wastewater is typically performed using activated carbon, nanoparticles-based adsorbents, low-cost adsorbents, and other types of adsorbents [115]. To achieve high efficiency, adsorbents must present high surface area and porous structures [116] to allow good diffusion in order to enable facile fluid passage.

One of the main advantages of adsorption compared to other physical treatment technologies is its potential to fully eliminate most dye types [117, 118]. It has also been widely employed for removing other contaminants, is simple to implement, and requires little or no secondary treatment after the process. In fact, when other less efficient technologies are implemented, adsorption can be used as a post-treatment to completely remove colour from discharged water [118]. Although the initial cost to produce some adsorbents remains a challenge, this process has proven to outperform conventional wastewater treatment technologies [77, 104], promoting research into low-cost adsorbents to make adsorption a more viable, economical solution for dye removal on a global scale [119].

Adsorption is a mass transfer process in which the adsorbate (gas or liquid) molecules agglomerate at the adsorbent interface (e.g. gas-liquid, gas-solid, liquid-liquid, and liquid-solid [120]). The main adsorption mechanism is physisorption, a non-reactive process driven by various forces, such as hydrogen bonding, electrostatic interactions, van der Waals forces and hydrophobic interactions [121]. In this process the solid surface isolates dye particles from the adsorbate solution, accumulating them on its surface, and thereby reducing the concentration of the adsorbate. When all the molecules have been adsorbed onto the surface and the system has reached a state of equilibrium, the result is typically a contaminant-free solution [77].

The other adsorption mechanism, chemisorption, which is less common than physisorption for dye removal, involves the chemical reactions between the

adsorbent and adsorbate, creating new chemical bonds on the surface of the adsorbent.

In summary, to achieve high adsorption efficiency, it is essential to understand the various parameters that can affect it, and as such, when testing suitable adsorbents, careful experimental design is crucial. For this purpose, the main parameters and their influence on the adsorption process are shown in Table 1.2:

Table 1.2: Main adsorption parameters [77].

Parameter	Description and influence	Optimum values
Adsorbent dosage	Mass of adsorbent. Increasing dosage improves adsorption.	≈ 10 g/L.
Contact time	Interval while adsorbent-adsorbate remain in contact. Higher time implies better adsorption.	≈ 3 h.
Dye concentration	Dye content in a solution. Larger amounts will be absorbed at higher dye concentrations.	≈ 0.1 g/L.
pH	Acidity of the solution. Adsorption can vary with pH depending on the dye and the point zero charge, PZC, of the adsorbent.	≈ 6 .
Temperature	Indicates the thermodynamic nature of the process (endo or exothermic). Not recommended to work at too high or low temperatures.	$\approx 30^\circ\text{C}$.

Adsorbents for dye removal:

Adsorbents are porous, insoluble materials capable of capturing and retaining adsorbate molecules. Adsorbents can be made from solid raw materials, but can also be derived from other sources, such as liquid-based materials, including enzymes or hydrogels [122-125].

The main characteristic of an adsorbent is its adsorption capacity, which quantifies the amount of adsorbate that it can retain per unit mass of the adsorbent. Other characteristics that define an adsorbent's efficiency are its porosity (surface area, pore distribution, pore size...), durability, regenerability and versatility towards different pollutants. It is also desirable for effective adsorbents to facilitate rapid dye removal and to be able to perform at different dye concentrations, pH levels and temperatures [77]. Examples of different adsorbents can be found in clays, bentonite, chitosan, cotton, coal or silica gel [126-130].

Of all these examples, activated carbons (ACs) are currently the most widely used adsorbents due to their excellent adsorption performance, including high adsorption capacity, versatility [131], potential for regeneration, and, importantly

from an industrial perspective, are low cost. Historically, ACs have been produced from carbonaceous materials derived from fossil fuels, resulting in materials that, although providing great adsorption results [120, 132, 133], depend on finite and non-renewable resources. To overcome this problem, innovative methods are being studied to produce ACs derived from sustainable sources such as biomass [134] or waste products [120]. These alternatives provide a renewable approach to conventional materials and are also more abundant than their fossil-based counterparts.

1.3. Advanced materials for energy and environmental applications

The previous sections have outlined some of the most pressing issues of our generation. However, to quote the renowned Brundtland report: “Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs” [135]. Under this premise, the following sections outline the sustainable strategies followed throughout the thesis, focusing on the use of biomass-derived materials and environmentally friendly synthesis methodologies.

1.3.1. Sustainable carbons from biomass

As mentioned previously, ACs have proven to be excellent materials for electrochemical and environmental applications, due to their good textural properties and rich functionality. For these reasons, extensive research has been carried out with the aim of developing ACs from sustainable sources, with biomass and waste being the main precursors.

The use of biomass from a variety of sources, such as plants, food waste or by-products, has gained prominence as a renewable and valuable resource due to its carbon neutrality and its wide-scale availability. For example, the total biomass in the biosphere accounts for approximately 450 gigatonnes of carbon (Gt C), primarily derived from plant matter [136]. In the EU-28, annual lignocellulosic biomass production from agriculture alone is estimated at 419 megatonnes of dry matter [137]. Interestingly only about 5% of this total biomass is used for competitive food and non-food applications, which, together with the additional 1.3 billion tonnes of food waste, represents a significant opportunity for conversion to higher value applications [138].

1.3.1.1. Cellulose

Cellulose is the most abundant and widely used biopolymer, with a global production of approximately 1.5×10^{12} tonnes per year [139]. The isolated form of this material dates back to the 1830s, when the French chemist Payen discovered a fibrous material remaining in plant tissues after purification with acid (hydrochloric, sulphuric) or ammonia, followed by extraction with water [140, 141]. Through elemental analysis, he found a molecule with the formula $C_6H_{10}O_5$, same as starch, which is known today as cellulose.

Cellulose has received considerable attention in research due to its specific structure and properties, as its repeating β -glucan units provide a wide variety of architectures, reactivities and functions. Its properties are strongly influenced by intermolecular interactions, chain length and distribution, degree of cross-linking, and functional group presence throughout the molecular chain. Some of the most notable features of cellulose are polyfunctionality, chain rigidity and susceptibility to hydrolysis and oxidation [142].

Cellulose is mainly found in plants, herbs and trees, such as cotton, sunflower, hemp, hazelnut, palm... with cellulose contents ranging from 15 to 90% [143-150]. However, it can also be obtained from other sources such as algae, bacteria and fungi [143, 151, 152]. In addition, cellulose and its derivatives are environmentally friendly as they can easily be disposed of after use [153], or returned to the natural carbon cycle when entering in contact with decomposers [154].

This environmentally friendly character, combined with its non-toxicity, hydrophilicity (despite being insoluble in water [155]) and relatively easy chemical modification, yield a promising material for adsorption applications (after chemical treatment). Natural cellulose presents a low adsorption uptake capacity [156] compared to activated carbons, but several studies have demonstrated the excellent efficiency of modified cellulose towards different pollutants, achieving adsorption capacities comparable to those of commercial activated carbons [157-161]. The use of cellulose-derived activated carbons in supercapacitors has also been reported, with capacitances exceeding 200 F/g [162-165].

However, the use and conversion of cellulose from diverse feedstocks into value-added materials remains challenging due to the vast differences in their chemical and physical properties. High costs can also be incurred due to their low calorific values (High Heating Values) and densities, and that they typically contain contaminants and high moisture levels. As a result, many processing methods are inadequate, whereas hydrothermal carbonisation (HTC), or wet torrefaction, can deal with all these issues in just one step [166].

1.3.1.2. Hydrothermal carbonisation

This process can convert mixed, wet biomass into carbonaceous materials with high heating values (HHV), and is applicable to any type of wet biomass, making it more energetically efficient for these types of materials than conventional carbonisation when producing carbonaceous materials [167]. It also prevents the

formation of metal oxide contaminants as ash residues after combustion, which are responsible for corrosion and fouling [168]..

The HTC process allows a rapid conversion of biomass into different products, namely a bio-oil, a gaseous fraction principally composed of carbon dioxide and, more importantly, a solid material resembling coal, known as a hydrochar. These products, which take millions of years to form in nature, can be produced in only a few hours [169]. The origins of HTC date back over a 100 years ago, initially introduced by Friedrich Bergius, who was awarded the Nobel Prize in 1913 for his work on “chemical high-pressure processes” [170]. In the hydrothermal process, biomass feedstock is subjected to subcritical water at temperatures ranging from 150°C to 250°C under autogenous pressure. When temperatures are higher than 250°C, this process is referred to as hydrothermal liquefaction or hydrothermal vaporisation [171]. A summary of HTC feedstocks, resulting materials and final hydrochar uses is shown in Figure 1.9.



Figure 1.9: Schematic of HTC precursors, primary products and main applications of the produced hydrochar [172].

After HTC, the resulting solid, a hydrochar, has similar properties to pyrochar obtained via pyrolysis. This hydrochar can be used in a wide range of applications, from improving soil fertility, greenhouse gas sequestration, and wastewater remediation [173-180], to the synthesis of quantum dots used in the therapeutic treatment of HCoV-229E, a strain of human coronavirus [181]. In the energy sector, the practice of co-firing hydrochars with coal as a cleaner solid fuel alternative is becoming increasingly popular due to hydrochar having higher

energy densities than the original precursor [182], while containing less ash and moisture [169], and H/C and O/C ratios similar to lignite and coal [183-185].

HTC has also proven to be an effective pretreatment strategy to produce carbonaceous, porous materials prior to activation or pyrolysis. Hydrochars display increased mass and carbon yields, and improved textural properties (after activation) when compared to non-hydrothermally treated materials [186, 187]. For this reason, HTC is attracting interest as a first step in the production of porous adsorbents designed for gas sorption and wastewater remediation applications. Recent studies have shown that straw-derived hydrochar has good adsorption efficiency for heavy metals, dyes, antibiotics and aromatic compounds owing to its diverse chemical functionality [188]. In the energy field, hydrochars are being investigated because of their sustainable character, and present a promising alternative to conventional carbonaceous materials, especially in the development of electrodes for fuel cells, batteries and SCs. However, it is important to note that for these applications hydrochars must undergo pyrolysis and activation beforehand.

Hydrothermal mechanistic pathway of cellulose breakdown and product formation:

The initial research carried out by Bergius on the conversion of cellulosic biomass into a carbonaceous material [189], and the subsequent studies conducted by Berl and Schmidt on the HTC of various biomass sources [190] show that the basic process hasn't changed.

The reactions that take place during the hydrothermal process depend on the biomass feedstock and the reaction parameters. It is generally accepted that the HTC mechanism consists of several stages. These include hydrolysis, in which the polymeric chain is broken down into smaller oligomers, dimers and monomers, dehydration of monosaccharides or oligosaccharides that produce furfural derivatives, and other processes such as decarboxylation, polymerisation and aromatisation.

Subcritical water conditions reduce the energy required to break the chemical bonds in biomass, enabling the reaction to occur at lower temperatures, and thus removes the dependence on catalysts [191]. After hydrolysis, the next stage in the HTC process depends on the nature of the produced sugar, whether it is a pentose (C5) or a hexose (C6). In the case of pentoses, dehydration takes place leading to furfural production, which can then be transformed into furfuryl alcohol through

alcohols acting as hydrogen donors [192]. Afterwards, levulinic acid is produced through a hydrolytic ring opening reaction [193]. Below, a sequential list presents the mechanistic phases:

- i) Xylose undergoing a de Bruyn-van Ekenstein transformation to produce 1,2 ene-diol and D-xylulose.
- ii) Retro-aldol reactions forming glyceraldehyde (and subsequently, glycoaldehyde and formaldehyde).
- iii) Glyceraldehyde producing dihydroxyacetone through another de Bruyn-van Ekenstein transformation.
- iv) Glyceraldehyde and dihydroxyacetone dehydrating to form pyruvaldehyde.
- v) Pyruvaldehyde hydrating to form acetic acid, formaldehyde, acetaldehyde, formic acid and lactic acid [194].

In the case of C6, dehydration also takes place, producing cyclic and intermediate linear products. These products are thought to directly produce humins, but in negligible amounts [195]. This process further leads to the generation of 5-hydroxymethylfurfural (HMF). Research suggests that HMF production from cellulose occurs through the de Bruyn-van Ekenstein transformation to fructose or mannose via an epimerisation reaction [196]. However, prolonged exposure of HMF to an aqueous medium can lead to a rehydration process, which ultimately results in the formation of formic and levulinic acids [197]. The result of this reaction is a reduction in the pH of the medium, which catalyses the dehydration reaction and subsequent polymerisation of HMF.

The HMF pathway is thought to involve a series of reactions involving 2,5-dioxo-6-hydroxyhexanal (DHH), resulting in the formation of an initial dimer that expands upon subsequent addition of HMF. DHH is thought to originate from the acid-catalysed hydrolysis and ring opening of HMF. However, the identification of DHH is still challenging, as it is a highly reactive intermediate and, therefore, more research is needed before this particular mechanistic process should be fully accepted.

Up to HMF production, there is a general consensus on the mechanism. However, understanding of the subsequent steps becomes more complicated due to the complex nature of humins and the number of reactions involved in producing them. Two types of humins can be distinguished depending on the reactant group, the

hydroxymethyl group, and the formyl group. A mechanistic overview of the reaction pathways to form the possible humin precursors is shown in Figure 1.10.

In the first case, the hydroxymethyl group can undergo nucleophilic substitution, acting as a leaving group to generate Product 1 (see Intermediate dehydration products in Figure 1.10), or it can take part in an etherification reaction resulting in the formation of Product 2. On the other hand, the formyl group can participate in several reactions, such as aldolic condensation, which is often observed with diketones at the α -position, leading to Product 3. Furthermore, acetalisation reactions can occur in the presence of alcohols within the medium, resulting in Product 4 [196]. Following the dissociation of the hydroxyl group in Product 4, highly reactive carbocations can be formed, initiating electrophilic substitution reactions that will go on to form Product 5.

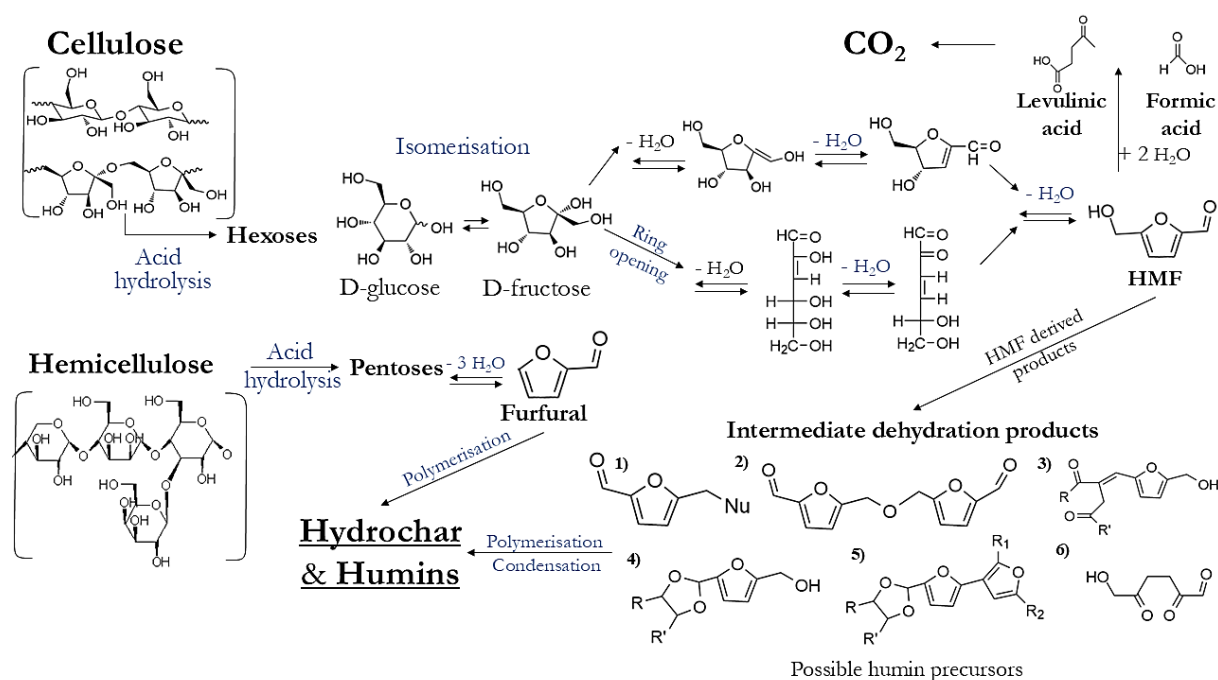


Figure 1.10: A mechanistic overview of cellulose and hemicellulose breakdown, and the formation of humin and hydrochar during HTC [172].

Nevertheless, HMF can take part in several reactions, including the previously mentioned rehydration process that results in levulinic and formic acids. It can also produce DHH (Product 6) and undergo Diels-Alder reactions [198]. The combination of these reactions is crucial for the formation of humin, which is thought to consist of around 60% furan rings and 20% ether or acetal linkers [199].

Parameters governing the HTC process:

In order to understand the characteristics of the resulting hydrochars, it is essential to analyse the influence of the parameters that control the HTC process, which include the following:

i) Temperature:

Temperature plays a crucial role as it provides the energy required to break the intermolecular bonds between the polymers. Temperature also influences the water properties that control the process. In the ionic reactions of this process, an increase in temperature leads to a decrease in water viscosity, which enhances the degree of degradation (as water can penetrate the polymeric chains more effectively [200]) and a decrease in the solvent's polarity, making it easier to dissolve organic components [191]. In cases where the temperature is insufficient to break down the biomass structure, a pyrolysis process may happen as a response opposed to the reactions of the monomers [169]. However, excessive temperatures should be avoided, as this can promote the formation of secondary char as a polymerisation by-product, which can affect the underlying mechanisms of hydrochar formation [201].

Several studies have shown a correlation between increasing temperatures and reduced solid yield in the HTC process. This decrease in solid yield is often followed by an increase in gas concentrations (CO_2 , CH_4 , H_2 ...), which can be attributed to dehydration, decarboxylation, and the reduction of volatile matter. Despite higher temperatures generally resulting in lower yields, there is a substantial increase in the High Heating Value (HHV) of the final hydrochar.

Although an increase in both HHV and solid yield is ideal, these two parameters trade-off with each other as temperature increases. However, as HHV is not a critical factor in electrochemical applications, it is recommended to work at lower temperatures in order to optimise the solid yield, even if this comes at the expense of HHV. For example, Lee's research [202] on *chlorella vulgaris* found a decrease in solid yield when temperature increased from 180°C to 240°C, with a maximum in HHV observed at 200°C. Similar trends have been observed in various materials such as cellulose [202], lignin [202], xylane [202], bamboo [203], nut shells [204] and tobacco stalk [205], as well as in smaller plants like *Humulus lupulus*, *Plumeria alba* or *Calophyllum inophyllum* [206].

A temperature range of 150-230°C is considered optimal for achieving the highest solid production, while the 250-350°C range is more appropriate for obtaining

liquid products. At higher temperatures, gas becomes the main product. These temperature ranges have been found to be independent of the origin of the feedstock used in the hydrothermal process. Examples of this are cellulose [207, 208], sugarcane bagasse, nut shells [204, 209], peat [210], and poultry wastes [211] with very little variation. For example, the maximum solid yield is obtained at typically 200°C for cellulose, while it is approximately 170°C for poultry wastes, and 150°C for different types of algae [212].

In addition to its impact on yield, temperature plays an important role in determining the final properties of the material. Carbon content increases with temperature, while hydrogen and oxygen content decrease significantly [207]. It has also been observed that the degree of aromaticity tends to increase with temperature [208, 213], which could be attributed to the reduced presence of reactive sites in the aromatic structures.

ii) Residence time:

Residence time is a critical factor in the process, since it determines the severity of the reaction, although its effect on solid yield is less significant than that of temperature. HTC can be a slow process, with residence times ranging from a few minutes to several days. In the case of hydrolysis, residence time has an impact over the first 6 hours (approximately), after which its effect reduces markedly [214, 215].

The formation of secondary compounds, such as furfural, is highly dependent on residence time, due to the polymerisation time required for these compounds [182]. Nevertheless, monomers are more affected by temperature than residence time. Research has shown that the residence time controls the degree of decomposition of the feedstock, which influences the hydrolysis and polymerisation of the monomers. Consequently, residence time has a major influence on the textural properties and particle size of the hydrochars [205, 207].

A relatively short period of time is required to achieve efficient bond rupture of the chemical components of the chosen biomass, as hydrolysis and bond cleavage are relatively rapid reactions. Research on cellulose [208] has shown that the hydrolysis process, which converts cellulose into soluble substances, is favoured at shorter residence times, inhibiting the decomposition of cellulose into heavy oils. As the residence time increases, solid yield reduces due to breakdown of the initially formed hydrothermal product, resulting in higher yield of heavy oil. Other materials such as tobacco plants [205] follow the same trend, showing a decrease

in yield decrease from 62% to 41% when the residence time increases from 1 to 12 hours at a temperature of 260°C. This trend is also true for peat [210], where the yield is reduced from 85% to 65% when the residence time varies from 1 hour to 8 hours at a temperature of 190°C. However, this effect is less pronounced in other materials like corn cobs [215], which shows a negligible variation in yield (around 1%) when the residence time increases from 1 to 6 hours at a temperature of 250°C.

In summary, research shows that long residence times lead to the production of soluble fractions, especially at lower temperatures (approximately 150°C). Furthermore, when temperatures increase to values close to 250°C, liquid yield decreases, with a subsequent increase in solid yield and an increment in gas production [208].

Residence time not only influences the solid, liquid and gas yields, but also impacts their final properties. Short residence times result in the generation of products with high HHV [215, 216], which can be attributed to the elimination of oxygen from biomass. Some studies show that longer residence times are related to improved textural properties of the hydrochar after activation, mainly porosity, pore volume, and BET surface area [217]. However, in other studies these properties reach their optimum values at intermediate residence times (1-6 hours), and after which they begin to decline [205].

iii) Feedwater acidity and catalyst:

The production of organic acids during HTC is highly dependent on pH. These acids are intermediates that facilitate the decomposition of biomacromolecules for the subsequent production of hydrochar. HTC is an autocatalytic process, meaning that it generates, *in-situ*, acids such as formic, acetic, lactic, and levulinic acids that reduce the pH of the media [218]. However, acids or bases can also be added to further catalyse the reaction by increasing the ionic strength and speed of the reaction, or to direct the process towards the formation of a particular type of hydrochar [219].

In Yang's studies with nut shells [204], the solid yield was measured across a pH range of 4 to 13. Results showed that the yield remained relatively stable within the pH range of 4 to 10, but decreased significantly (from 60% to 20%) at a pH of 13. This decrease suggests an increase in water soluble products, which could be due to the liquefaction of the feedstock at higher pH levels. Research on pH involving wheat straw [220] demonstrated that at both 200°C and 260°C, the solid yield remained constant within the pH range of 2 to 12. Elemental analysis of the

products indicated that cellulose and hemicellulose exhibit lower reactivity under alkaline conditions compared to lignin. Studies involving sewage sludges [221, 222] showed the same results, with less than 5% change in solid yield within a pH range of 2 to 12. Sawdust [223] presented similar results at 250°C, while at 200°C, the yield variation was around 10%. In general, raw materials processed by HTC under high pH conditions yield materials with increased surface area and pore volume after activation, and subsequently reduced pore diameters [220].

The hydrolysis process can be improved by the addition of catalysts: acidic catalysts such as sulphuric, nitric or hydrochloric acid [224-226], are usually more effective for hydrolysis, while basic catalysts, such as RbOH, NaOH or CsOH [225-228], usually improve bio-oil production [217]. Furthermore, catalytic addition can help to reduce NO_x emissions by converting them into nitrogen and water [217].

iv) Feedstock:

The composition and structure of biomass can vary significantly depending on factors such as its origin, growing environment, time of planting or harvesting, and duration of biomass growth [229, 230]. Furthermore, each biomass component behaves differently to changes in temperature. For example, it is known that biomasses with higher cellulose and hemicellulose content produce mainly bio-oil [231], whereas lignin-rich feedstocks present higher solid yields [232]. This difference can be attributed to the branched and aromatic lignin structure, which makes it more resistant to degradation [185, 204, 206]. The composition of cellulose and lignin in biomass are considerably different. However, most agricultural residues generally consist of about 40–50% cellulose, 25–30% hemicellulose, and 10–20% lignin [233-235]. Depending on the feedstock, biomass can contain as little as 9% or as much as 90% cellulose, over 80% hemicellulose, and more than 40% lignin [236-238]. Consequently, selection of the appropriate biomass type is critical in achieving the desired end product.

As noted previously, the process of HTC is known to involve different mechanistic pathways. However, these mechanisms are also influenced by the specific type of biomass feedstock, which plays a significant role in the development of porosity in the final hydrochar after activation. To date, there is scarce literature on the effect of feedstock in HTC. Some studies suggest that high levels of dissolved biomass could accelerate the polymerisation of soluble compounds, resulting in larger spherical particles [169]. However, further research in this area is needed in order to substantiate this hypothesis.

v) Heating rate:

Heating rate, when reaching high levels, does not usually promote the formation of solid products, as there is not enough time for polymerisation and carbonisation reactions that ultimately form the char to take place. Depending on the final product, the use of relatively high heating rates (10-20°C/min) is common, as this method reduces the time for secondary reactions and results in higher oil yields, with a corresponding reduction in solid yield [169]. For example, when rapeseed was heated at rates from 5 to 50°C/min it was found that with increased rates mass loss was greater [239]. A similar observation was found in studies on wood chips [240]. These results support the known theory that lower heating rates promote higher degrees of carbonisation, and thus, higher solid yields, while higher heating rates maximise liquid and volatile product yields [241].

vi) Pressure:

Pressure is a critical factor in the HTC process as it influences the decomposition rate and hydrolysis process. It is essential to keep a tight control on the pressure level of the medium in order to obtain the desired final products [217]. The control of pressure is vital as it can control the reaction pathways, as pressure changes are closely related to temperature. High-density solvents have been found to accelerate decomposition, thereby promoting reactions during liquefaction [242]. Pressure plays a key role in the use of these solvents since they can be obtained by applying elevated pressures.

To summarise, the evaluation of the influence of different parameters in hydrothermal carbonisation reveals that, in order to maximise the solid yield (as desired in this project), it is necessary to follow a careful experimental design. Specifically, moderate temperatures (200-250°C) and intermediate residence times (4 hours) are desired to obtain a stable hydrochar with higher carbon content and improved textural properties (after activation). Other conditions, such as acidic pH, lower heating rates, and subcritical pressure are also desired to enhance char production. Understanding these parameters is essential for the development of materials with optimal properties that can be tailored to specific applications.

1.3.2. Biopolymers

Sections 1.1.2 & 1.2.2.1 demonstrate the suitability of biomass-derived activated carbons for energy and environmental applications, and their preference over conventional materials due to their sustainable nature. However, their powdery

form can limit their use, especially in adsorption, where recovering them at the end of life can be difficult and costly. To overcome this problem, the use of scaffolds, especially polymeric ones, has gained prominence in recent years. In this field, polymeric nanocomposites stand out due to the synergistic properties offered by the polymer matrix and the incorporated nanoparticles. The combination of, for example, metal nanoparticles with biopolymers yields electrically conductive materials with good mechanical properties and chemical stability, with improved electrochemical performance [243-245]. In the adsorption field, the combination of porous materials with biopolymers results in biocompatible materials with increased surface area and chemical functionality that promotes chemisorption processes, as well as enhancing physisorption, leading to more effective adsorption and easier industrial implementation of adsorbents for wastewater removal [246, 247].

Although research on bionanocomposites (combination of biopolymers and nanoparticles) has received special interest over the last 20 years, there are works on the synthesis of organic/inorganic hybrid networks dating from the 1980s [248] and 1990s [249]. The rapid progression in this field is due to the vast knowledge gained during the 20th century, since the birth of synthetic plastics. Initially, petrol-derived polymers offered several advantages over traditional materials (metals, wood, etc.), such as low cost, light weight, ease of processing and adequate mechanical properties. However, the production of these materials presents several disadvantages, such as increasing fossil fuel price, cross-contamination issues and aiding global warming [250, 251]. In addition, some of these polymers, like bakelite, polyethylene, nylon are poorly biodegradable, which leads to significant polymer-generated waste [252].

For this reason, research into renewable, biodegradable polymers (such as cellulose, chitosan, chitin, alginic acid [253]) has attracted considerable interest over recent years, due to their more environmentally friendly nature. From these biopolymers, a wide variety of materials can be obtained for plastic applications (bioplastics). Among these bioplastics, Poly-Lactic Acid (PLA) remains the most used material in terms of production, with a total production of 0.92 million tonnes as of 2024 [254] (see Figure 1.11). This biopolymer finds its main use in flexible and rigid packaging, but it can be also used to produce consumer goods, in agriculture or in fibre production [254].

Global production capacities of bioplastics

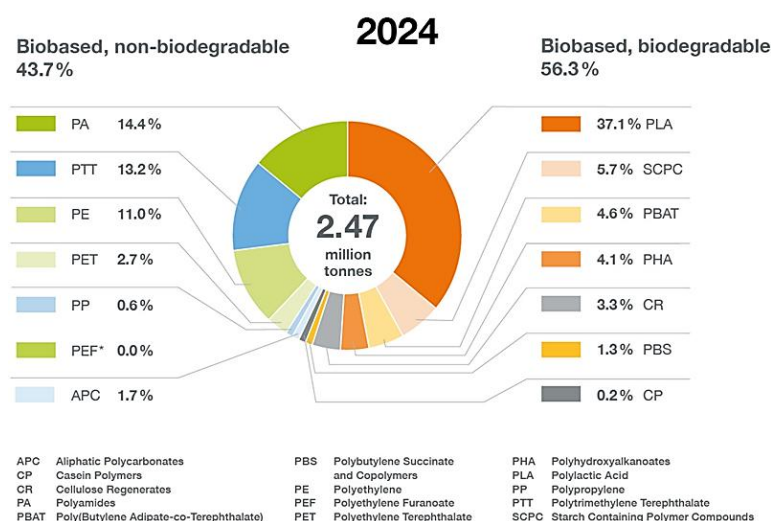


Figure 1.11: Global bioplastic production for the year 2024, divided into biodegradable and non-biodegradable polymers [254].

1.3.2.1. Poly-L-lactic Acid

Poly-L-lactic acid (PLLA) is a polymer derived from natural sources [255, 256], such as corn, wheat or straw, and it is biodegradable, decomposing into water and CO₂. The production of polylactic acid (PLA) also presents benefits over other biopolymers in that it is derived from the fermentation of sustainable sources, minimising the volume of landfill and allowing to tailor its properties through process modifications [257]. Currently, PLLA is the most widely used biopolymer in the packaging industry, with a global production capacity of approximately 900 ktonnes, which is expected to exceed 2.4 million tonnes before 2030 [254]. PLLA has also been classified as Generally Recognised As Safe (GRAS) by the U.S. Food and Drug Administration (FDA) [258].

PLLA production consists of three stages summarised below [259]:

- i. Lactic acid (LA) production: 2-hydroxypropionic (or lactic) acid is typically produced by microbial fermentation, although it can also be produced by chemical synthesis. There are two enantiomers of this material, L- and D-lactic acid, with the first one being used for PLLA production [260]. Common strains used in the microbial process are *Lactobacillus bulgaricus*, *Lactobacillus amylophilus*, *Lactobacillus leichmanii*, and *Lactobacillus delbrueckii*, working at 40°C with low O₂ supply [261].
- ii. Polycondensation of LA: PLA polymerisation is carried out at 150°C-250°C and pressures from 1 bar to vacuum. This process yields average molecular

weight oligomers which then undergo transesterification resulting in ring structures (lactide). While this process can be carried out without catalysts, their use is common to avoid by-product generation [259].

- iii. Ring opening polymerisation is a process used to obtain high molecular weight PLA. In this process, catalysts are employed in order to open the ring structure of the lactide. Furthermore, a precise control of the reaction parameters (time, temperature, type and concentration of catalyst) can help to control the ratio of L- and D-lactic acid polymer obtained [262].

PDLA is a polymer with poorer mechanical properties, produced in lower volumes and is more costly compared to PLLA, which typically exhibits good tensile strength, ductility and good biocompatibility [263, 264]. These properties are influenced by the molecular weight as well as its crystallisation behaviour. Highly crystalline PLLA usually displays high resistance to metabolic degradation, whereas the low crystalline amorphous form can be degraded in a few weeks and is more soluble. For example, amorphous PLLA is soluble in organic solvents like acetone, acetonitrile and methylene chloride [265], while crystalline PLLA is only soluble in dichloromethane and benzene at high temperatures.

PLLA also presents other valued properties including good thermal stability, which facilitates easier thermal processing, permeability, water resistance, oxygen barrier capacity, resistance to oils and fats and resistance to UV degradation. All of these features result in a sustainable polymer that has found application in a wide variety of fields, most notably for biological applications [265], medical uses [266], food packaging [261] or 3D printing [257]. In the adsorption field, this polymer has also shown great applicability for the removal of dyes [267-269], antibiotics [270], heavy metals [271-273], pesticides [274] and proteins [275, 276] acting as a scaffold for nanoparticles to adsorb, or as the adsorbent itself.

PLLA can be processed into various morphologies but for adsorption purposes, PLLA fibres are typically preferred over films or membranes [277]. This form provides a high surface-to-volume ratio, maximising the area available for adsorption and facilitates access to active centres. In addition, the porous structure of the fibres, the ability to control the diameter of the fibre and the ability to incorporate nanoparticles within the fibre are key factors in order to increase adsorption performance [278, 279]. Electrospinning is the most common technique to obtain polymer fibres [280, 281].

1.3.2.2. Electrospinning

Electrospinning is a technique used to produce extremely thin fibres with widths in the nanometre to micrometre range [282]. Typically, polymer solutions or melts are fed through a syringe which, upon application of a voltage (usually greater than 10 kV), creates an electric field that results in an electrified jet that flows towards a metallic collector [283, 284]. The resulting product is a nano-microfibre mat with a high surface-to-volume ratio that finds application in adsorption processes [285], smart textiles [286], tissue regeneration [287], drug delivery systems [288] or even facemask production for aerosol filtration [289, 290]. To successfully achieve fibre generation, several electrospinning parameters must be evaluated:

- **Solvent system:** The polymer must be completely dissolved in the chosen solvent, otherwise fibres will not be produced. In addition, solvents should display low boiling points and intermediate-to-high dielectric constants to ensure that they evaporate easily and do not interfere with the electric field. Common examples of solvents used for electrospinning PLLA are acetone, butanol, chloroform, dichloromethane, dimethylformamide, dimethylsulfoxide, ethyl formate, hexafluoroisopropanol, N-methylpyrrolidone, tetrahydrofuran, and 2-methyl tetrahydrofuran [291-294].
- **Polymer concentration:** Changes in polymer concentration (as well as viscosity) can significantly alter the final structure of the fibre. Studies on different biopolymers have shown that increasing the concentration from 5% to 20% w/w can reduce bead formation and produce continuous fibres, but also lead to fibres with increased diameter (not typically recommended for adsorption applications) and a non-uniform structure [295, 296]. However, viscosity also plays an important role in the final fibre as it is directly related to chain entanglement [297]. If a solution does not have sufficient viscosity (and chain entanglement), the resulting polymer jet will break up into low surface tension droplets, which will reach the collector in the form of beads [298]. Figure 1.12 shows the main electrospinning products obtained as a function of viscosity and polymer concentration.

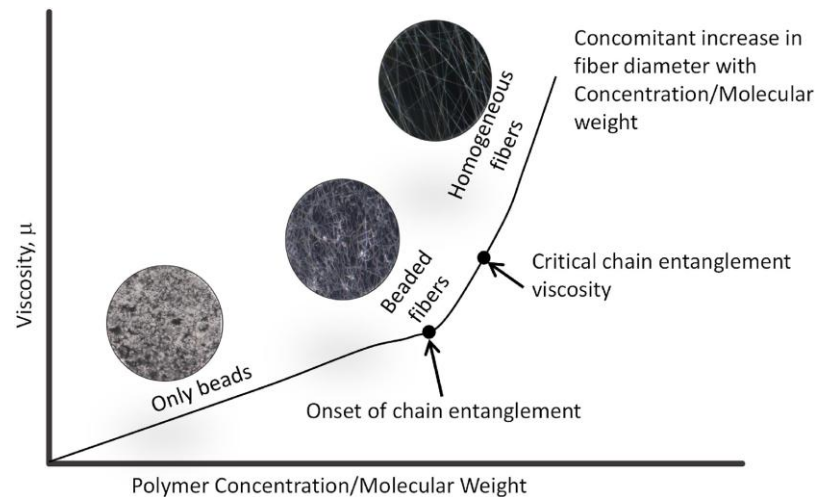


Figure 1.12: Electrospinning products as a function of viscosity and polymer concentration [298].

- Voltage:** It is also a critical parameter as it creates the electrical field responsible for fibre development. If the chosen voltage is too low, then the solvent will not evaporate completely, resulting in the formation of droplets instead of fibres. Previous studies have shown that, as the voltage increases, the fibre diameter can markedly decrease, to the point where selecting an excessive voltage leads to the formation of beads or beaded nanofibres [299-301]. The choice of voltage varies considerably for each polymer.
- Needle-to-collector distance:** Several studies determined that the needle-to-collector distance plays a key role in the path of the charged polymer jet. It is known that short distances (and therefore, short travel times) involve shorter solvent vaporisation times, which can result in fibre defects and bead morphology [298]. On the other hand, increasing distance usually promotes longer and thinner fibres. However, beyond a certain threshold, the influence of electrical field diminishes, resulting in a larger fibre diameter, bead formation and defects in the final fibres [295, 302] (a phenomenon called Rayleigh instability). For this reason, a needle-to-collector distance between 10 to 16 cm is typically chosen.
- Solution flow rate:** Very low values (< 1 mL/h) result in small, short fibres rather than a continuous mat. On the other hand, if the flow rate is too high (> 5 mL/h), there is a high probability that aggregates will form at the end of the needle, blocking the flow and making it impossible to obtain a useful product.

- **Electrospinning time:** Although there is not extensive literature on this parameter, some studies have confirmed that the electrospun product is likely to display a continuous fibrous structure as the settling time increases, improving the stability of the process [303]. Furthermore, studies on gelatin and polyurethane fibres indicate that fibre diameter can increase with spinning time [303, 304]. Moreover, the study on polyurethane also showed that the tenacity of the mat increases linearly with electrospinning time.

1.3.3. Transition metal dichalcogenides (TMDCs)

As previously noted, the incorporation of nanoparticles is a common approach in order to improve the properties/performance of a material. For example, in the electrochemical field, it is common to find nanoparticles based on carbonaceous materials (graphite [305], graphene [306], graphene oxide (GO) [307], carbon nanotubes [308]) as well as transition metal oxides (FeO [309], MnO₂ [310], NiO [311]), mixed metal oxides [312]) or metal oxide frameworks, MOFs [313]. However, more recent approaches are focusing on the use of MXenes [314] and, in particular, transition metal dichalcogenides (TMDCs) [172, 315] due to their better environmental profile compared to traditional nanomaterials.

The structure of TMDCs was first determined by Pauling approximately 100 years ago [316], in 1923, but it was not until the second half of the century that research on TMDCs became widespread. By the 1960s, more than 60 types of TMDCs were known, 40 of which had a layered structure [317]. In the following years, research was focused on improving the synthesis of TMDCs. In the case of MoS₂, for example, the first methodology (1963) was based on the use of adhesive tapes to develop ultrathin layers [318], but it was not until the mid-80s that MoS₂ monolayers were successfully produced, following an exfoliation process [319]. Extensive research on carbon nanotubes and fullerenes (1D materials) during the 1990s also stimulated the research on inorganic fullerenes and nanotubes [320], leading to the development of various layered TMDCs, such as WS₂ nanotubes [321] (2D) or MoS₂ nanotubes and nanoparticles [322], which have been used for several applications, as discussed later.

TMDCs present a layered structure in which a transition metal atom (such as W or Mo) is inserted between layers of chalcogen atoms (mainly S, Se and Te), forming a MX₂ unit. Each layer is covalently bonded, while the different layers are bonded

by weaker Van der Waals forces [323]. This arrangement allows the exfoliation of single TMDC layers [324], which is important because multi-layered TMDCs exhibit typical semiconducting behaviour, but when reduced to a single layer their conductivity is enhanced [325], improving their performance in field emitting transistors and optoelectronics [326]. Furthermore, TMDCs typically crystallise in two different phases: the 2H phase (trigonal prismatic, stable, semiconducting) and the 1T phase (octahedral, less stable, metallic) [324]. The arrangement of these phases influences not only the electronic behaviour of the TMDCs but also their mechanical properties. TMDCs are flexible materials due to the Van der Waals forces between layers, but also mechanically resistant due to the presence of covalent bonds. Additionally, they display a high Young's modulus [327], making them suitable for flexible, durable electronic and optical devices.

TMDCs have received particular attention owing to their potential use in environmental applications, as well as the improvements they offer in electrochemical devices when combined with hydrochars [172]. These materials can increase the conductivity of the carbonaceous matrix, thereby increasing capacitance values, and consequently, energy and power densities. One of the main features of TMDCs is their anisotropy, including different structural forms (0D, 1D and 2D structures are available), which leads to excellent mechanical and tribological properties. These properties, together with their biocompatibility, have led to their use in polymer composites to improve wear resistance and crystallisation behaviour [328-335], as well as in medical lubricants and coatings [336], transistors [337], and energy storage devices, such as batteries and supercapacitors [315].

In the latter field in particular, the combination of biomass-derived, hydrothermally treated carbons with TMDCs presents an excellent opportunity for environmentally friendly energy storage materials, due to the sustainable nature of these blends. Although literature on this topic is scarce, Table 1.3 and Table 1.4 provide a summary of representative successful examples of TMDC+HTC combination for superior electrochemical performance, where MoS₂ stands out as the most used TMDC for these devices, mainly due to studies reporting that monolayer MoS₂ can exhibit good surface areas, is easy to disperse, and can also enhance thermal and mechanical properties within the polymer matrix [338], combined with the barrier properties they provide [328].

Table 1.3: Examples of TMDC+HTC prepared carbon combinations for batteries.

Li-ion Battery				
Electrode material		Electrolyte	Capacity	Stability
Biomass source	TMDC		mA h/g	
Corn stalk [339]	MoS ₂	LiPF ₆ in EC/DEC/DMC ^a	>1300	1129 after 200 cycles
Chitosan [340]	MoS ₂	LiPF ₆ in EC/DMC	>1000	Stable over 100 cycles
Glucose [341]	MoS ₂	LiPF ₆ in EC/EMC/DEC	484	>480 after 50 cycles

^a Ethyl carbonate (EC), Diethyl carbonate (DEC), Dimethyl carbonate (DMC), Ethyl methyl carbonate (EMC); ^b Specific capacitance measured at 1 A/g unless specified otherwise.

Table 1.4: Examples of TMDC+HTC prepared carbon combinations for batteries and supercapacitor electrodes.

Supercapacitor				
Electrode material		Electrolyte	Capacitance ^b	Stability
Biomass source	TMDC		F/g	
Tendu leaf [342]	MoS ₂	1M Na ₂ SO ₄	261* (2mV/s)	89% after 5000 cycles
Glucose [343]	MoS ₂	1M Na ₂ SO ₄	186*	95% after 1000 cycles
Corn cob [344]	MoS ₂	1M Na ₂ SO ₄	38 */333 **	82% after 7000 cycles
Pomelo peel [345]	MoS ₂	3M KOH	361 **	94% after 2000 cycles
Corn stalk [339]	MoS ₂	1M Na ₂ SO ₄ in EC/DEC/DMC	338 **	79% after 5000 cycles
Glucose [346]	MoS ₂	3M KOH	210 **	Increase 5% after 1000 cycles

* In a 2-electrode setup ** In a 3-electrode setup.

Beyond the excellent results obtained through use of TMDC-modified carbons, it is interesting to compare the influence of these nanofillers on the electrochemical behaviour of the produced electrodes. For example, studies on corn stalk-based electrodes for Li-ion batteries report a capacity of 504 mA h/g after 100 cycles [347], that is less than half of the capacity displayed by the TMDC-doped material (see Table 1.3). The same can be observed for these types of material used in supercapacitor type applications, displaying substantially higher capacitances than those of hydrothermally-treated, non-doped carbons (presented in Table 4.12).

1.3.3.1. Tungsten disulphide

Among TMDCs, MoS₂ is typically preferred over other chalcogenides due to its previously mentioned features. However, tungsten disulphide (WS₂) also presents interesting characteristics that can make it a sustainable alternative to molybdenum disulfide. Firstly, WS₂ displays a higher corrosion resistance than MoS₂ [348]. It also presents higher thermal stability and is able to work at a much broader temperature range than MoS₂, therefore displaying greater durability [349]. Furthermore, WS₂ presents a slightly lower electronic bandgap (1.50 eV vs. 1.58 eV) [350], and toxicity studies prove that tungsten is not considered an important human health hazard, while molybdenum can be poisonous by inhalation and ingestion [351]. All these features favour the use of tungsten disulphide instead of MoS₂.

Apart from the comparison with molybdenum, tungsten disulphide has attracted considerable interest because of its graphene-like, layered structure. Furthermore, WS₂ nanosheets display excellent Young's modulus and flexibility, superior to other tungsten chalcogenides [352]. This material has a semiconducting behaviour [353], which finds applications in optoelectronics and electrocatalysis [354-357]. In addition to its electronic features, it exhibits good lubrication properties, even under high temperatures and pressures, making it an optimal material for the automotive industry [358, 359]. As noted before, WS₂ also shows high thermal conductivity and resistance to corrosion (widely applicable in coatings [360, 361]), apart from being very biocompatible, promoting its use for biomedical applications [362, 363].

Finally, although research into the use of MoS₂ for energy storage applications is more prevalent than in WS₂, some examples of this material have already been reported [364, 365]. For example, in the case of supercapacitors, a highly stable symmetric device was developed by growing WS₂ nanoflowers on a nickel foam support. The EDLC obtained an impressive specific capacitance of 204 F/g at 5mV/s and maintained 100% stability over 10000 cycles [366]. Additionally, WS₂/PPy nanowires were synthesised and used as EDLC electrodes, achieving a specific capacitance of 338 F/g [367], demonstrating the potential of these materials for electrochemical applications.

1.3.4. TMDC-Polymer nanocomposites strategies

The incorporation of TMDCs into other materials paves the way for the development of hybrid composites that combine the properties of both components, resulting in flexible, conductive, tunable and easy to process materials. Depending on the desired end property (or application), different materials or processes can be used. With respect to TMDC-polymer nanocomposites, there are various reports using polyurethane [368], polypropylene [369], polyvinyl alcohol [370], or polyetheretherketone [334], among many other examples [329, 333, 335, 371-376]. However, TMDC / PLLA blends, and in particular WS₂, are of growing interest due to their strong sustainable profile, low cytotoxicity, and importantly, good compatibility – the latter resulting in synergistic improvements in crystallisation, thermal stability, processability, and wear resistance [331, 332, 377]. Although WS₂ nanoparticles can be found in 0D, 1D, and 2D forms, there are only a few reports on the preparation of 0D and 1D-WS₂ / PLLA blends. For 0D nanoparticles (WS₂ inorganic fullerenes), the authors prepared PLLA-WS₂ nanocomposites via direct melt compounding using a micro-extruder [328]. In order to prepare PLLA nanocomposites containing WS₂ nanotubes (1D), the authors dispersed small amounts of TMDC (1% w/w) and polymer in an ethanol solution, followed by melt-mixing in an extruder to efficiently disperse the nanofiller. For both 0D and 1D morphologies, results showed that the TMDCs exerted a nucleating effect on PLLA, which increases crystallisation enthalpy and enhances the mechanical properties of the polymeric blends (increase of 16% compared to neat PLLA) [327]. On the other hand, blends of PLLA and 2D-WS₂ have also been reported [328], following the same procedure as that for the 1-D morphology. Results from this study showed that the incorporation of these nanofillers induced a significant reduction on the crystallisation rate of PLLA.

Furthermore, some studies have reported that TMDCs possess antimicrobial properties [378, 379]. This last factor is of special interest, as water treatment experiments carried out using biopolymers are often associated with the growth of algae and bacteria (biofouling), which can severely compromise the adsorption performance [380, 381].

2. Objectives

As discussed in the Introduction, the inability to fully harness the energy potential of renewable sources, and the widespread pollution of water as a result of extensive dye usage are two of the most critical challenges of our generation. Energy storage systems and contaminant adsorption technologies offer promising pathways to address these problems. Nevertheless, these solutions still encounter several limitations, which this thesis seeks to address.

The primary objective of this work is the development of functional, sustainable materials that serve three key roles: i) supercapacitor electrodes for rapid, durable and optimal energy storage, ii) electrocatalysts to promote efficient oxygen reduction reactions, and iii) adsorbents for the effective removal of dyes from aqueous media.

To this end, the thesis will adhere, where possible, to the “12 Principles of Green Chemistry” set out by Anastas and Warner in 1998 [382]. Specifically, the carbonaceous materials will primarily be derived from cellulose, the most abundant biopolymer in nature. These materials will be synthesised through hydrothermal carbonisation, a green methodology that yields highly carbonaceous structures with minimal environmental impact compared to conventional carbonisation techniques, followed by activation.

To further enhance the properties of these cellulose-based carbons, different additives will be incorporated. In particular, albumin—a sustainably sourced egg-derived protein—will be used to increase the carbons’ nitrogen content, while WS₂ nanosheets will be added to enhance conductivity and electrochemical performance. The influence of these substances on the nature of the carbon will be assessed through physicochemical characterisation techniques, including TGA, XPS, EDX, FTIR, Raman and gas sorption analyses.

Afterwards, their performance in energy storage applications will be evaluated. Symmetrical supercapacitors will be assembled using these ACs as electrodes, and an evaluation of their electrochemical performance will be carried out through different techniques (Cyclic voltammetry, galvanostatic cycling and electrical impedance spectroscopy). Additionally, solutions of these materials will be prepared and deposited onto glassy carbon electrodes to assess their

electrocatalytic activity in ORR, a key reaction in fuel cells, and compared to commercial Pt-based catalysts.

For wastewater remediation, the ACs will be combined with a biopolymeric matrix consisting of PLLA. Various PLLA-AC forms will be prepared and their adsorption capacity evaluated. After screening, the optimum morphology will be further enhanced with WS₂ nanosheets addition and the hybrid material's mechanical and thermal properties assessed before extensive adsorption testing.

Finally, four different dyes will be tested for adsorption: two anionic dyes (Congo Red and Methyl Orange) and two cationic dyes (Methylene Blue and Rhodamine B). The adsorption capacity, isothermal and kinetic properties of the PLLA-WS₂-AC material will be evaluated to elucidate the adsorption mechanism.

The specific aims of the selected applications will be detailed in the corresponding sections. Figure 2.1 illustrates the procedural framework and applications that will be explored in relation to these objectives and aims:

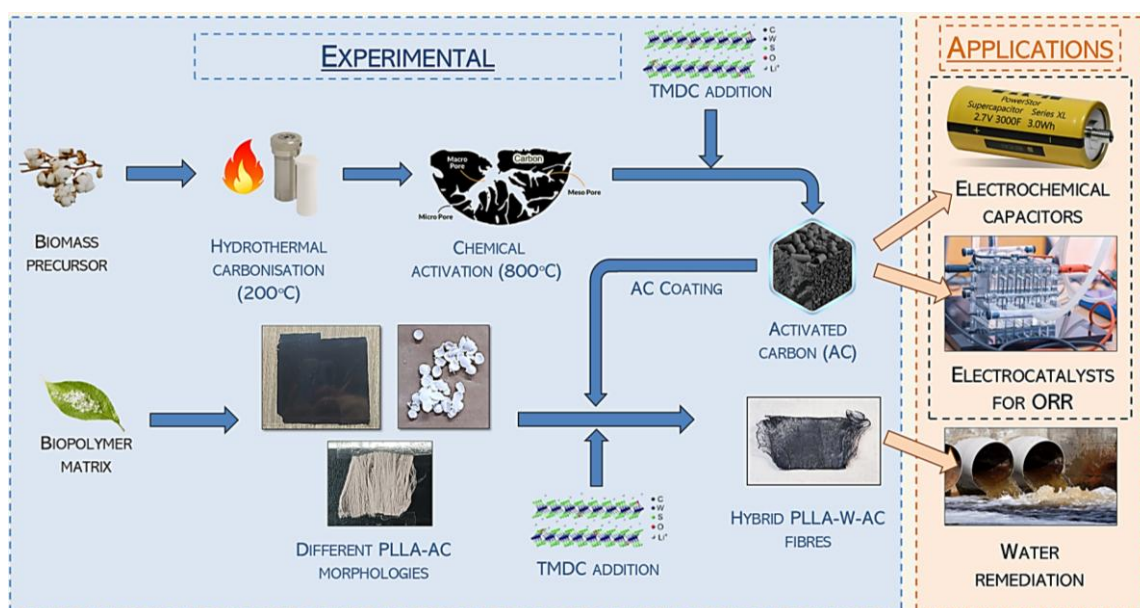


Figure 2.1: Schematic of the proposed objectives for the thesis.

3. Materials and experimental techniques

3.1. Materials

3.1.1. Cellulose

Microcrystalline cellulose in form of powder was purchased from Sigma Aldrich® (Ref: 435236) and used as supplied. This material contains approximately 7% moisture by mass and 0.001% heavy metals. Its particle size distribution is approximately >40% +200 mesh.

3.1.2. Albumin

Chicken egg albumin (powder) was supplied by Sigma Aldrich® Ref: A7641) and used without further modification. It has a purity of 98%, and a water content of <6%. It is soluble in water (40 g/L) and has a nitrogen content from 13% to 16%.

3.1.3. Poly-L-lactic Acid

Poly-L-lactic acid, PLLA, (Ref: ME336310/1) was purchased in granular form from Goodfellow® and used as received. This granular material has a molecular weight of approximately $1.5 \cdot 10^5$ g/mol and a density of 1.25 g/cm³.

3.1.4. Tungsten disulphide

WS₂ nanosheets (Ref: WS2PN005) were acquired from ACS Material® and used as supplied. This material has a density of 7.5 g/cm³ and a diameter and thickness of approximately 20-500 nm and 1 nm, respectively.

The rest of chemical reagents (potassium hydroxide, isopropyl alcohol, sulphuric acid, hydrochloric acid 36%, and chloroform) were purchased from Sigma Aldrich and used as received. The analysed cationic dyes (Methylene Blue and Rhodamine B) were supplied from ACROS Organics, and the anionic dyes (Congo Red and Methyl Orange) were purchased from Fisher Scientific. All were used as supplied.

3.2. Characterisation techniques

This section describes the fundamentals and experimental procedure of each technique used to characterise the structure, composition, as well as thermal, electrical and mechanical properties of the synthesised materials:

3.2.1. Gas sorption porosimetry

Theory:

Gas sorption porosimetry is a technique used to characterise porous materials, particularly porous solids and powders. It typically involves the use of subcritical fluids (e.g., nitrogen at $T = 77$ K, argon at 87 K, carbon dioxide at 273 K), but also organic vapours and supercritical gases, and is based on the interaction between the adsorbate and the solid [383]. This process yields an adsorption/desorption isotherm, which helps detail the porous structure of the material. According to IUPAC, gas sorption isotherms can be divided into 6 different types, as shown in Figure 3.1.

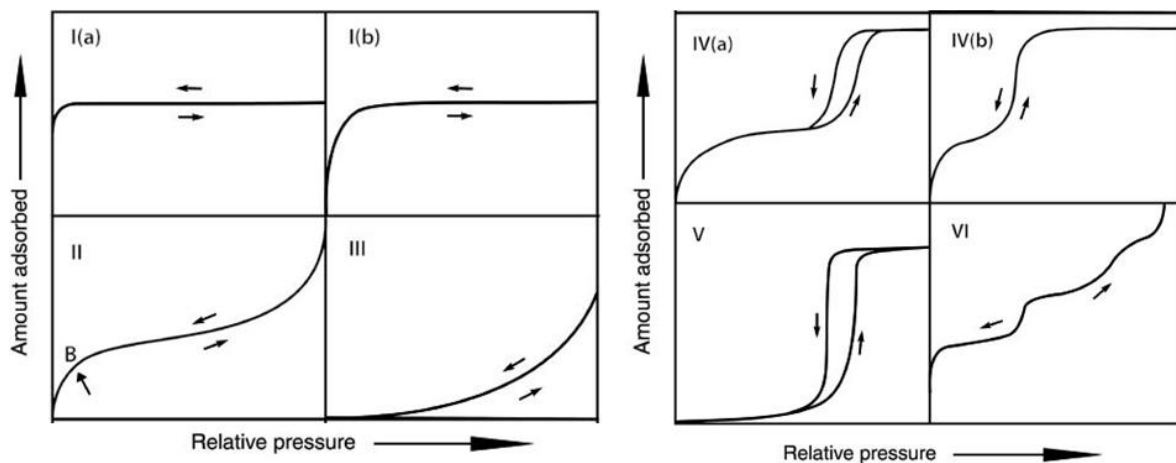


Figure 3.1: Classification of adsorption isotherms according to IUPAC [383].

- Type I isotherms are representative of microporous solids. Their concave shape indicates a rapid adsorption at low pressures. Type I (a) is characteristic of samples with narrow micropores whereas type I (b) represents samples with wider micropores and narrow mesopores.
- Type II and III isotherms are common in macroporous and non-porous adsorbents. The main difference between both is the existence of the B-point, which represents the coverage of the monolayer and the onset of multilayer adsorption.

- Type IV isotherms are present in mesoporous materials, combining monolayer and multilayer adsorption with pore condensation (only in type IV (a) isotherms, represented by hysteresis loops). The occurrence of pore condensation implies that pores exceed a critical width (4 nm when working with N₂ at 77 K). On the other hand, type IV (b) represents a reversible sorption process for mesopores with diameters < 4 nm.
- Type V isotherms show a similar shape to type III at lower pressures (weak adsorbent-adsorbate interaction), followed by a hysteresis loop at higher pressures. These isotherms are characteristic of water adsorption on hydrophobic microporous and mesoporous materials.
- Finally, Type VI isotherms represent layer-by-layer adsorption on uniform, non-porous surfaces. It is common to observe these isotherms for the adsorption of argon or krypton on graphitised carbon blacks [383].

Experimental conditions:

Two different gas sorption tests were carried out. First, as a preliminary test to assess the influence of the activating agent on the prepared activated carbons, different samples were sent to INCAR-CSIC for testing using their external services. Testing was carried out using a Micromeritics ASAP 2000 instrument, with nitrogen as the adsorbate at 77 K. Before testing, samples (100 mg) were degassed at 200 °C for 6 hours (and measured in a P/P_0 range of 10^{-6} -0.99 for adsorption and 0.99-0.15 for desorption).

After these preliminary tests, the porosity of the final carbons was thoroughly characterised using both N₂ (77 K) and CO₂ on a Micromeritics 3Flex analyser. This was carried out personally during a stay at the ICGM-CNRS (Montpellier, France). For N₂ experiments, samples (approximately 100 mg) were degassed at 200 °C for 12 hours and measured in the P/P_0 range of 10^{-6} -0.995. CO₂ sorption experiments were performed in the same instrument at 273, 298 and 323 K using an ethylene glycol/water mixture (20% v/v) as a refrigerant. Measurements were conducted in the partial pressure range of 10^{-4} -0.03.

Specific surface area was calculated using the Brunauer-Emmet-Teller (BET) method in the pressure range of 0.05-0.3, applying the Rouquerol criteria. Total pore volume was determined through N₂ adsorption isotherms. Micropore area and volume were calculated using the t-plot method with at least 10–15 points using Microactive software. Mesopore volume was calculated using NLDFIT method for slit-shaped pores, and pore distribution was determined through a NLDFIT method

combining both nitrogen and carbon dioxide isotherms using the SAIEUS® software, fixing a value of $\lambda=2.75$ and keeping standard deviation values below 5.

3.2.2. Scanning electron microscopy (SEM)

Theory:

Scanning electron microscopy is a characterisation technique that generates images of the surface of a material with very high spatial resolution, in the micrometre range. SEM is based on the application of a voltage difference that directs an electron beam toward the sample, with electromagnetic lenses that maintain the electrons' path. When the electrons hit the sample, they scatter in two ways, resulting in two types of detectable electrons:

- Secondary electrons which are scattered in non-horizontal or vertical directions are captured by a positively charged detector (around 3000 V). They are primarily responsible for the SEM image.
- Back-scattered electrons are reflected back to the source and are captured by a detector located near the electron beam. These electrons play a minor role in the generation of the SEM micrograph.

The main difference between the two types of electrons is that secondary electrons interact directly with the sample's surface, while back-scattered electrons penetrate deeper into the sample. The combination of both types of electrons generates a high-resolution image of the samples' surface [307].

Experimental conditions:

A Hitachi SU8000, ultra-high field emission scanning microscope (FE-SEM), available at ICTP-CSIC, was used to assess the surface structure of the developed materials. Micrographs were taken in a magnification range from x400 to x100,000 under voltages of 1-2 kV and analysed using ImageJ software.

3.2.3. Transmission electron microscopy (TEM)

Theory:

TEM is a morphological characterisation technique with strong similarities to SEM. In this technique, a power source emits a beam of electrons towards a very thin sample. Depending on the samples' thickness and atomic composition, some electrons will scatter after colliding with the sample. These electrons are

subsequently directed and collected by lenses, creating an image of the structure of the sample consisting of different shades of grey, corresponding to the degree of scattering of the incident electrons [384].

Experimental conditions:

Samples were sent to the ICGM-CNRS and analysed on a JEOL2200 FS microscope operating at 200 kV. Prior to measurement, the samples were ground for 5 minutes in an Agate mortar and less than 1 mg of each sample was dispersed in 1 mL of ethanol and sonicated for 3 minutes. 3 drops of this dispersion were placed on a carbon film supported copper grid and sent to measure. During testing, samples were measured at different angles with an angular increment of 2°, ranging from -40° to 40°.

3.2.4. Fourier-transform infrared spectroscopy (FTIR)

Theory:

Infrared spectroscopy is an absorption technique that analyses the infrared region of the electromagnetic spectrum to identify functional groups. It is based on the absorption of specific vibrational frequencies, each characteristic of a particular molecular bond. Molecules will absorb IR radiation when the energy of the light beam matches the vibrational energy of the molecule, producing an IR spectrum of vibrations associated with a change in the dipole moment.

There are two main types of vibration with several subtypes: stretching (symmetric and asymmetric), which is associated with changes in the interatomic distance between atoms, and bending (including scissoring, rocking, wagging and twisting), which alters the angles between bonds. The combination of both creates a unique spectrum for each material, making it possible to determine the structure and functional groups of a sample [385].

Fourier-transform infrared spectroscopy (FTIR) is an advanced version of this technique that uses an interferometer to eliminate dispersive elements, increase the signal-to-noise ratios and allow faster data acquisition. FTIR measures the amount of transmitted light at each frequency (transmittance), which can be converted into quantitative information using the Beer-Lambert law [386].

Experimental conditions:

Cellulose and carbon precursors were analysed by FTIR. Samples were ground and mixed with powdered KBr (1 mg of sample with 150 mg of KBr). These materials

were further dried and pressed into pellets for measurements at room temperature. Spectra were obtained using a Perkin Elmer 2000 instrument available at ICTP-CSIC with 100 scans per sample over a wavenumber range from 4000 to 400 cm^{-1} , at a resolution of 4 cm^{-1} . Spectra were analysed using SpectraGryph software.

3.2.5. Raman spectroscopy

Theory:

Raman spectroscopy, like FTIR, is a characterisation technique based on the vibrational study of molecules. Raman analyses molecular vibrations and rotations by studying the inelastic scattering of monochromatic light. In this technique, a sample is irradiated with high-energy monochromatic radiation. The majority of the photons will undergo elastic scattering, a phenomenon known as Rayleigh radiation. However, a small fraction of photons will scatter inelastically, providing insight into the molecular properties of the sample.

The Raman effect occurs when photons interact with a molecule's electron cloud, raising the molecule from its ground state to a higher energy state and then allowing it to relax into an excited vibrational state, producing Stokes Raman scattering. Conversely, anti-Stokes Raman scattering occurs when the molecule is already in an excited vibrational state before interaction. Typically, Stokes scattering is more intense than anti-Stokes, due to a higher number of electrons in a ground state than in an excited vibrational state [387].

For the Raman effect to be observed, the interaction must cause a change in the polarizability of the molecule; larger shifts in polarisability result in more intense Raman scattering. Since the fraction of inelastically scattered light is small, Raman spectroscopy requires the use of monochromatic radiation, using lasers in the visible, near UV and near IR range.

In order to determine the nature of the carbonaceous materials analysed by Raman spectroscopy, it is necessary to deconvolute the acquired spectra. To perform an accurate deconvolution, it is recommended to follow Sadezky's methodology for soot and carbonaceous materials [388]. Briefly, this methodology aims to describe the Raman spectrum of carbonaceous materials as a sum of 5 different peaks:

- i) G peak: A strong peak centred around 1580 cm^{-1} . It is associated with the vibration of ideal graphite lattices [389]. Present in carbons as well as disordered and highly ordered graphites.
- ii) D1 (D) peak: Very strong peak when measuring soot, but slightly less intense in disordered graphite. It appears at frequencies close to 1350 cm^{-1} and it is related to the breathing mode of sp^2 carbon atoms [390]. Not present in highly ordered graphites.
- iii) D2 (D') peak: Intense peak in carbons, but weak in disordered graphite. This peak appears at 1620 cm^{-1} . The related vibrational mode is also a disordered graphite lattice, but is associated with the surface of the graphene layers [390].
- iv) D3 (D'') peak: Appears only in carbons, not in graphite, with medium intensity. It usually shows a peak centred around 1500 cm^{-1} and it is related to the amorphous structure of carbons (can be fitted using either Gaussian [391] or Lorentzian [392] curves).
- v) D4 (I) peak: Weak peak showing only in carbons at frequencies close to 1200 cm^{-1} . This peak is also related to the vibration of the disordered graphitic lattice [393].

Experimental conditions:

The activated carbons were analysed through Raman spectroscopy using a confocal Raman microscope (Renishaw Raman in via Reflex) at the ICTP-CSIC. The Raman spectra of the samples were collected at room temperature in the frequency range between 2000 and 540 cm^{-1} using a solid-state diode laser (785 nm wavelength) as the excitation source. The spectra were analysed using Wire 3.0 software.

3.2.6. Elemental analysis

Theory:

Elemental analysis, or microanalysis, is a technique that determines the elemental composition of a sample in terms of its carbon, hydrogen, nitrogen, and sulphur content. This method is based on the combustion of samples in an oxidative atmosphere at approximately 1000°C . The resulting gases (CO_2 , H_2O , NO_x , and SO_x) are carried by helium and further converted to CO_2 , H_2O , N_2 , and SO_2 . These gases are then separated using dedicated columns and quantified by infrared detectors (for CO_2 , SO_2 and H_2O), and by a thermal conductivity detector for N_2 .

Finally, the content of each element is calculated based on the initial sample weight [387].

Experimental conditions:

Elemental microanalysis tests were performed at least in duplicate using a Leco Analyzer CHNS 932 (at ICTP-CSIC characterisation service). To test the samples, carbon, hydrogen, nitrogen and sulphur content were measured using a mass of 5 mg for each sample. Since further thermogravimetric analyses (TGA) confirmed the absence of inorganic ash, oxygen content was calculated using Equation 3.1:

$$\%O = 100\% - \sum \%C, H, N, S \quad \text{Equation 3.1}$$

3.2.7. Energy dispersive X-Ray spectroscopy (EDX)

Theory:

Energy dispersive X-Ray spectroscopy (EDX) is a characterisation technique commonly coupled with SEM measurements. It allows the determination of the chemical composition of a sample by detecting the characteristic X-Rays emitted by the sample. In brief, when a sample is bombarded with high-energy electrons, the electrons in the inner surface of the sample are ejected, creating an electron deficiency that is filled with electrons from higher energy levels. This excess energy is released in form of X-Ray photons, which have a specific energy for each atom. An EDX detector can measure this energy and generate a spectrum whose peaks represent the characteristic energies of the elements present. This technique provides both qualitative and quantitative information about the elemental composition of the sample by analysing the generated peaks [394].

Experimental conditions:

EDX measurements of the final carbons were obtained using an ultra-high field emission scanning microscope (Hitachi SU8000) at the ICTP-CSIC, measuring each sample twice under a voltage of 15 kV.

3.2.8. X-Ray photoelectron spectroscopy (XPS)

Theory:

X-Ray photoelectron spectroscopy is a spectroscopic technique based on the photoelectric effect, in which X-rays irradiate a material and cause the ejection of

core electrons from the surface atoms of the sample [394]. The kinetic energy of the electrons ejected from the surface can be measured to determine their binding energy. Since each element and its chemical functionalities produce characteristic binding energies, this technique can be used to determine the chemical composition of a sample.

Experimental conditions:

Samples were sent to the ICGM-CNRS for XPS testing using a Thermo Electron ESCALAB 250 instrument. Experiments were conducted using an Al K α excitation source at 1486.6 eV. The photoelectron spectra were calibrated using the binding energy peak of C-Si (SiC) at 282.5 eV. The charge was compensated by a low-energy electron beam (-2 eV).

3.2.9. Thermogravimetric analysis (TGA)

Theory:

TGA is a technique used to determine the thermal stability of a sample. In TGA tests, a high precision microbalance continuously measures the mass of a sample as it is heated under a controlled atmosphere (inert or oxidative). This process can be isothermal or, more commonly, dynamic, where the sample is heated at a constant rate. In addition, TGA instruments can also display the derivative of the mass-temperature curve, called DTG, which shows the rate of mass change as a function of temperature or time. A constant mass results in a DTG value of 0, while a peak indicates the maximum rate of mass loss [307].

This technique is extremely useful for studying decomposition, thermal stability, composition, purity, moisture content and volatiles. In the context of this work, its main use is to analyse the thermal stability of the developed carbons.

Experimental conditions:

For all experiments a TA Instruments Q50 Thermogravimetric analyser was used. Typical experiments consisted of heating samples of approximately 10 mg from an equilibrated temperature of 50 °C to 800 °C at a heating rate of 10 °C/min under both inert and oxidising atmospheres followed by cooling to room temperature. Universal Analysis software was used to analyse the data.

3.2.10. Differential scanning calorimetry (DSC)

Theory:

DSC is a thermal analysis technique that measures the heat flow exchanged between a sample and its surroundings. In a heat flux DSC, the sample and an inert reference material are subjected to identical heating or cooling processes. During transitions such as melting, crystallisation and glass transition, the sample absorbs or releases heat at a different rate from the reference. This creates a temperature difference between both materials, proportional to the heat flow. This temperature difference is recorded and provides detailed thermodynamic information about these transitions. In addition, by integrating the area of the peaks associated with each transition, the enthalpy of each process can be determined [387].

Experimental conditions:

The crystallisation behaviour of the samples was investigated through dynamic DSC tests. Experiments were performed using a TA Instruments DSC25 calorimeter, at both the ETSII-UPM and ICTP-CSIC, under a nitrogen purge. Samples (2-4 mg) were sealed in aluminium pans and heated to 225 °C (at a ramp of 10 °C/min) and held at this temperature for 5 minutes to erase any thermal history. Afterwards, melted samples were cooled down to 0 °C under different cooling rates (1,2,5,10 and 20 °C/min), and again heated to 225 °C at a heating rate of 10 °C/min. DSC results were evaluated using TRIOS software.

3.2.11. Tensile tests

Theory:

The mechanical properties of a material can be determined by destructive tensile testing. Tensile testing equipment generally consists of an extensometer, a load cell, and two clamps (one fixed and one movable). A dumbbell-shaped sample is attached between the clamps. These experiments can monitor the applied force and the resulting deformation as the clamps separate at a controlled rate along the vertical axis. The instrument can measure the elongation of the material and the contraction of its cross section until it breaks. These measurements yield a plot correlating stress (ratio of applied force to initial cross-sectional area) and elongation (expressed as a percentage of the initial length). Several properties can

be determined from this, such as Young's modulus (stiffness of the material), tensile strength (maximum stress in the curve) and strain at break [387].

Experimental conditions:

The mechanical properties of the prepared samples were evaluated using an INSTRON 3366 dynamometer at the ICTP-CSIC. Samples were measured under a load cell of 1 kN, with a crosshead speed of 2 mm/min and a distance between clamps of 2 cm. The dumbbells were made from fibres using a 35.2 mm high and 2 mm wide die.

3.2.12. Electrical conductivity

Theory:

The determination of electrical conductivity is based on the movement of electrons through a material under application of a voltage difference, which creates an electric field. Conductivity measures the ability of a material to conduct an electric current and is dependent on factors such as the structure of the material, density and mobility of charge carriers and temperature. According to Ohm's law, conductivity can be calculated as the relation between the current density and the applied electric field. In practice, it is determined using specific equations according to the measurement technique. Conductivity measurements are typically undertaken using a four-point probe [387] or impedance spectroscopy [395].

Experimental conditions:

Tests were performed on a Solartron 1480 multichannel potentiostat/galvanostat available at the ICTP-CSIC, using the CorrWare software in a 4-probe system. For this measurement, an amount of powdered material was inserted into a poly(methyl methacrylate), PMMA, container with metallic ends connected to the potentiostat. An image of the material container, and its dimensions is presented in Figure 3.2.

In order to determine the resistance of the material, 4 measurements were carried out at a constant current over a voltage range of 10-25 mV. Conductivity results were analysed using CView® software.

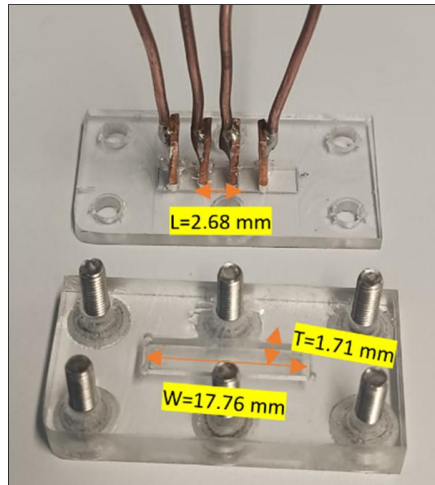


Figure 3.2: In-house manufactured 4-probe conductivity sample holder used to test the prepared samples.

3.2.13. Electrochemical characterisation

3.2.13.1. Cyclic voltammetry (supercapacitors)

Theory:

Cyclic voltammetry (CV) is an electrochemical characterisation technique in which a potential difference is applied cyclically to an electrode at a constant scan rate, measured in V/s. This technique is useful for analysing the charging and discharging processes, as well as for identifying the energy storage mechanism. These mechanisms primarily include the electrochemical double layer, typically associated with a rectangular shaped voltammogram, and pseudocapacitance, which appear as redox peaks in the voltammogram, as depicted in Figure 3.3.

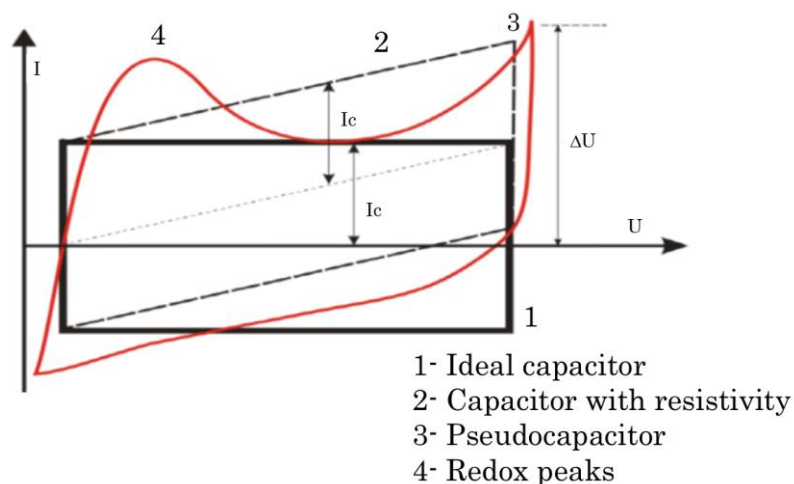


Figure 3.3: Types of voltammograms according to the energy storage mechanism (modified from [396]).

The technique also provides information on the reversibility of the reactions, as reversible reactions produce symmetrical oxidation and reduction peaks, whereas irreversible ones result in asymmetric or shifted peaks [397]. By studying the influence of scan rate and the structure of the electrode-solution interface, CV allows the study of reaction mechanisms, kinetic parameters, and the properties of redox-active materials.

Experimental conditions:

A Solartron 1480 multi-channel potentiostat/galvanostat was used for CV tests. Data were acquired through CorrWare software and analysed with OriginPro. Details on the cell assembly and electrode preparation are given in Section 4.3.3.

Samples were measured at scan rates ranging from 1 to 100 mV/s within a potential window of 0-1 V. Each test was repeated for 5 cycles in order to ensure stability and measure reproducibility. Voltage and current values were obtained for each sample, and the specific capacitance was calculated from these values.

3.2.13.2. Galvanostatic cycling

Theory:

Galvanostatic cycling, also known as constant current charge and discharge analysis, is an electrochemical characterisation technique mainly applied in the determination of the electrochemical parameters of a supercapacitor (namely capacitance, stability, energy density and power density). In this technique, a constant current is applied to the electrochemical cell for a certain period of time [307]. The resulting graph shows the variation of voltage over time, during the charging and discharging process, as demonstrated in Figure 3.4 & Figure A8.

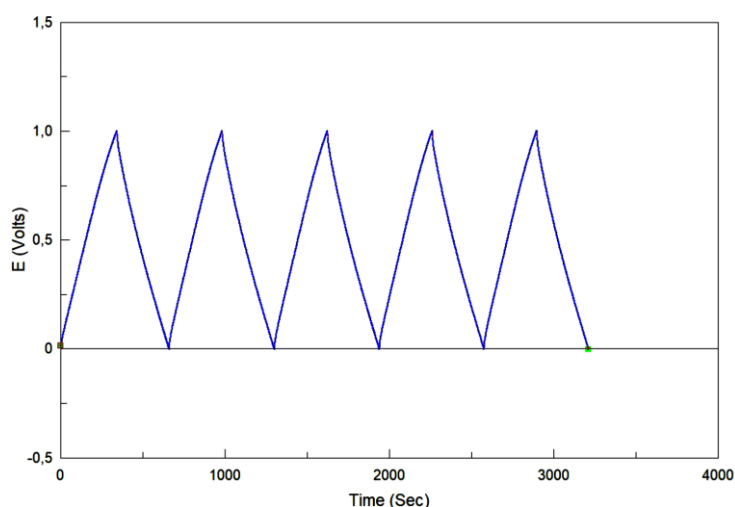


Figure 3.4: Charge-discharge curves of a carbon-based symmetrical supercapacitor [307].

Experimental conditions:

Galvanostatic charge/discharge cycles tests were performed in a Solartron 1480 multi-channel potentiostat/galvanostat. Data were acquired through CorrWare software and analysed using CView and OriginPro software. Charge and discharge cycles were performed at increasing currents starting at 1 mA until cells stopped working. Using voltage and discharge time data, the electrochemical parameters of the cells were calculated (specific capacitance, power density and energy density).

3.2.13.3. Electrical impedance spectroscopy (EIS)**Theory:**

Impedance spectroscopy is a technique used to determine the behaviour of the electrochemical capacitor in response to a low amplitude sinusoidal potential stimulus in the frequency range from 10^{-3} to 10^6 Hz. The graphical representation, known as the Nyquist diagram, represents the real part of the impedance (Z' , on the abscissa axis) against the imaginary part (Z'' , on the ordinate axis) over the frequency range studied. Figure 3.5 illustrates a typical Nyquist plot of an electrochemical capacitor with its differentiated parts:

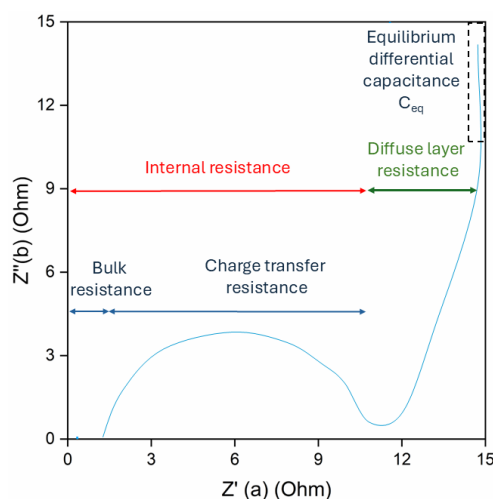


Figure 3.5: Schematic of a typical Nyquist plot for a supercapacitor material [398].

The Nyquist plot can be divided into four characteristic regions, which are studied to characterise the electrochemical behaviour of the capacitor over the entire frequency range. The first part of the Nyquist diagram is the point where the curve intersects the X-axis at high frequencies. This point refers to the bulk resistance, which represents ionic resistivity in the electrolyte and the hindrance of electron flow due to cell components (current collectors, separator, contact resistance...)

[399]. The second part is the semicircle that can be seen in Figure 3.5, which is due to the charge transfer resistance (related to the ion transfer at the electrolyte-electrode interface), in the mid-to-high frequency range [400]. The third part is a small slope at the end of the semicircle, which is associated with resistance due to the Warburg diffusion (reflecting ion diffusion limitations in the electrode pores) at slightly low frequencies. The last part is the slope that can be seen at the end of the graph, associated with a capacitive process at lowest frequencies. If this slope is a straight line, it means that it indicates an ideal capacitive behaviour at this stage. On the other hand, if the angle of the slope takes values between 0° and 90° , this is due to diffusion restrictions [307].

Experimental conditions:

Impedance spectroscopy tests were carried out in a Solartron 1470B frequency analyzer. Supercapacitors were tested over a frequency range of 10^6 to 10^{-3} Hz. Frequency and impedance values were acquired with ZPlot software. Data was analysed using ZView and OriginPro software.

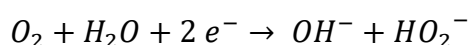
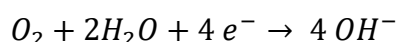
3.2.14. Fuel cell characterisation

To characterise these materials as electrocatalysts in ORR, it was necessary to also perform cyclic voltammetry. However, these experiments are based on a 3-electrode setup rather than a 2-electrode symmetrical cell. As such, the assembly employed is different (a Rotating ring disk electrode apparatus, RRDE) and the theoretical foundations of the technique differ significantly from those of the aforementioned process.

3.2.14.1. Cyclic voltammetry (Rotating Ring Disk Electrode)

Theory:

RRDE is a powerful technique applied for the determination of reaction mechanisms, as well as the identification of intermediate species. In the case of ORR, it is extremely useful to determine the reaction pathway (and number of electrons transferred) between the two possible oxygen reduction reactions:



As previously explained, among these two ORR pathways, the 4-electron reaction is strongly preferred, mainly because this reaction does not generate the corrosive

hydroperoxyl anion (HO_2^-), which is also responsible for the formation of atmospheric NO_x [401] and subsequent tropospheric ozone formation [402].

In order to determine the kinetic parameters of this reaction, hydrodynamic methods are preferred, as they involve the controlled rotation of an electrode to force the solution to move, and in this way, the effects of convection can be controlled. Rotating disk electrode (RDE) and RRDE are the most popular hydrodynamic methods [403]. Typically, RRDE is preferred over RDE as the latter cannot be used to determine the concentration of hydroperoxyl ions generated.

In RDE, a solution containing the oxidised form of a molecule or ion is placed in contact with a rotating glassy carbon, disk-shaped electrode. This electrode is set at a potential that decreases over time (cathodic sweep). As this potential approaches the standard reduction potential of the molecule, electrons begin to flow and a cathodic current is observed, increasing as potential passes the standard potential and approaches negative values. Eventually, when the reduction process is complete, the current stops increasing and reaches its maximum value, known as limiting current. Repeating this experiment at different rotation speeds enables the number of electrons transferred to be determined.

In RRDE, a concentric ring electrode (usually made out of platinum) is placed around the rotating disk electrode, as shown in Figure 3.6:

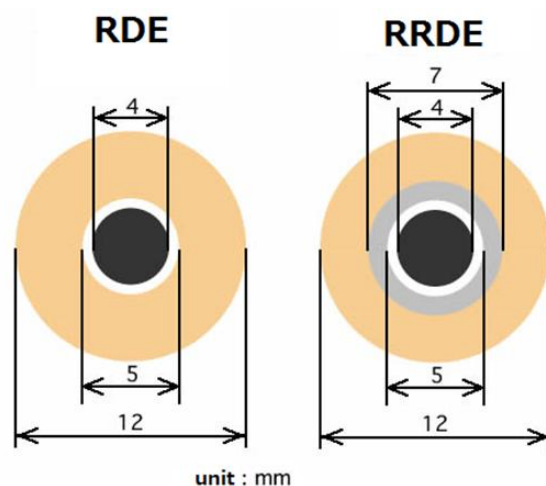
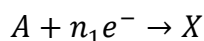


Figure 3.6: Schematic representation of typical RRDE and RDE electrodes [404].

This technique is extremely useful to determine the reaction pathways when there are two competing pathways. In cyclic voltammetry performed using a RRDE apparatus, the original flow carries molecules and ions to the disk electrode (set at the same potential as in RDE). A fraction of these molecules is then carried to the

surface of the ring electrode (set at a different potential). In order to determine the number of molecules transferred to the ring electrode it is necessary to know the collection efficiency of the apparatus (theoretical and experimental determination of this value are provided in Annex 7). Considering an oxidised species A, the determination of competing pathways in the RRDE follows the mechanism:

- Reduction of A to the unstable intermediate X at disk electrode:



- Chemical decay of X to form electrochemically inactive Z:



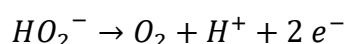
- Chemical decay of X to form electrochemically active Y:



- Detection of Y at the ring electrode by oxidation to B:



In this way, the selection of a different ring electrode potential allows the oxidation of a chemical species previously reduced in the disk electrode. As such, the calculation of the ratio between the ring and disk currents enables the concentration of species produced to be quantified. In the case of ORR, the reactions happening at the disk electrode are the ones presented at the beginning of this section, while the reaction occurring at the ring electrode is the oxidation of the hydroperoxyl ion:



This method allows the determination of the amount of water generated by the 4-electron pathway and compare it to the amount of by-product (HO_2^-) produced by the 2-electron pathway [403], thus indicating the extent to which the two reduction reactions are taking place.

Experimental conditions:

Cyclic voltammetry experiments were carried out in a RRDE-3A apparatus from ALS Japan, connected to a Biologic VSP-300 potentiostat, both available at ICGM-CNRS. Data was collected using EC-Lab software and analysed using OriginPro. Typical experiments consisted of a 3-electrode setup with a Pt counter electrode and an Ag/AgCl a reference electrode inserted in a 0.1 M KOH aqueous electrolyte solution. Details on the catalyst preparation are provided in Section 4.3.4.

CV tests were performed at a scan rate of 10 mV/s in a disk potential range of 0.25 V to -1.2 V vs Ag/AgCl at a rotation rate of 1600 rpm. The ring potential was fixed at 0.43 V vs. Ag/AgCl, and chronoamperometry was used to monitor the current over time. The measurements were repeated three times to ensure reproducibility, all under an oxygen flow of 2 mL/min.

3.2.15. Ultraviolet-visible spectroscopy (UV-Vis)

Theory:

UV-Vis spectroscopy is an analytical technique that measures the absorption of ultraviolet and visible light by certain molecules, providing information about their electronic structures. When chromophores (the functional groups responsible for the absorption of radiation) absorb light in the UV-Vis region (at wavelengths typically between 200 and 800 nm), electrons are promoted from lower energy molecular orbitals (σ , π and non-bonding orbitals, from lower to higher energy level) to higher energy unoccupied orbitals (σ^* and π^*)[405]. Since different molecules absorb at characteristic wavelengths, the analysis of the absorption spectrum of a sample provides information about the electronic configuration and functional groups present in the species. In addition to qualitative measurements, UV-Vis can also provide quantitative results, as in the determination of the concentration of aqueous solutions.

UV-Vis experiments require the use of a spectrophotometer, comprising a light source, a sample holder, a monochromator which separates the light into its component wavelengths, and a detector. This equipment first passes a beam of light without the sample (blank), then the sample is placed, and the same beam is passed through a cell containing the sample so that transmittance can be calculated. However, if a double-beam spectrophotometer is used, this step is unnecessary, because in this instrument the light is split into two before it reaches the sample, directing one beam through the sample and the other through a reference (two detectors are required for this equipment).

The theoretical basis of UV-Vis spectroscopy relies on the Beer-Lambert equation, which can be used to determine the concentration of a substance in a solution. Once absorbance or transmittance is measured, the analyte concentration can be calculated knowing the path length of the beam and the molar adsorption coefficient of the analyte. Nevertheless, the concentration of a solution can also be

determined by plotting calibration curves generated from known analyte concentrations and comparing with the spectrum of the analyte solution.

Experimental conditions:

UV-Vis spectra were acquired using a UV-NIR LAMBDA 1050+ InGas (Perkin Elmer) spectrometer available at the ICTP-CSIC. A 10% v/v ethanol water solution was used as reference, as the analysed dyes were also dissolved in this solution. Samples were analysed in the wavelength range of 200-800 nm, with a scan speed of 240 nm/min and a slit of 2nm. The slit of a spectrophotometer determines the amount of light that travels through the system.

4. Activated carbon from cellulose

4.1. Introduction

As explained in Chapter 1, in the context of the global transition toward sustainable energy systems, the development of environmentally friendly and energy-efficient electrodes and catalysts is critical. Under this premise, hydrothermally-treated, biomass-derived carbons have emerged as promising materials for energy related applications, particularly as electrodes in supercapacitors and electrocatalysts for the ORR in fuel cells. As discussed in Section 1.3.1.2, the HTC process is regarded as a sustainable and efficient method for pre-treating biomass prior to activation, being more energy efficient than conventional carbonisation processes, while reducing by-product generation [172].

Importantly, HTC pre-treatment has shown to significantly enhance carbons' porosity after activation, resulting in higher surface areas and improved electrochemical performance [406]. Experiments comparing ACs prepared via conventional and hydrothermal carbonisation report that the latter exhibit superior textural properties and increased capacitance [406]. Capacitances exceeding 250 F/g have been achieved in some HTC-derived materials, underscoring their potential for energy storage applications [33].

Beyond supercapacitors, HTC has also been successfully employed in the preparation of non-Pt-containing, carbon-based electrocatalysts for their application in ORR. Different biomass sources have been studied [407-413] and, in many cases, the catalytic activity of these materials is comparable to that of commercial Pt/C catalysts, further highlighting the versatility of the HTC process for the development of cost-effective alternatives to Pt-based catalysts.

Taken together, the environmental, performance and economic benefits presented so far (i.e. sustainable precursors, lower energy consumption, reduced by-product generation...) make HTC an attractive route for the preparation of ACs. The present chapter details the synthesis of HTC-derived carbons and evaluates their structural, physical and electrochemical properties in the context of supercapacitor and fuel cell technologies.

4.2. Aim of this chapter

The following specific objectives have been set for this Chapter:

- Evaluate of the influence of KOH dosage on the development of a porous structure within the biomass-derived carbon.
- Understand the underlying mechanism behind the addition of albumin and WS₂ nanosheets to the carbonaceous matrix.
- Assess the impact of these particles on the properties of the ACs.
- Analyse the electrochemical performance of supercapacitor electrodes, with special attention to the contribution of albumin and tungsten disulfide nanosheets to the total capacitance.
- Perform a post-mortem study of the supercapacitor electrodes after electrochemical tests to understand the chemical and structural changes that have taken place within it after supercapacitor testing.
- Evaluate the potential use of the synthesised ACs as electrocatalysts, comparing their performance to a commercial state-of-the-art Pt/C catalyst and a standard glassy carbon electrode.

4.3. Synthesis procedure

Cellulose aqueous mixtures (320 g/L) were prepared and added to a 140 mL stainless steel autoclave, heated in an oven at 200 °C for 5 hours, and afterwards left to cool overnight. The product was then filtered using a cellulose Whatman filter paper and dried under vacuum in a desiccator at 50 °C overnight to obtain the solid hydrochar, named C200 (Cellulose at 200 °C), as depicted in Figure 4.1.



Figure 4.1: Obtained cellulose hydrochar (C200) before and after drying.

After HTC, the char needs to be mixed with KOH in order to develop porosity. However, direct carbonisation led to the separation of KOH and C200. Therefore, C200 underwent a pre-carbonisation step to avoid separation (see Figure 4.2):



Figure 4.2: Residue after activation without (left) and with (right) pre-carbonisation step.

Pre-carbonisation of the C200 product entailed heating it at 5 °C/min in a tube furnace until 300 °C, and then maintaining it under isothermal conditions for an hour before leaving it to cool. The prepared samples were named C (Cellulose), C200 (Cellulose after HTC) and C300 (Hydrothermal cellulose after pre-carbonisation at 300 °C)

Chemical activation was performed to enhance the porosity of the samples, with potassium hydroxide chosen due to extensive supporting research on its effectiveness as an activator [38, 39, 414, 415]. In order to achieve this, KOH was dissolved in ethanol (20 g/mL), and then the solid (C300) mixed into the solution for



QR 1: Rotovapor use for sample drying.

2 hours to ensure homogeneity at different C300 to KOH ratios, from 1:1 to 1:6. Subsequently, the mixture was dried under vacuum in a rotary evaporator (see QR 1), and the obtained powder moulded into a pill using a press.

The prepared pills were heated at 10 °C/min from room temperature to 800 °C under an inert atmosphere (100 mL N₂/min) in a tube furnace. They were then repeatedly neutralised and washed with a 5% HCl solution and water before drying. Finally, to ensure no residual potassium remained within the samples, EDX and TGA measurements were carried out. The final samples (see Figure 4.3) were named C 1-x, with x being the C300-to-KOH ratio employed.

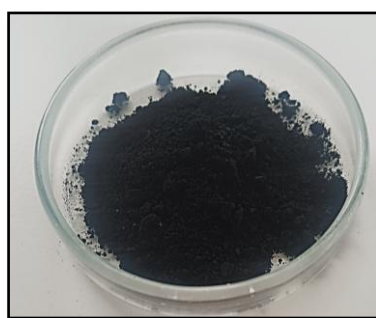


Figure 4.3: Image of the resulting activated carbon derived from cellulose.

For the purpose of imparting additional functionality and properties to the chosen carbons for the assigned applications, different preparation methodologies were carried out as detailed below:

4.3.1. Albumin addition

Typically, to introduce nitrogen functionality, cellulose is mixed with urea or ammonia. However, the N fixation in the final carbons using these chemicals is poor, typically resulting in 5-10% N incorporation [416, 417]. This added waste, along with handling issues and reactor corrosion, lead to the use of other more natural and safer nitrogen sources.

In this study, albumin was chosen as the N source for this study, since it is one of the biopolymers with highest nitrogen content, which can be sourced from egg waste or those that don't meet food criteria, making it a sustainable choice.

Cellulose was mixed with egg albumin (A) in ratios ranging from 1:1 to 5:1, and then hydrothermally treated as explained in Section 4.3. It was found that a 4:1 ratio was optimum due to a combination of superior yield and higher N retention, as shown in Table 4.1:

Table 4.1: Product yields and nitrogen content at different cellulose to albumin ratios.

C:A ratio	HTC Yield (%)	N before HTC (%)	N after HTC (%)	N retention (%)
1:1	51.0	6.48	1.88	29.0
2:1	64.4	4.36	1.52	34.9
3:1	71.5	3.30	1.19	36.0
4:1	77.4	2.66	1.05	39.5
5:1	78.0	2.24	0.76	33.9

In bold, the chosen material

The chosen sample (CA 4:1) after HTC also underwent a pre-carbonisation step and activation (data on the final N content is displayed in Section 4.4.1.2), with the final products named CA 1-x depending on the chosen C300-to-KOH ratio.

4.3.2. Tungsten disulphide addition

To the materials prepared in 4.3 and 4.3.1 (both without and with added nitrogen), tungsten disulphide (WS_2) nanosheets were added after activation. To obtain this, two batches were prepared in parallel: one containing WS_2 nanosheets in isopropanol (1 g/L), which was stirred at 500 rpm at 30 °C until complete dissolution, and another containing the prepared AC in isopropanol (19 g/L), that in this case was stirred for 2 hours at 500 rpm (30 °C). Afterwards, the two batches were combined and stirred for a further 2 hours to obtain a homogeneous mix and then dried using a rotary evaporator. The final products had a WS_2 concentration of 5% w/w (total solid mass) and were named C 1-x W or CA 1-x W depending on the KOH ratio and presence of albumin. Figure 4.4 summarises the experimental procedure and terminology for each sample.

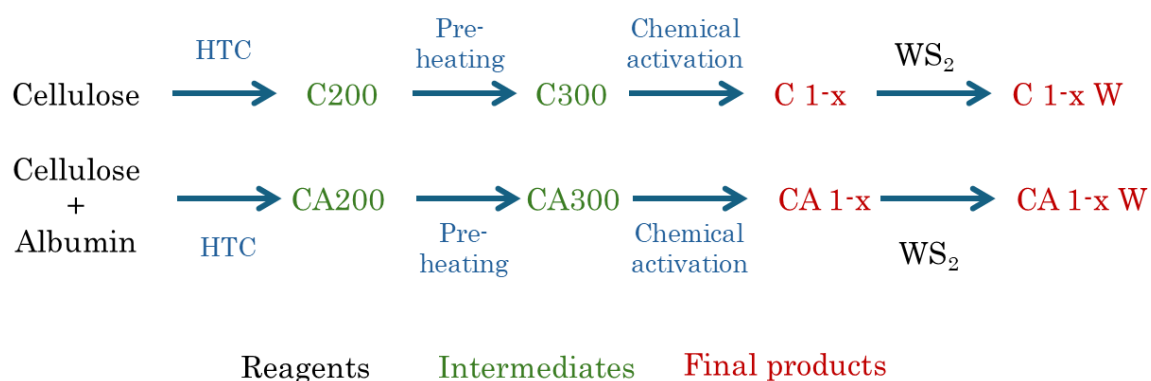


Figure 4.4: Flow diagram representing the synthesis methodology, with the nomenclature for each sample.

After completing the experimental procedure, the yields of the total process were calculated and are summarised in Table 4.2, where the first number represents the total yield (ratio between initial mass and mass after each stage) and the number in brackets represents the yield at each stage (ratio between mass before and after each stage). This table only displays the yields of the final materials, prepared using the C300-to-KOH ratios of 1-1.5 and 1-4 in order to maximise meso and microporosity, respectively.

Table 4.2: Yields for the total carbon preparation process.

Precursor mass (g)	HTC Yield (%)	Pre-carbonisation yield (%)	Activation & neutralisation yield (%)
12 (cellulose)	84.8	39.0 (46.0)	2.10 (5.30) ^a 0.78 (2.00) ^b
12 (cellulose and albumin)	77.4	36.8 (47.6)	2.80 (7.60) ^a 0.79 (2.15) ^b

^a For the sample with a 1:1.5 C300-to-KOH ratio; ^b For the sample with a 1:4 C300-to-KOH ratio.

4.3.3. Assembly of the supercapacitor electrochemical cells

Supercapacitor electrodes (40 mg approx.) comprised a physical mixture of the prepared AC (60% wt.), PTFE binder (30% wt.) and conductive carbon black (10% wt.), grinded in an Agate mortar and finally pressed into 12 mm cylindrical pellets by applying a load of 0.8 tonnes for 10 minutes.

Symmetric supercapacitors were assembled into homemade Teflon SwagelokTM-type cells using A20 stainless steel current collectors, and an aqueous 2M H₂SO₄ solution as electrolyte. A glassy microfibre paper (Whatman 934 AH) was used as a separator (see Figure 4.5).

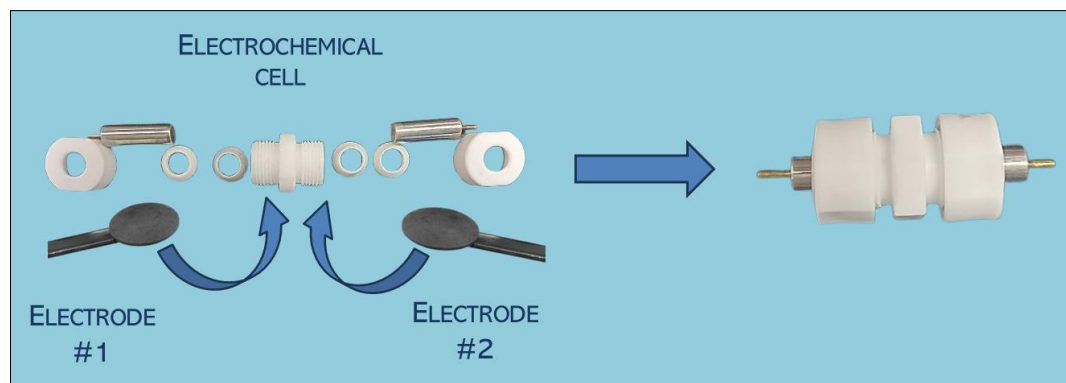


Figure 4.5: Components and assembly of the EDLC electrochemical cell.

These cells were further subjected to direct current (cyclic voltammetry & galvanic cycling) and alternating current (impedance spectroscopy) tests in order to assess the electrochemical performance of the developed carbons. Prior to the analysis, samples were dried overnight at 100°C under vacuum.

4.3.4. Preparation of inks for the ORR electrocatalytic application

In order to measure the electrocatalytic activity of the samples, carbon inks were prepared and deposited onto a glassy carbon electrode for ORR testing.

For ink preparation, 10 mg of each carbon was mixed with 100 μL of Nafion and put in an ultrasound bath with ice for 20 minutes. After, 700 μL of ethanol was added to the mixture and sonicated again for 20 minutes. After sonicating, the dispersions were kept in a fridge at 6 $^{\circ}\text{C}$ for 48 hours. Finally, 2 μL of the prepared ink was deposited onto a previously dried glassy carbon electrode and dried in an oven at 60 $^{\circ}\text{C}$ for 60 minutes to fully evaporate the solvent.

After drying, the electrode was connected to the RRDE equipment along with the counter and reference electrode, all immersed in a 0.1 M KOH solution working as electrolyte, as presented in Figure 4.6 (for more details on test procedures see Section 3.2.14):

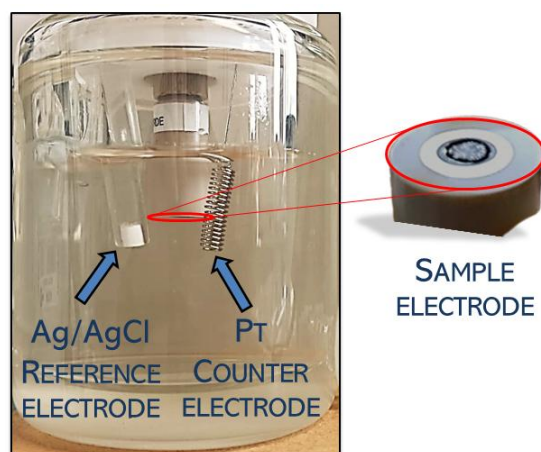


Figure 4.6: Detail of the electrodes used for the ORR tests.

4.4. Results and discussion

4.4.1. Carbon properties and morphology

4.4.1.1. Structural and morphological properties

Gas sorption analysis:

In order to obtain information about the porous structure of the developed carbons (precursors were not analysed as they do not display any porosity before activation), gas sorption analyses were employed. N₂ was used for all samples, and CO₂ only when more detailed microporosity information was required.

The first test was nitrogen sorption on the samples prepared with different C300-to-KOH ratios, ranging from 1-1 to 1-6. This was carried out in order to assess the optimum amount of activating agent needed to produce materials with different porosities, so as to evaluate the influence of porosity in energy and adsorption applications. Figure 4.7 shows the nitrogen microporosity (micropore-to-total pore volume ratio); higher KOH dosage (1-6) leads to a Type IV (b) isotherms, similar to those prepared with KOH ratios of 1-2 or lower. This sorption isotherms obtained from this experiment:

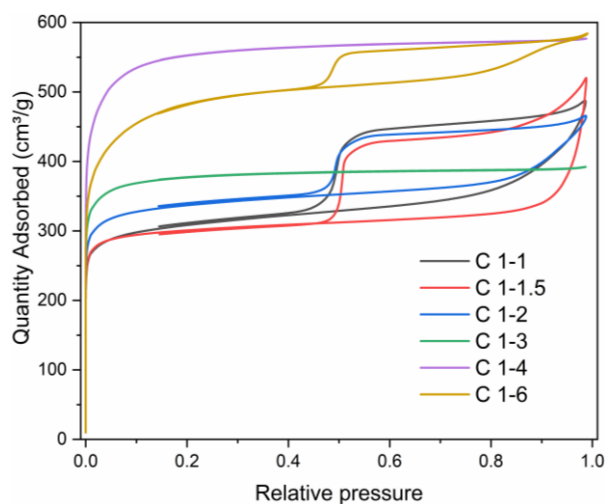


Figure 4.7: Nitrogen sorption isotherms for different C300-to-KOH ratios.

It can be seen that the volume of nitrogen adsorbed generally increases at higher KOH dosages. At elevated temperatures (>700°C), carbon gasification reactions occur due to the presence of CO₂ in the alkali, resulting in the release of volatiles and subsequent pore formation [418]. This CO₂ can react with carbon atoms, leading to the creation of new pores and enlargement of the existing ones.

Furthermore, the presence of K-containing molecules results in the formation of metal potassium, which can enter the carbonaceous matrix and increase the pore volume. It is therefore expected that samples with a higher KOH content will display higher micropore volume and, consequently, higher microporosity (micropore to total pore volume ratio). This metal can either sublime or interact with functional groups from the carbonaceous matrix in order to promote catalytic sites for gasification reactions. However, at temperatures exceeding 800 °C, the (hard) carbon undergoes a breakdown of its cross-links, which leads to a decrease in the textural properties of the resulting material [418]. This is the primary reason for the selected temperature for these carbons. A summary of the structural changes in the carbonaceous structure of the materials is presented in Figure 4.8:

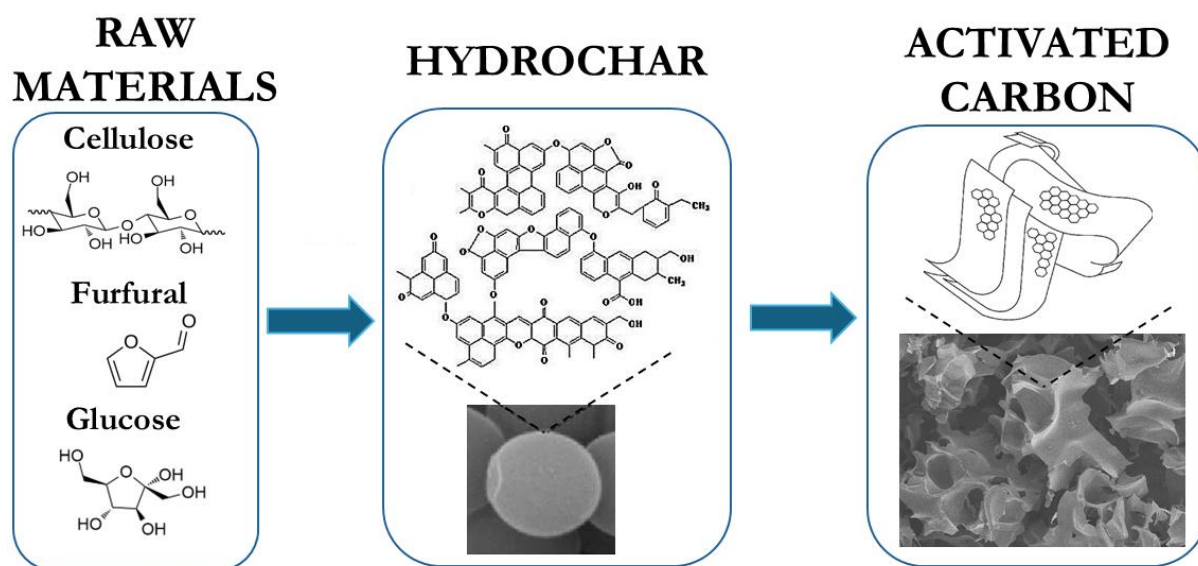


Figure 4.8: Changes in the precursor structure during the different stages of the AC (adapted from [419-421]).

Moreover, analysis of the isotherms reveals that the samples with lower KOH dosage (1-1; 1-1.5 and 1-2) exhibit Type IV (a) adsorption isotherms with hysteresis loops. These loops are indicative of the presence of mesopores with a width exceeding a critical threshold (4 nm for N₂ adsorption [383]). This finding suggests that these materials display a combination of micropores and mesopores wider than 4 nm. Conversely, at higher KOH dosages (1-3 and 1-4), Type I (b) isotherms are observed, which are related to mainly microporous samples with a minor mesopore contribution. Specifically, it is associated with samples with wide micropores and narrow mesopores with a width of 2.5 nm or less [422].

It is noteworthy that C 1-4 has the maximum microporosity (micropore-to-total pore volume ratio); higher KOH dosage (1-6) leads to a Type IV (b) isotherms,

similar to those prepared with KOH ratios of 1-2 or lower. This phenomenon has also been documented by other authors for other biomass sources [38, 187, 419], where it can also be seen that a KOH ratio of 1-4 results in a maximum in microporosity with the selected activation.

Figure 4.7 also demonstrates that the maximum micropore volume is reached with C 1-4, indicating that there is no need to increase KOH dosage beyond this point (besides from the fact that C 1-6 exhibits a combination of micro and mesopores that can be reached with lower KOH amounts). Consequently, the KOH ratios selected were 1-4, in order to enhance microporosity and surface area, and 1-1.5, in order to optimise mesoporosity (C 1-1-5 exhibits the most extensive hysteresis loop, indicating its mesoporous nature). The results of N₂ sorption are outlined in Table 4.3:

Table 4.3: Textural properties of carbons with different KOH dosages.

Sample	BET area (m ² /g)	Micropore area (m ² /g) ^a	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g) ^a	Mesopore volume (cm ³ /g) ^b
C 1-1	1190	1051	0.76	0.45	0.25
C 1-1.5	1188	1118	0.81	0.41	0.26
C 1-2	1304	980	0.73	0.49	0.18
C 1-3	1465	1294	0.61	0.57	0.09
C 1-4	1938	1783	0.89	0.83	0.09
C 1-6	1776	1678	0.91	0.65	0.25

^a Calculated using t-plot method. ^b Calculated using the NLDFIT method.

It must be noted that these results are derived from experiments conducted using a different equipment and measuring less points (as these experiments were conducted as part of a preliminary test) compared to the following measurements. Consequently, the calculated textural properties of the final samples (C 1-1.5 and C 1-4) are likely to present discrepancies compared to those presented in subsequent tests, which were performed using a more up to date apparatus and were combined with CO₂ sorption tests. Nevertheless, these analyses are useful for understanding how the KOH ratio affects the carbons' textural properties.

After determining the optimum KOH ratios, the final carbons were tested more extensively using N₂ and subsequently CO₂ sorption. The nitrogen sorption isotherms are displayed in Figure 4.9:

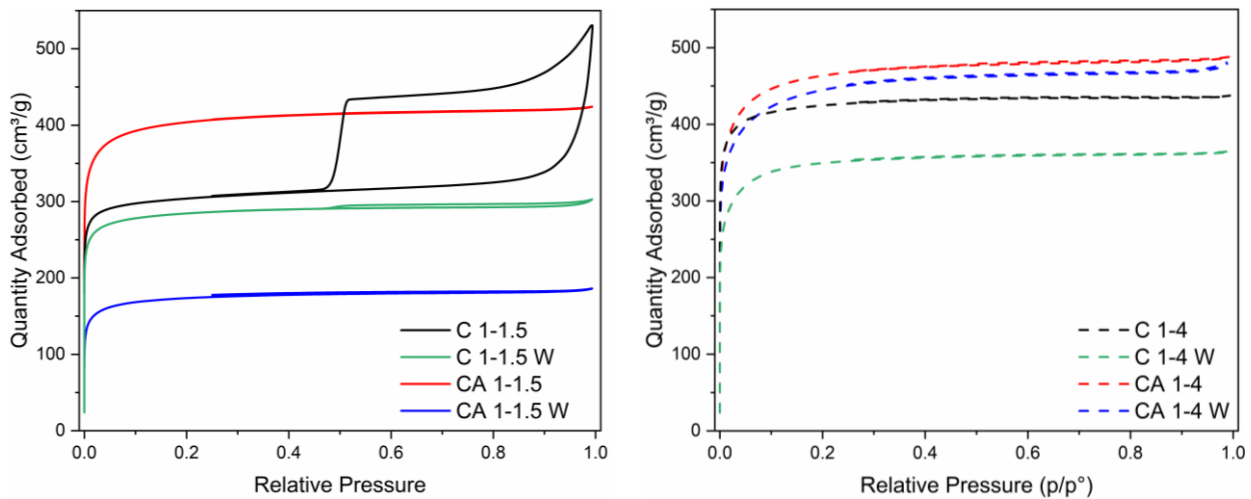


Figure 4.9: Nitrogen sorption isotherms of the final carbons.

From these more detailed isotherms, it can be deduced that both sample types (C 1-1.5 and C 1-4) contain micropores from the sharp uptake of adsorbed gas at low P/P_0 , and display Type 1(b) isotherms, with the exception of C 1-1.5 (and to some extent, C 1-1.5 W) that from the hysteresis loop (characteristic of Type IV (a) isotherms), consists of both micro and mesopores, as previously outlined. Furthermore, analysis of the desorption isotherm of C 1-1.5 shows a sudden pressure drop at $P/P_0=0.5$ that is due to cavitation – the spontaneous nucleation of nitrogen bubbles within the pores, leaving the pore body empty, while the neck remains filled [422]. The occurrence of cavitation indicates the presence of ‘bottle-necked’ mesopores with a diameter of 30-60 nm, and pore neck diameters smaller than the critical width of 5-6 nm when using nitrogen at 77 K. Figure 4.10 illustrates the relationship between the type of hysteresis loop and the porous structure:

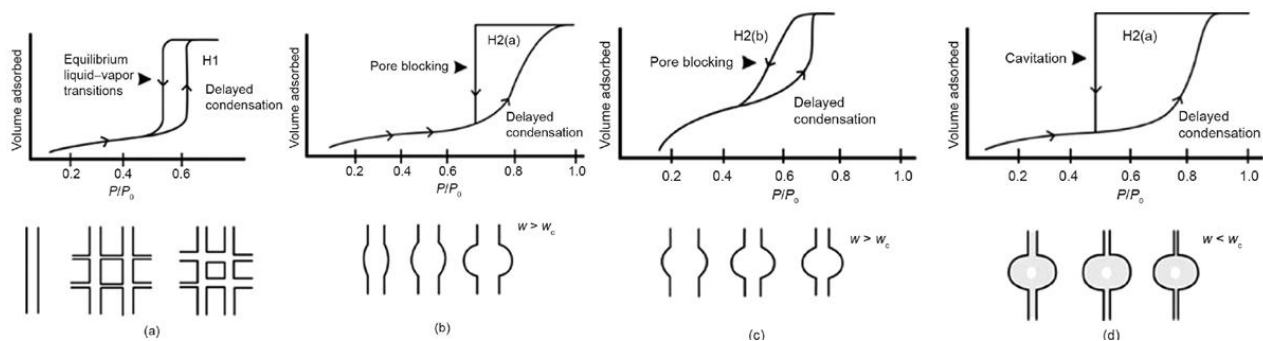


Figure 4.10: Porous structures according to the hysteresis loop type associated to Type IV a) isotherms (from [422]).

The difference in porosity between C 1-4 and C 1-1.5 has already been addressed; however, the distinction between the original ACs and their doped homologues (albumin and WS₂ nanoparticles) is of particular interest. It is observed that most

albumin-containing samples exhibit higher micropore volume than the carbons which do not contain N atoms. This suggests that nitrogen atoms significantly increase the number of active centres on the carbon surface, which substantially affects the final pore structure and its adsorption capacity [423].

The presence of active centres can stimulate the formation of micropores [424], hence the theory of higher KOH ratio resulting in samples with predominant microporosity, and lower ratios increasing the possibility to have mesopores [423, 425]. However, this reasoning is only valid up to a KOH ratio of 1-4, beyond which the probability of the formed active centres being located near each other increases, and as such, the formation of a mesoporous structure become more likely.

Furthermore, the obtained isotherms displayed in Figure 4.9 demonstrate that the addition of WS₂ nanosheets results in a decrease in adsorption capacity compared to their non-doped counterparts. This observation can be attributed to the deposition of the tungsten disulfide nanosheets on the carbon surface, rather than being inserted within its porous carbonaceous matrix, thereby blocking access to the developed pores. Further SEM analyses will develop this on this conjecture. The data acquired from the more detailed nitrogen isotherms are presented in Table 4.4:

Table 4.4: Textural properties of the final carbons calculated from their N₂ sorption isotherms.

Sample	BET area (m ² /g)	Micropore area (m ² /g) ^a	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g) ^a	Mesopore volume (cm ³ /g) ^b
C 1-1.5	1206	1151	0.83	0.45	0.20
CA 1-1.5	1589	1540	0.66	0.61	0.011
C 1-1.5 W	1134	1029	0.47	0.43	0.012
CA 1-1.5 W	680	655	0.29	0.26	0.012
C 1-4	1674	1636	0.68	0.65	0.002
CA 1-4	1759	1701	0.76	0.70	0.014
C 1-4 W	1330	1291	0.57	0.53	0.005
CA 1-4 W	1660	1591	0.75	0.67	0.044

^a Calculated using t-plot method. ^b Calculated using the NLDFIT method.

The results in this table reinforce the main conclusions, confirming that most samples are highly microporous due to the active centres provided by either high KOH dosage or albumin incorporation, as detailed in Figure 4.11. This figure compares the ACs' micropore and total pore volumes, where it can be observed that

WS₂-doped samples present lower volumes than the non-WS₂ ACs, again suggesting that pore blockage is the underlying cause. On the contrary, albumin containing samples display the highest micropore volume for both sets of samples, reinforcing the theory of N atoms promote micropore development.

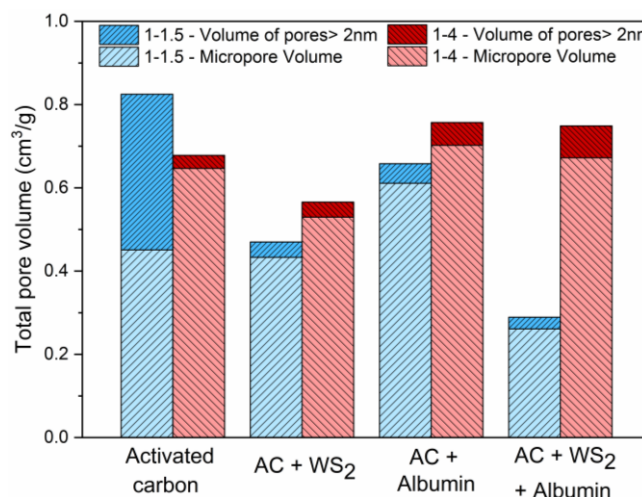
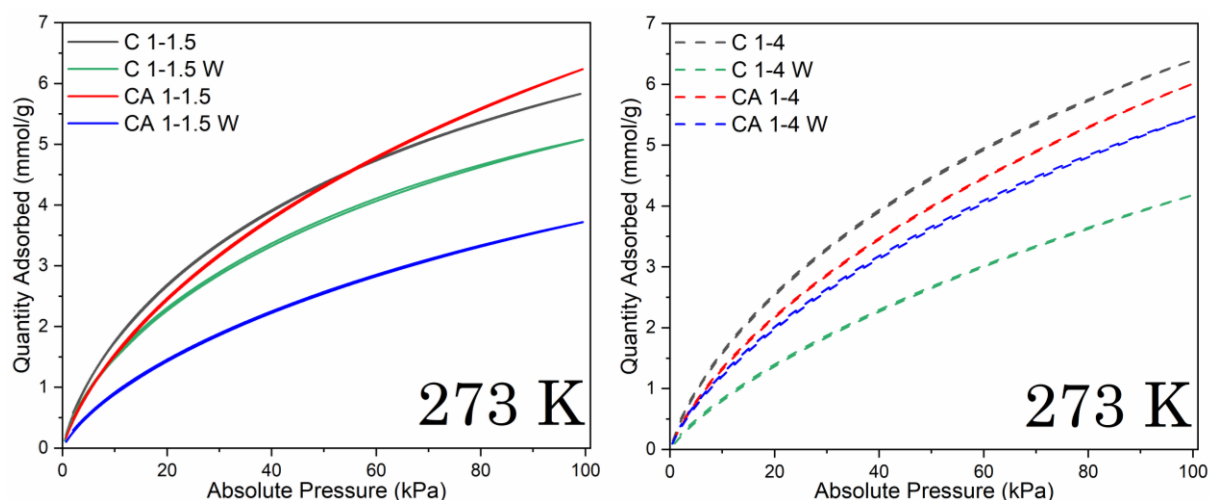


Figure 4.11: Total pore volume of the final ACs, highlighting the contribution of micropore volume, and volume of pore with a diameter >2nm.

Sorption tests using CO₂ were undertaken at different temperatures to obtain more detailed information about the samples' micropores and understand better the nature of the gas sorption mechanism, as can be seen from the isotherms presented in Figure 4.12:



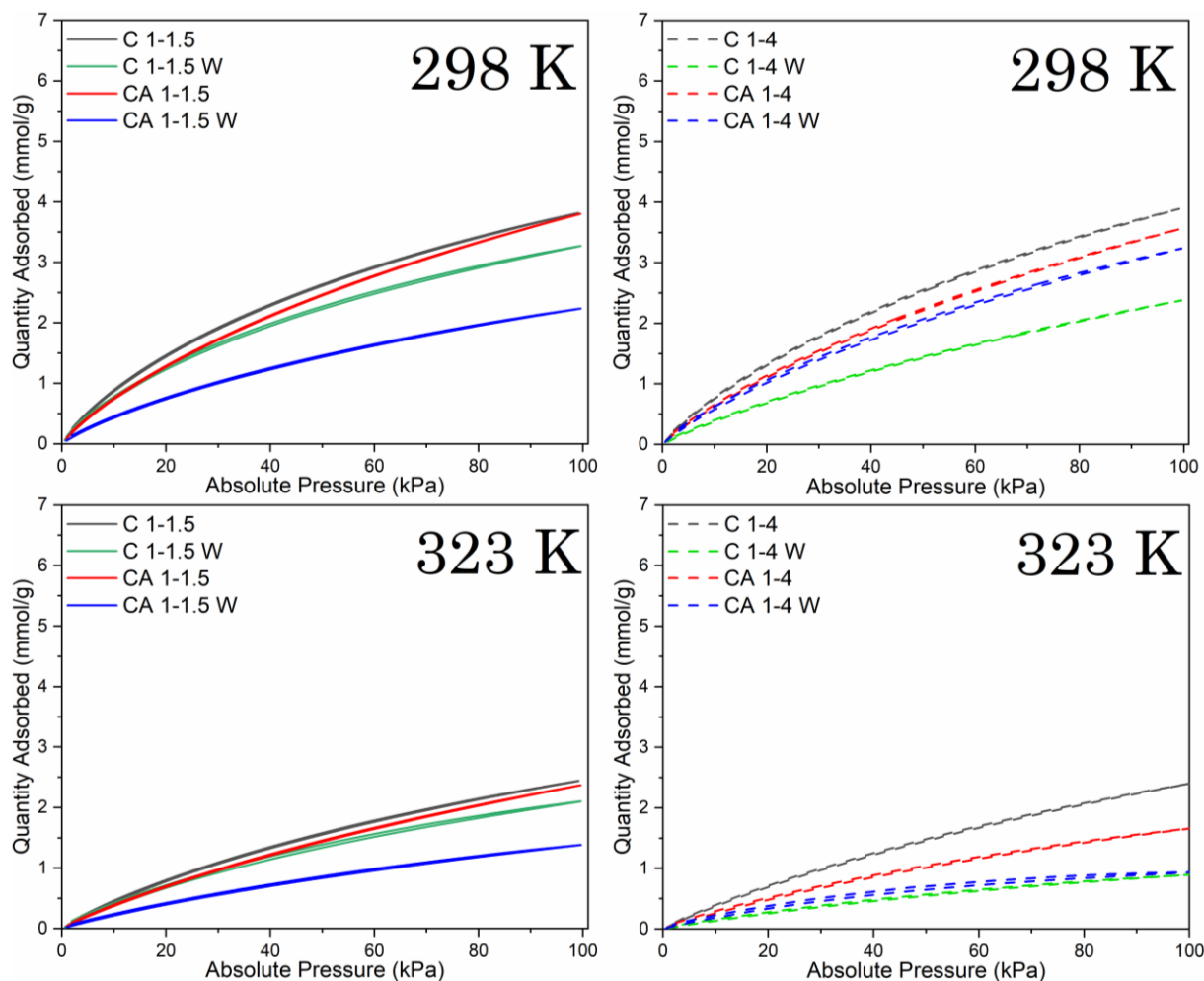


Figure 4.12: CO₂ sorption isotherms of the final ACs at temperatures of 273 K, 298 K and 323 K.

Consistent with N₂ sorption isotherms, Figure 4.12 shows that the WS₂-doped samples adsorb less CO₂ than C and CA samples, irrespective of the activating agent ratio or temperature. Interestingly, it can be observed that the adsorption capacity of each set of samples follows the same trend as the micropore volume (see Table 4.4). This finding is consistent with previous literature, as recent studies have already shown a correlation between higher CO₂ adsorption and larger BET areas and micropore volumes [426].

Moreover, the nitrogen and carbon dioxide sorption isotherms were combined using SAIEUS software and then analysed using the Non-Local Density Functional Theory (NLFDT) method to obtain the pore size distribution (PSD) of the samples (see Figure 4.13). The results confirm that the main contribution to the pore volume of all samples comes from the micropores, agreeing with the previous data (see Table 4.4 and Figure 4.11). Specifically, the set of C 1-1.5 samples presents a prominent peak around 0.51-0.59 nm. In the case of the

samples with a 1-4 KOH ratio, there is a negligible shift, displaying a peak in the microporous region of the PSD at 0.61-0.79 nm. Furthermore, the majority of the samples present a second, significantly smaller peak centred at around 1.4-1.6 nm, indicative of the presence of micropores with a range of sizes. In addition, in the C 1-1.5 sample, noticeable peaks at 3.7 and 5.7 nm are observed, along with a minor peak at 32.1 nm, thereby confirming the presence of mesopores with diverse pore diameters, as evidenced from its Type IV (a) isotherm.

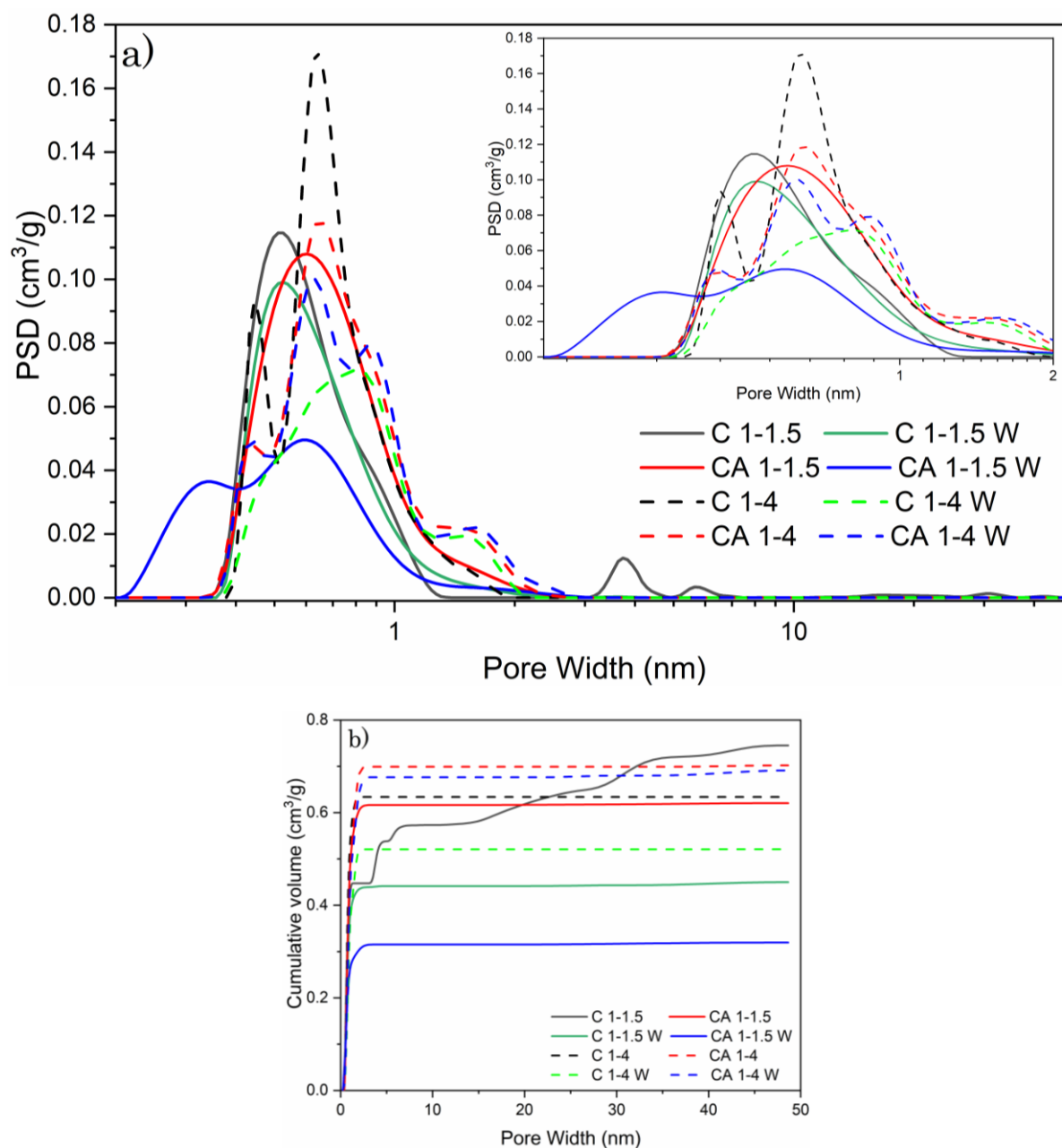


Figure 4.13: Results of the NLDFT method to obtain a) the PSD of the final ACs and b) cumulative pore volume of the ACs.

The cumulative volume of the samples was analysed (Figure 4.13 b) using the NLDFT method, where it is seen that for most samples, more than 95% of their maximum volume is reached at pore widths lower than 2 nm, again confirming that the samples are predominately microporous. For the C 1-1.5 sample, it also exhibits a cumulative volume curve that increases up to a pore sizes of 2 nm, but at pore widths > 2 nm it also continues to increase substantially, confirming its diverse combination of pore sizes.

Finally, CO₂ sorption isotherms at different temperatures were used to determine the enthalpy of adsorption of each sample, and hence, to better understand their CO₂ sorption mechanisms (Note: details of the calculation can be found in Annex 1). This data was used to plot the enthalpy of adsorption of the prepared ACs versus the CO₂ adsorption capacity at equilibrium (Q_e), as shown in Figure 4.14.

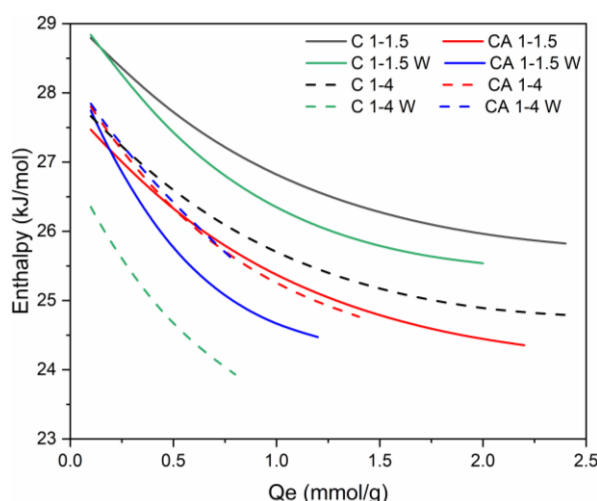


Figure 4.14: Enthalpy of adsorption of the prepared ACs versus Q_e (CO₂).

From Figure 4.14, a correlation between the size of the micropores and calculated enthalpy can be established, as narrower pore sizes generate stronger adsorption sites and, consequently, higher enthalpy values [427, 428]. It can be seen from the graph that the C 1-1.5 set of samples exhibit higher enthalpy values for the majority of the measurement range (with the exception of CA 1-1.5 W, which presents lower adsorption due to its poor textural properties, see Table 4.4). The findings are consistent with the results of the PSD analyses, which demonstrate that the C 1-1.5 set of samples presents an average micropore size approximately 0.1-0.2 nm smaller than that of C 1-4 (from 0.51 nm in C 1-1.5 to 0.59 nm in CA 1-1.5 W vs. 0.62 nm in CA 1-4 W to 0.79 nm in C 1-4 W).

In addition, the gas sorption mechanism can be characterised by these calculations. Typically, enthalpy of adsorption values below 40 kJ/mol are

indicative of a physisorption process, while higher values are associated with a chemisorption mechanism [427]. According to this theory, it can be understood that all of the studied samples present a physisorption mechanism. This hypothesis is supported by the absence of residual KOH, which would be required to provide the active centres for chemisorption, as evidenced by both XPS and TGA analyses (as shown in Sections 4.4.1.2 & 4.4.1.3). Furthermore, the amounts of remaining sulphur and nitrogen within the final ACs, which could potentially provide other adsorption sites for chemisorption are low (< 2.5% of the total mass, as detailed in Table 4.6).

Scanning electron microscopy:

In order to understand the macroscopic structure of the carbons, SEM was performed on the precursors and the final ACs. These micrographs confirm that only activated samples display porosity, as both cellulose and C300 (Figure 4.15 a and b) exhibit a continuous, non-porous structure. As noted earlier, from the results presented in Table 4.4, KOH dosage plays a fundamental role in the development of the porous structure, with each sample containing a significant contribution of both micro and mesopores. However, from Figure 4.15 c and d, it can be seen that KOH dosage also significantly alters the macroporosity of the samples, in this case C 1-1.5 has pore diameters in the 300-400 nm range, while C 1-4 exhibits much larger pores of 10-20 μm .

Albumin addition (CA 1-4) appears to promote the amount of macropores formed, but not increasing their size (compare Figure 4.15 c and Figure 4.15 e). On the other hand, when the WS_2 nanosheets are inserted into the carbonaceous matrix, (as seen in Table 4.4), a significant reduction in surface area can be observed. This, from the SEM images (displayed in Figure 4.15 f and Annex 2), is due to the nanosheets depositing on the carbons' macroporous external surface and blocking many of these porous structures. The images of the rest of the samples are presented in Annex 2. Furthermore, this annex also contains TEM micrographs taken at different angles of the C 1-4 W sample. These images were then compiled together to enable visualisation of this material's internal three-dimensional structure.

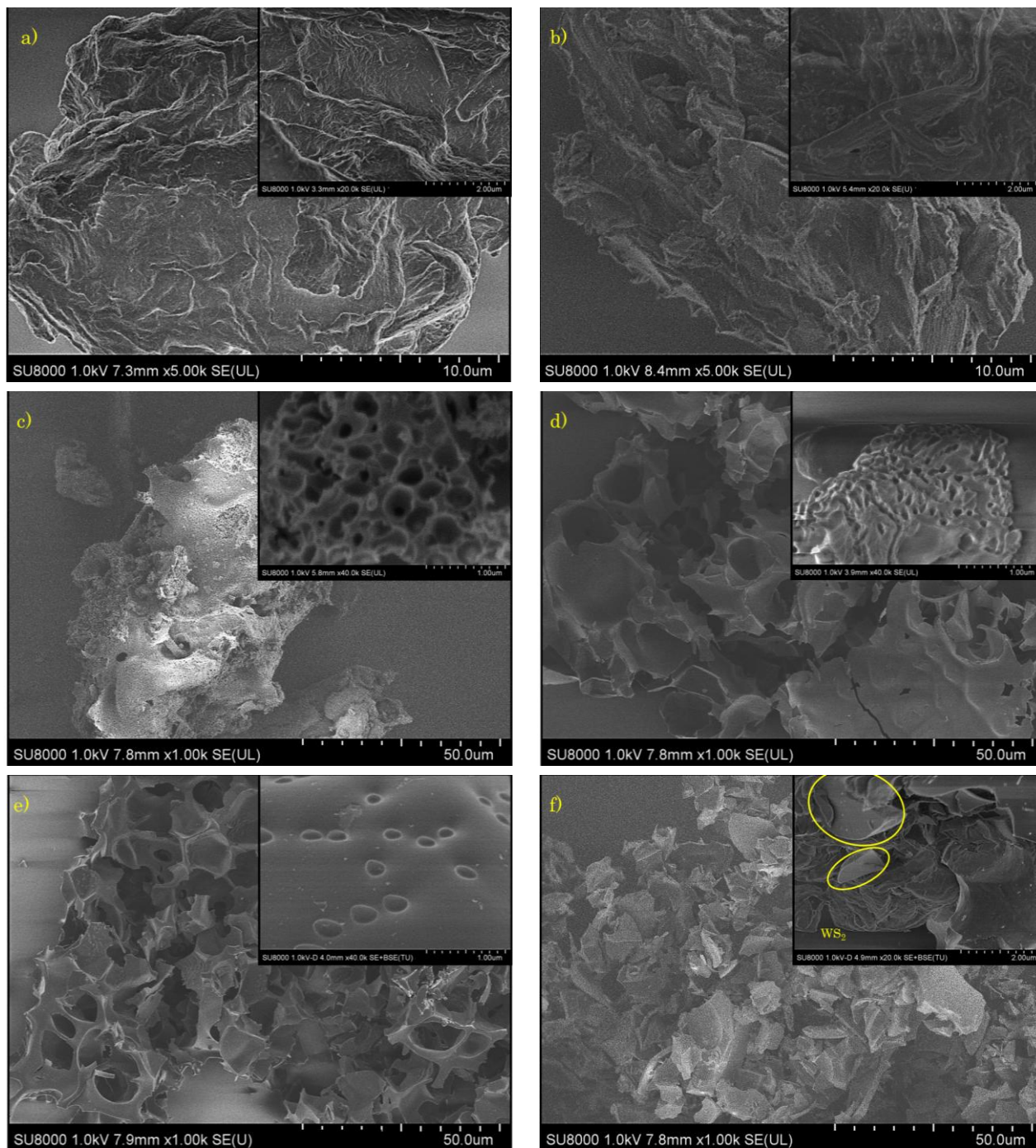


Figure 4.15: SEM micrographs of a) Cellulose; b) C300; c) C 1-1.5; d) C 1-4; e) CA 1-4 and f) C 1-4 W. The main images are at a resolution of x1k, and the insert images at x20k or x40k.

Fourier-transform infrared spectroscopy:

Spectroscopic techniques were employed to determine the chemical functionalities of the starting materials and prepared carbonaceous products. To understand the chemical changes taking place in the HTC process, FTIR analyses were performed on cellulose, C200 and C300, with the resulting spectra presented in Figure 4.16.

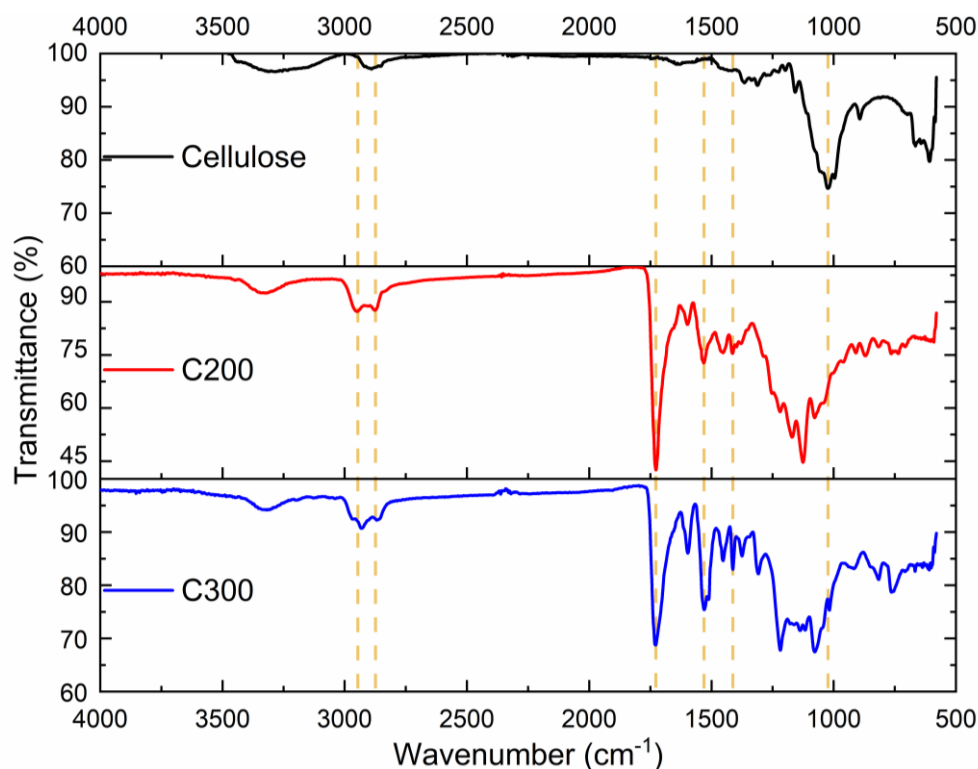


Figure 4.16: FTIR spectra of cellulose, C200 and C300.

A number of bands in the spectra can be used to differentiate between cellulose and the hydrochars prepared at 200 and 300 °C (see dashed lines). For example, cellulose displays a strong band around 1020 cm^{-1} , characteristic of the stretching vibration of the C-O bonds [429], which is considerably less intense in the C200 and C300 samples, indicating rupture of the C-O links as the hydrothermal process advances. Furthermore, a band at approximately 1730 cm^{-1} is present in C200 and C300, but not in cellulose. This band has been associated by several authors to the stretching vibration of the C=O bond [430]. This is possibly due to an oxidation of the samples, but could also be ring-opening of the acetal function and/or conversion of a pyranose (i.e. glucose) to a furanose (i.e. fructose) and possibly further dehydrations to HMF [431].

Additionally, a band around 1530 cm^{-1} is also observed in the hydrothermally treated materials, but not in the cellulose. This band is due to the aromatic C=C stretching [432], confirming that the samples have undergone some aromatisation and conjugation during the HTC process, as explained in Section 1.3.1.2. Moreover, the three samples present a peak in the wavenumber range of $2920\text{--}2870\text{ cm}^{-1}$, associated to the CH_2 stretching vibration [433]. Finally, a minor peak is observed at 1413 cm^{-1} , which can be attributed to the CH_2 in-plane vibrations, specifically scissoring, which typically appears in the region of $1422\text{--}719\text{ cm}^{-1}$ [433].

Furthermore, a FTIR analysis of albumin and the C:A precursors was carried out to confirm the presence of nitrogen functionality within the carbonaceous materials.

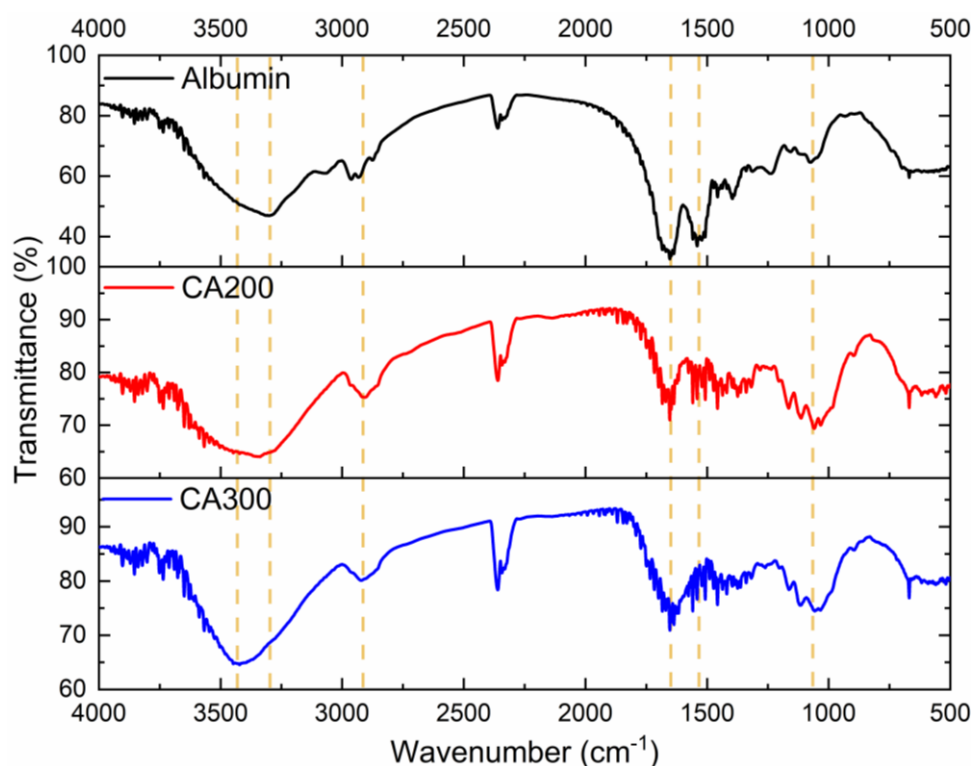


Figure 4.17: FTIR spectra of albumin, CA200 and CA300.

As demonstrated in Figure 4.17, all three samples exhibit a prominent peak around 1050 cm^{-1} , which is attributed to the stretching of C-N peptide bonds in the molecules [434], confirming the presence of nitrogen after thermal treatment (at least up to $300\text{ }^{\circ}\text{C}$). Furthermore, a noticeable peak at 1650 cm^{-1} can be observed, which previous studies in egg albumin have attributed to the C=O stretching of the amide I group, in addition to a band at 1550 cm^{-1} , corresponding to N-H bending of the amide II group [435]. However, given the low intensity of this peak, it can also be attributed to an artifact of sampling.

These samples also display a broad band at $3300\text{--}3450\text{ cm}^{-1}$, characteristic of N-H stretching vibrations of peptide bonds. The exact nature of the nitrogen functionality within the HTC prepared samples will be discussed further within the XPS section of this chapter. The bands at 2350 cm^{-1} are due to atmospheric CO_2 [436].

Raman spectroscopy:

Raman spectroscopic analysis of the samples C 1-1.5 and C 1-4, and their derivatives are shown in Figure 4.18 and Figure 4.19, respectively.

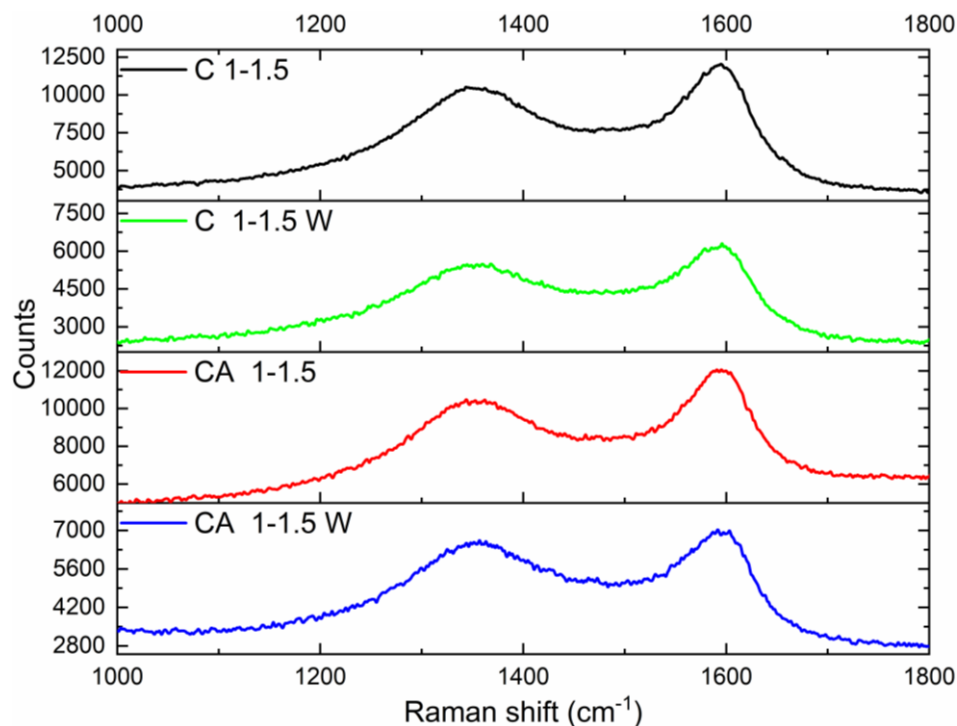


Figure 4.18: Raman spectra of the C 1-1.5 set of samples.

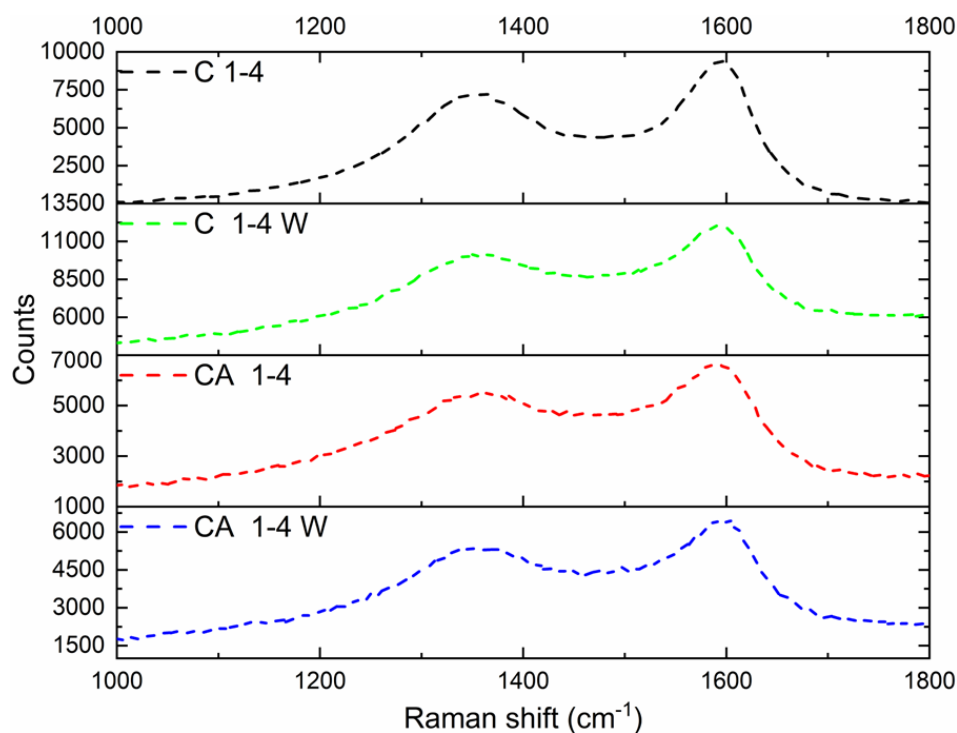


Figure 4.19: Raman spectra of the C 1-4 set of samples.

Following the acquisition of the spectra, peaks were deconvoluted according to Sadezky's methodology for turbostratic carbons [388] using OriginPro® software. Turbostratic carbons are defined as a class of carbon with a structural ordering in between that of an amorphous carbon phase and a crystalline graphite phase, but lack the regular AB-stacking and long-range ordering of graphite [437]. An example of the deconvolution is presented in Figure 4.20, and the parameters obtained from this procedure are shown in Table 4.5:

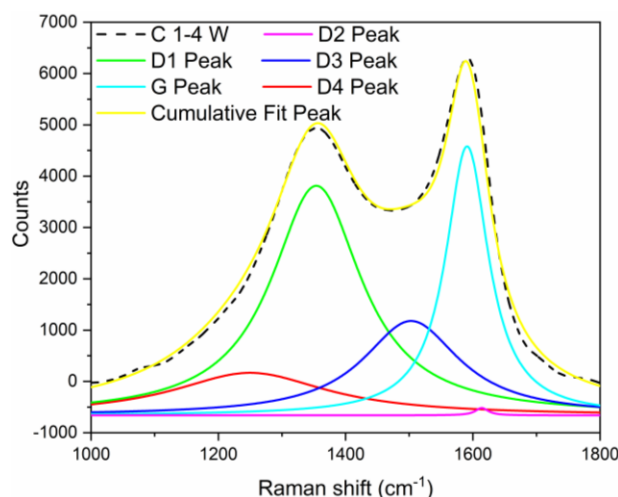


Figure 4.20: Example of deconvolution of the AC Raman spectrum (C 1-4 W), with peak identification labels presented.

Calculation of the D/G ratio (peak height or area) using the deconvolution of the D1 and G peaks enables the ratio between structural defects (peak D1) in the carbon and the ideal graphitic lattice (peak G) to be determined, as shown in Table 4.5.

Table 4.5: Raman deconvolution results for the C 1-1.5 and C1-4 series of samples.

Sample	Peak maxima (cm ⁻¹) ^a					D/G ratio	
	D1	D2	D3	D4	G	Area	Height
C 1-1.5	1349 (50%)	1557 (3%)	1501 (18%)	1238 (3%)	1594 (26%)	1.89	0.97
CA 1-1.5	1348 (50%)	1557 (2%)	1501 (18%)	1239 (4%)	1595 (27%)	1.87	0.92
C 1-1.5 W	1351 (42%)	1553 (4%)	1503 (20%)	1250 (10%)	1597 (24%)	1.77	0.90
CA 1-1.5 W	1348 (46%)	1561 (3%)	1501 (22%)	1250 (6%)	1597 (23%)	2.05	0.97

C 1-4	1350 (48%)	1616 (3%)	1504 (19%)	1217 (7%)	1588 (23%)	2.08	0.99
CA 1-4	1348 (47%)	1608 (4%)	1524 (22%)	1222 (10%)	1591 (17%)	2.72	1.27
C 1-4 W	1346 (51%)	1603 (4%)	1526 (24%)	1227 (4%)	1590 (18%)	2.82	1.32
CA 1-4 W	1350 (44%)	1611 (4%)	1519 (22%)	1236 (11%)	1589 (18%)	2.39	1.16

^a In brackets, the area contribution from each peak compared to the total area.

The D1 peak contributes the most to the total cumulative area of the deconvoluted region of all samples, underscoring the disordered nature of the prepared ACs. These results are expected, given that thermal treatment at 800 °C is not enough to generate a graphitic structure [438, 439]. However, the strong influence of the G band reveals that there is some graphitic character, placing the material structurally between a hard carbon (non-graphitisable) and a soft carbon (graphitisable). Typically, hard carbons are materials with a high degree of cross-linking (and disorder) that cannot be graphitised. These materials usually present a large number of small pores, intercalation active sites, and relatively high specific surface area, which makes them favourable for energy storage applications [440]. On the other hand, soft carbons present a higher degree of order in its carbon chains, and at high temperatures these chains can organise and form graphitic structures (with a subsequent lower porosity). Figure 4.21 shows the required temperatures to achieve graphitisation:

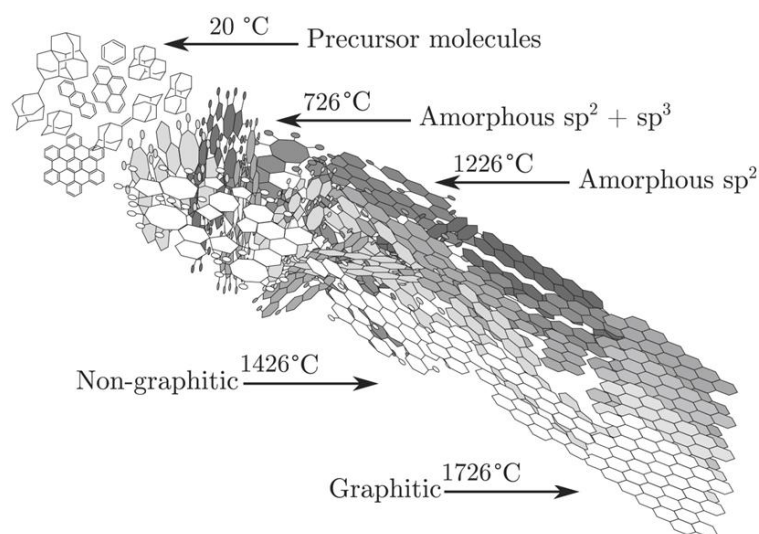


Figure 4.21: Carbon structure and changes with temperature increase (for soft carbons) [438].

In relation to peak position of the deconvoluted maxima of all samples, the D1 and G peaks remain almost unchanged, whereas the low-intensity D3 and D4 peaks exhibit the greatest shift (D4 most). Although D4 shows the greatest variation, it contributes less than 10% of the deconvoluted area, underscoring the influence of edge-defects in these samples' graphitic structures. Regarding D3, the greatest peak shifts were seen in samples with the highest D/G-ratios (CA 1–4, C 1–4 W, CA 1–4 W), consistent with its association to amorphous-carbon vibrations [388]. Comparing the D/G height ratios of all samples (see Figure 4.22), minimal variation is observed, ranging from 0.9 to 1.3. These values are consistent with other sustainably sourced turbostratic ACs, thereby confirming the nature of the developed materials [441, 442].

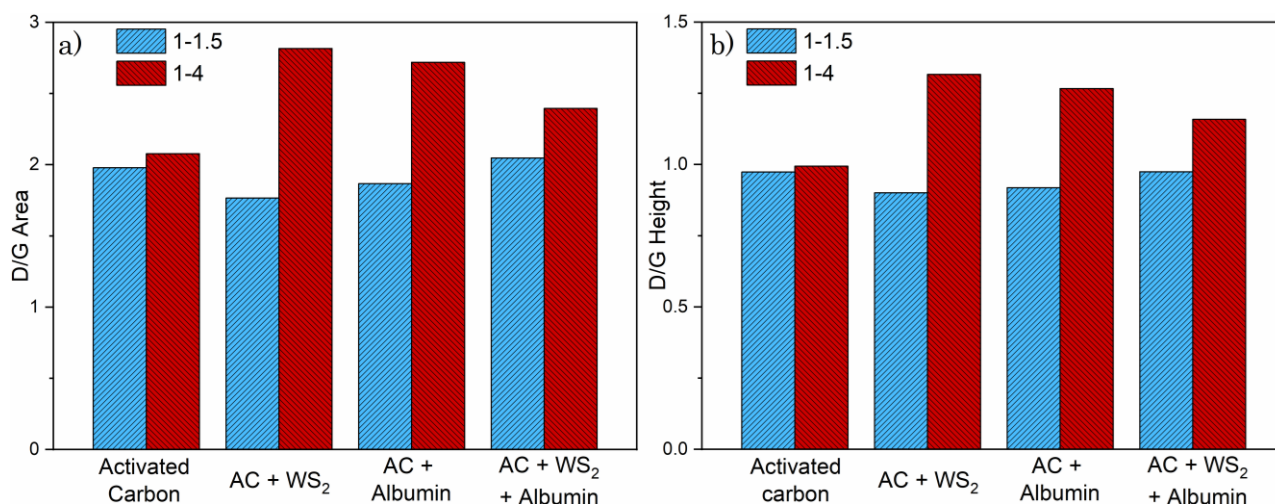


Figure 4.22: D/G ratios of all the analysed samples, a) calculated from the ratio of area and b) from height.

4.4.1.2. Elemental and atomic composition

Elemental microanalysis:

In order to determine the atomic carbon, hydrogen, nitrogen and sulphur content of the developed carbons, elemental microanalysis was initially performed. Subsequent TGA tests showed no inorganic ash content, enabling oxygen to be calculated by subtracting the total (100%) from the sum of the rest of the atoms (C, H, N, S, W). Tungsten was calculated from the results of EDX measurements.

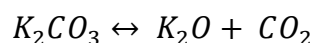
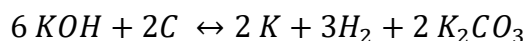
To this end, the pristine material, as well as the hydrochar (at 300 °C) and the final ACs were evaluated through CHNS and EDX analyses, to understand the influence of both HTC and chemical activation on the composition of the final material. All samples were analysed twice with a maximum variation of 0.5% between measurements. The results of these experiments are shown in Table 4.6:

Table 4.6: Atomic composition from elemental analysis and EDX testing.

Group	Name	C (%)	H (%)	N (%)	S (%)	W (%)	O (%)
Precursor	Cellulose	42.8	6.4	0.2	0.1	0.0	50.6
	Albumin	46.7	6.8	13.3	1.6	0.0	31.6
Intermediate	C300	61.7	4.8	0.1	0.1	0.0	33.4
	CA300	60.9	5.6	2.5	0.2	0.0	30.8
Final carbon	C 1-1.5	83.8	1.1	0.1	0.0	0.0	15.0
	CA 1-1.5	83.2	1.3	1.1	0.1	0.0	14.4
	C 1-1.5 W	79.2	2.3	0.1	0.6	3.7	17.8
	CA 1-1.5 W	79.9	2.7	1.0	0.5	2.6	15.9
	C 1-4	82.5	1.0	0.1	0.1	0.0	16.3
	CA 1-4	80.6	1.3	1.2	0.3	0.0	16.5
	C 1-4 W	80.2	2.0	0.2	0.4	2.4	17.3
	CA 1-4 W	75.5	2.1	1.0	0.8	2.8	20.6

Table 4.6 underscores the significance of the HTC, improving %C content by approximately 50% from the pristine cellulose to the C300 and CA300 samples. This increase is mainly attributed to carboxylic group presence as a result of oxidation occurring during HTC and heating to 300 °C (see Figure 4.16). Furthermore, conjugation and aromatisation reactions can also start at 300 °C, as demonstrated by previous FTIR results (see section 4.4.1.1), increasing the C/O ratio of the samples prepared at 300 °C [432].

Following chemical activation, carbon contents of around 75-85% are obtained, representing a 100% increase in %C compared to the precursor. These values are consistent with the literature on hydrothermally treated, chemically activated cellulose [419, 443], which depends strongly on parameters such as activation temperature, KOH dosage, and hydrothermal conditions. During chemical activation, the following reactions take place [444], resulting in the volatilisation of oxygenated and hydrogenated functional groups, which ultimately increase the final %C content of the materials:



In addition, analysis of AC nitrogen content reveals that after blending albumin with the cellulose, it remains throughout all the processing stages. Typically, albumin-doped samples exhibit %N concentrations of approximately 1-1.2%. However, a significant decrease in nitrogen content is observed after the activation

process, from 2.5% in CA300 to 1-1.2% in albumin-doped samples activated at 800 °C. This decline can be attributed to decreasing thermal stability of N-containing functional groups (principally pyrrole and pyridone groups) that remain in negligible amounts after 700 °C, and pyridine groups, which lose approximately 85% of their original mass at 800 °C [445]. These changes are mainly related to the degradation of functional groups, a surface rearrangement of the groups, and decomposition that leads to the formation of volatile HCN [445]. The specific types and relative proportions of nitrogen-containing groups in the samples will be described in the XPS analysis (see page 92).

Finally, WS₂ nanosheets presence can also be verified by comparing the %S in the final carbons. In all cases, WS₂ doped carbons present a %S of around 0.4-0.8%.

Energy dispersive X-Ray spectroscopy:

Although EDX is not commonly used as a quantitative measurement technique, it provides crucial information about the samples. EDX tests were conducted on the final ACs with two main objectives: i) to confirm the elemental analysis results, and ii) to verify the presence of tungsten within the carbons doped with WS₂ nanosheets. It can also be used to detect other metals, such as potassium, which helps assess whether the activating agent was completely removed.

As the example in Figure 4.23 shows, EDX tests demonstrate the presence of tungsten within the WS₂-doped samples, again verifying WS₂ presence within the carbons. Secondly, this spectrum also revealed no trace of potassium, implying that neutralisation and cleaning were effective in the removal of KOH after chemical activation.

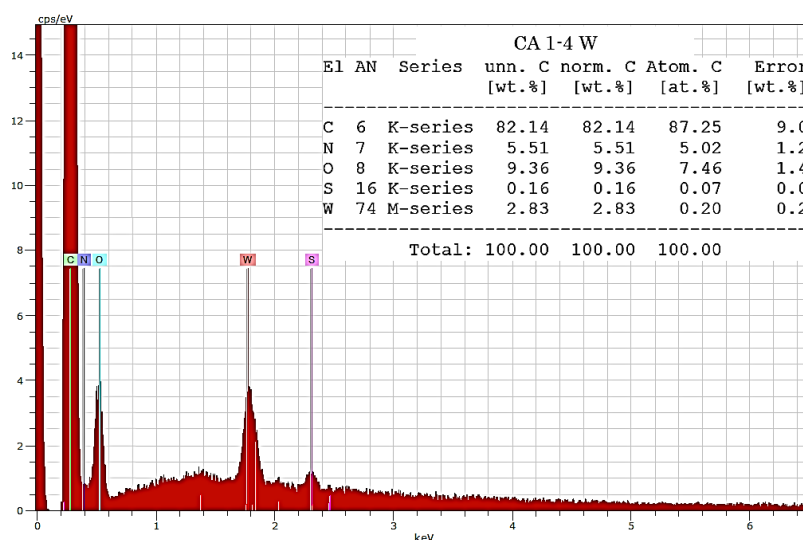


Figure 4.23: Example of EDX spectrum of the developed AC (CA 1-4 W).

X-Ray Photoelectron spectroscopy:

To understand the impact of WS₂ and albumin addition on the functionality of the prepared carbons, C 1-4, CA 1-4 and C 1-4 W were examined using XPS, focusing on the N 1s spectrum of CA 1-4, and the S 2p spectrum of C 1-4 W. The spectra of C 1s and O 1s were not evaluated as all three samples present very similar spectra, indicating that the carbon and oxygen functionality do not vary between the tested samples. Regarding the nitrogen functionality, the N 1s core level spectrum was deconvoluted using OriginPro®. The process yielded three different peaks, as shown in Figure 4.24a.

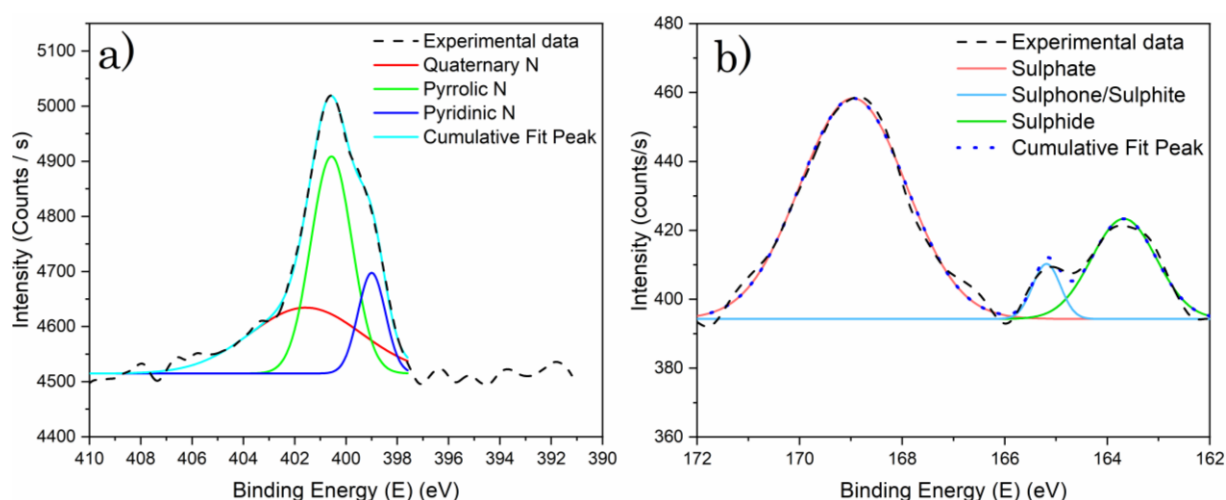


Figure 4.24: XPS deconvolution of a) the N 1s spectrum of CA 1-4 and b) the S 2p spectrum of C 1-4 W.

The three main peaks identified at 399 eV, 400.5 eV and approximately 401.5 eV correspond to pyridinic nitrogen [446], pyrrolic nitrogen [447] and quaternary nitrogen [423, 448], respectively. The deconvolution of these peaks also enabled determination of each peak's area and its contribution to the final nitrogen makeup, as presented in Table 4.7. The obtained nitrogen functionalities in the modified ACs are expected as they originate from peptide bonds, which, upon carbonisation, typically reorganize into pyridinic and pyrrolic nitrogen [449, 450].

Table 4.7: Details of functional group contribution from XPS fitting of the N 1s spectrum and S 2p spectrum of CA 1-4 and C 1-4 W, respectively.

Group	Binding energy (eV)	Area contribution (%)
Nitrogen 1s spectrum		
Pyridinic	399.0	14.5
Pyrrolic	400.6	46.9
Quaternary	401.6	38.6

Sulphur 2p spectrum		
Sulphide	163.7	20.6
Sulphone/Sulphite	165.2	4.9
Sulphate	168.9	74.5

The same procedure was applied to the S 2p sulphur spectrum of C 1-4 W. Deconvolution (see Figure 4.24b) revealed three main peaks at 163.7, 165.2, and 168.9 eV. The expected peak at 163.7 eV (reported values in the literature between 163.7 and 163.8 eV) [451, 452] is related to sulphide (S^{2-}) in the 2H (or 1T) lattice of WS_2 , and has a 20.6% area contribution. The main peak with a binding energy of 168.9 eV can be associated with sulphate (168.5-169.2 eV) presence [452, 453]. This finding indicates that the WS_2 nanosheets deposited on and within the prepared AC have been partially oxidised, which is reinforced by the finding of a peak at 165.2 eV that corresponds to either sulphone ($-SO_2-$) or sulphite groups [452, 453], both being oxygenated functional groups. This oxidation is likely due to air exposure of the nanosheets and may adversely affect the conductivity and electrochemical stability of the final ACs, as discussed in sections 4.4.1.3 and 4.4.2.

4.4.1.3. Thermal and electrical properties

Thermogravimetric analysis:

TGA tests were performed with the following aims:

- Determine the influence of the HTC process on the thermal stability of the carbonaceous materials compared to conventionally carbonised samples.
- Analyse the influence of albumin, WS_2 , and KOH dosages on the thermal stability of the carbons.
- Verify complete removal of potassium after chemical activation and washing.

Figure 4.25 presents a comparison between the C300 samples heated without (red) and with (black) prior HTC. The first sample was directly heated to 300 °C at a rate of 10 °C/min under nitrogen atmosphere in a tubular furnace. In contrast, the second sample was initially hydrothermally treated at 200 °C in a reactor and subsequently heated to 300 °C in a tubular furnace at the same heating rate. Detailed information about this procedure is provided in Section 4.3.

The influence of the HTC step is evident from the thermograms, as it significantly enhances the thermal stability of the carbons. This is due to the hydrothermal reactions that release volatiles and promote depolymerisation of the cellulose, followed by subsequent repolymerisation into more cross-linked aromatic structure (see Figure 1.10 and Section 1.3.1.2) that ultimately increase the thermal stability of the hydrochar [172].

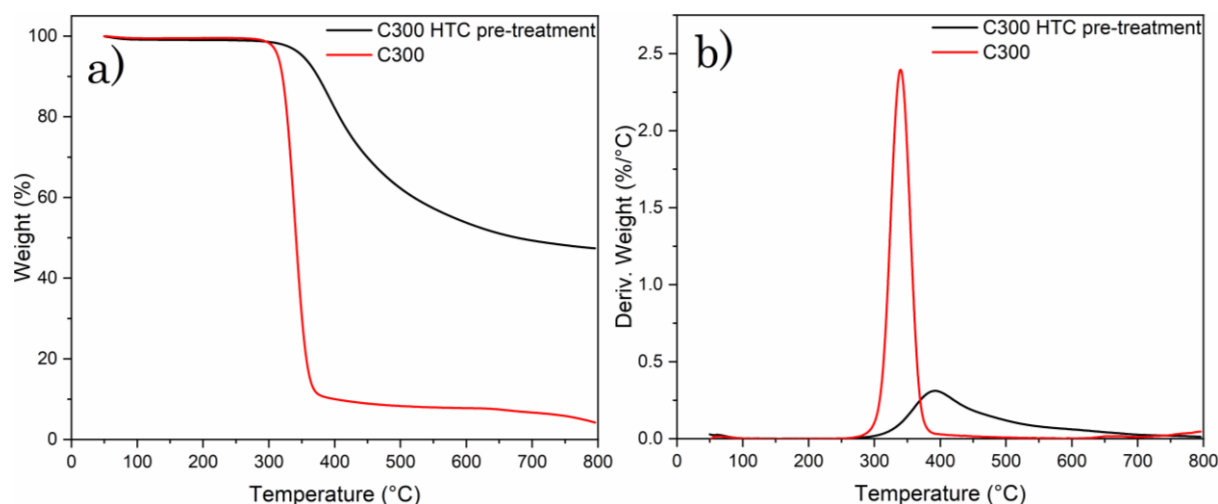


Figure 4.25: a) TGA of C300 (red) and C300-HTC (black) under N₂ atmosphere and b) DTG of the same samples.

Table 4.8: TGA results of the HTC pre-treated and untreated cellulose after preliminary heating to 300 °C under inert atmosphere.

Sample	Temperature at %wt. loss (°C)			Temperature at max. wt. loss (°C)	Residue at temperature (%)		
	2%	5%	10%		400°C	600°C	800°C
C300-HTC	319	352	375	394	82	54	47
C300	302	314	321	340	10	7.8	4.2

From this data, it can be observed that the non-hydrothermally treated carbon starts its decomposition around 302 °C, with a $T_{\max}$ (temperature of maximum weight loss) of 340 °C. This material only retains 10% of its original mass at 400°C, a value that is reduced to less than 5% at 800 °C. In contrast, the hydrothermally treated cellulose begins to decompose at approximately 319 °C, and reaches its $T_{\max}$ at 394 °C, which is approximately 60 °C higher than the untreated carbon. Remarkably, this material retains more than 80% of its original mass at 400 °C, and nearly 50% remains at 800 °C—more than 10 times the residue of the non-HTC carbon. Following these tests, the ACs were analysed under nitrogen and air

atmospheres. Initially, samples were heated from room temperature up to 800 °C under nitrogen, with the results shown below in Figure 4.26 and Table 4.9.

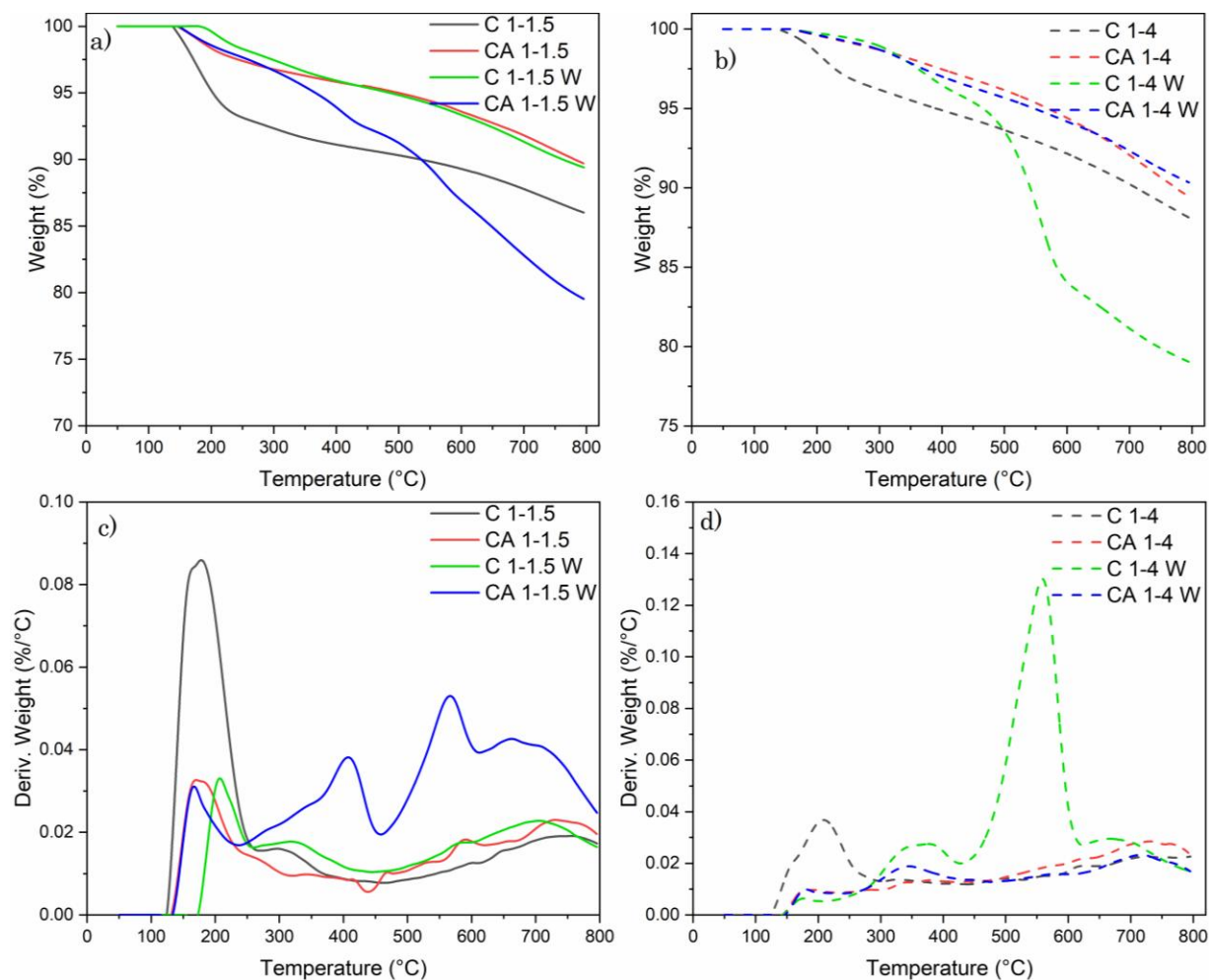


Figure 4.26: TGA and DTG of the C 1-1.5 (a,c) and C 1-4 (b,d) set of samples under N₂ atmosphere.

Table 4.9: TGA results of the final activated carbons under inert atmosphere.

Sample	Temperature at %wt. loss (°C) ^a		Temperature at max. wt. loss (°C) ^a		Residue at temperature (%) ^a		
	5%	10%	T ₁	T ₂	400 °C	600 °C	800 °C
C 1-1.5	203	535	178	311	91	89	86
CA 1-1.5	500	780	171	-	96	94	90
C 1-1.5 W	486	762	208	322	96	93	89
CA 1-1.5 W	367	536	406	567	94	87	80
C 1-4	401	711	207	-	95	92	88
CA 1-4	574	775	180	-	98	94	90
C 1-4 W	467	541	374	560	96	84	79
CA 1-4 W	551	800	180	351	97	94	90

^a Weight loss from surface water was excluded from analysis.

All samples exhibit a weight loss maximum between 100-200 °C, corresponding to the removal of physisorbed water. These peaks are notably more intense in C 1-1.5 and C1-4, indicating that the unmodified carbons retain more water than their doped counterparts. This suggests that nitrogen and sulphur heteroatoms are able to alter the carbon surface chemistry, reducing hydrophilicity and water retention, consistent with previous studies [454].

With respect to the profile of the C 1-1.5 and C 1-4 samples and their derivatives, they all present very similar thermogram profiles, suggesting that there is little difference between how they degrade and carbonise. These samples likely lose formed oxygen functionality generated during the activation process between approximately 200-400 °C and then continue to slowly reorganise and carbonise from 450 °C onwards [455]. The exception to this are the samples C 1-4 W and CA 1-1.5 W, which lose substantially more mass ($\approx 15\%$) and with T_{max} maxima around 350-370 and 560 °C. For clarity, Figure A15 displays a thermogram of pure WS₂, where a clear peak at approximately 560 °C can be distinguished. This peak is associated with nanosheet degradation, and therefore, it can be understood that these peaks (see Table 4.9) are related to the degradation of WS₂. However, they are significantly less intense—or absent—in CA 1-4 W and C 1-1.5 W, despite also containing WS₂.

The hypothesis for this difference from the post mortem analysis (see Section 4.4.2.4) is that for the samples that follow the same degradation profile as the other samples, the WS₂ nanoparticles are only deposited on the samples' surface. On the contrary, for the two samples with the greatest mass loss, the nanoparticles are incorporated to a better extent within the pores, and that when they degrade, the formed radicals can act upon the carbon matrix, catalysing the decomposition and, therefore, increasing mass loss, as observed in Figure 4.26. Furthermore, this pore filling hypothesis also explains the significantly lower surface area of these samples compared to the rest of the samples in their sets (see Table 4.4).

Subsequently, samples were tested under the same conditions in an oxidative atmosphere, as shown in Figure 4.27 and Table 4.10.

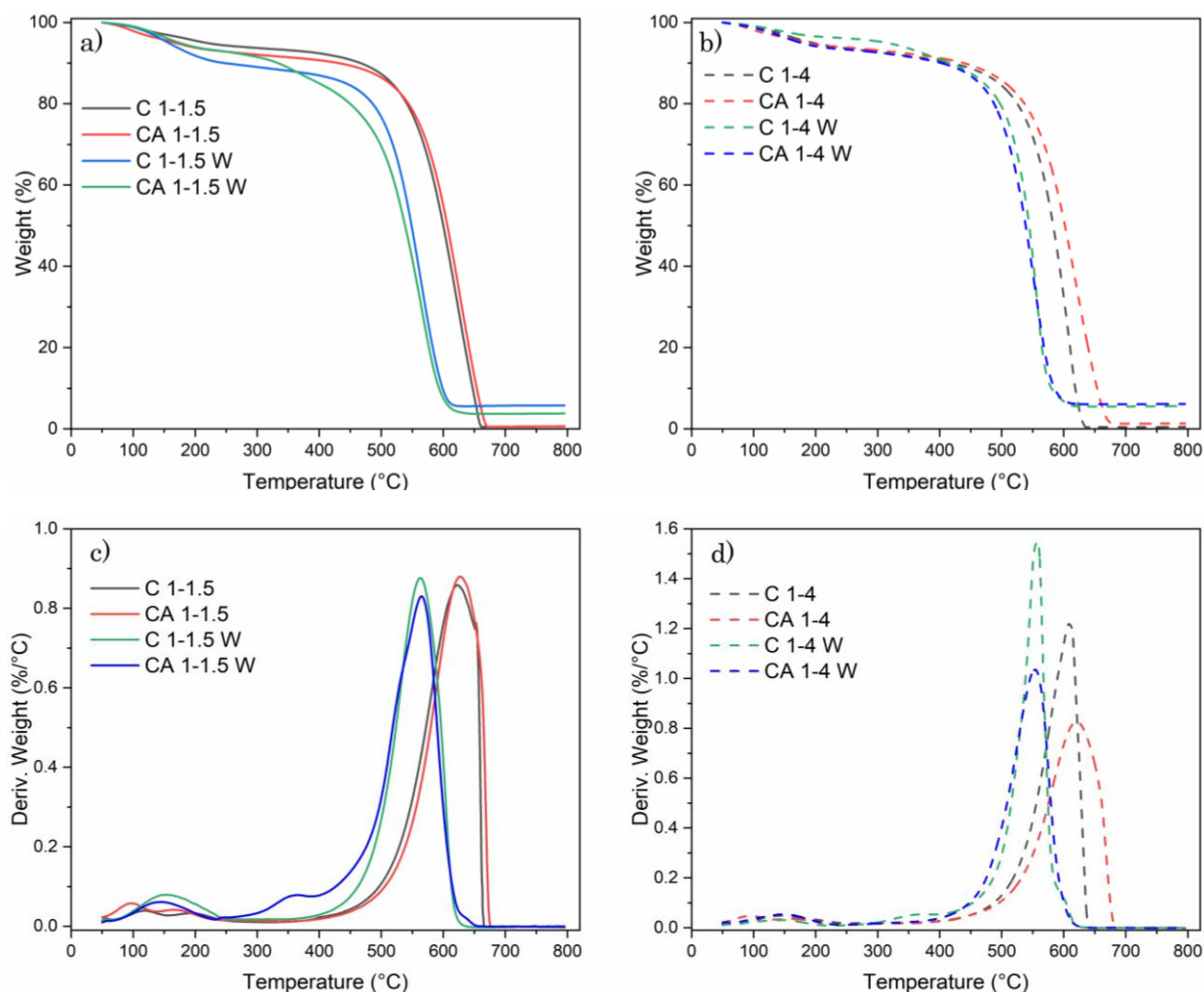


Figure 4.27: TGA and DTG of the C 1-1.5 (a,c) and C 1-4 (b,d) set of samples under oxidative atmosphere.

Table 4.10: TGA results of the final ACs under oxidative atmospheric conditions.

Sample	Temperature at %wt. loss (°C)			Temperature at max. wt. loss (°C)	Residue at temperature (%)		
	2%	5%	10%		400 °C	600 °C	800 °C
C 1-1.5	123	218	467	624	92	50	0
CA 1-1.5	99	168	431	628	91	55	0
C 1-1.5 W	123	175	334	563	85	7	4
CA 1-1.5 W	117	157	248	564	87	9	6
C 1-4	128	196	419	609	91	32	0
CA 1-4	103	187	439	622	91	51	1
C 1-4 W	141	315	417	558	91	7	6
CA 1-4 W	117	176	406	554	90	7	6

From the obtained thermograms, it is observed that C 1-x and CA 1-x samples exhibit a $T_{\max}$ around 610-630 °C, associated with oxidative degradation of the

carbon [456, 457], and they were fully consumed during the heating process, verifying the absence of any KOH residue. In contrast, WS₂-containing samples reach their $T_{\max}$ approximately 50 °C earlier, further confirming the catalytic effect of the WS₂ nanosheets during the oxidative degradation of carbons, as other authors have previously reported [458]. Furthermore, approximately 5% of the original mass remains in the WS₂-doped ACs after 800 °C, attributed to the residual presence of nanosheets, or tungsten sulphate, given the oxidising conditions.

Electrical conductivity:

The bulk electrical conductivity of the prepared ACs was evaluated by measuring the current over a voltage range of 10-25 mV.

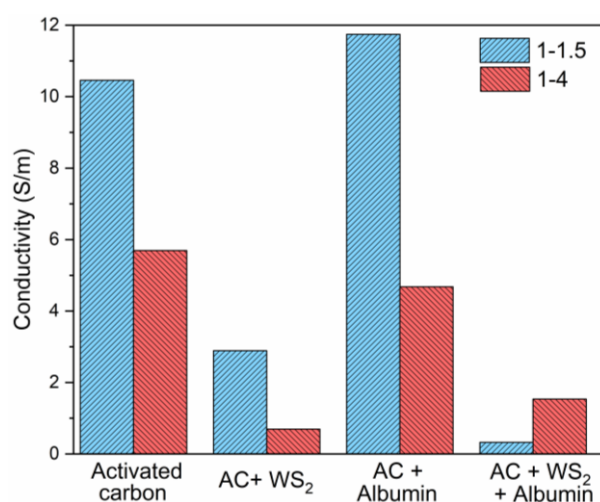


Figure 4.28: Conductivity of the prepared ACs and their derivatives.

Figure 4.28 reveals how KOH dosage influences the conductivity of the prepared ACs. In general, samples prepared with a C300-to-KOH ratio of 1:1.5 are approximately twice as conductive as those with a 1:4 ratio, likely due to multiple factors. Among the unmodified ACs, C 1-4 is notably more porous than C 1-1.5, with a respective 39% and 44% higher BET surface area and micropore volume (see Table 4.4)—an increase in porosity that effectively reduces the solid cross-section available for current flow [459]. Moreover, Raman analysis shows that the 1-1.5 set of samples exhibits higher G peak intensities (and thus lower D/G ratios, as detailed in Table 4.5). The stronger G-peak implies a higher fraction of sp²-hybridized carbon and thus more extensive π -electron delocalisation, which also promotes electrical conduction [460].

The WS₂-doped samples, however, exhibit significantly lower conductivity than their undoped counterparts. As demonstrated by XPS analysis (see Table 4.7), more than 75% of the sulphur species present in WS₂ are in oxidised forms. These oxygenated functional groups can disrupt the graphitic structure of the carbon (introducing sp³ defects) and, therefore, decrease its conductivity [461].

The effect of albumin on the samples' conductivity does not show a clear trend overall. However, it can be observed that, for C 1-1.5, albumin addition results in an increase in the C/O ratio of the sample (5.58 vs 5.78), which, in turn, leads to increased conductivity. In contrast, the C/O ratio of C 1-4 decreases (see Table 4.6) when albumin is present (5.06 vs 4.88), negatively affecting the conductivity.

Furthermore, Raman analysis of the samples reveals a slightly higher graphitic content in CA 1-1.5 (D/G ratios of 1.89 vs. 1.87, respectively; as shown in Table 4.5), linked to enhanced conductivity, while C 1-4 also exhibits a greater degree of graphitisation compared to CA 1-4 (D/G ratios of 2.08 vs. 2.72, respectively), explaining its increased conductivity compared to its albumin-doped homologue. Further details regarding the methodology used for conductivity measurements are provided in Annex 3: Electrical conductivity calculations.

4.4.2. Supercapacitor application

After analysis of the prepared samples chemical and morphological properties, they were assembled in supercapacitor cells for electrochemical testing. Samples were assessed using direct current (cyclic voltammetry and galvanostatic tests) and alternating current (impedance spectroscopy) tests to fully understand their energy storage potential.

4.4.2.1. Cyclic voltammetry

To investigate the electrochemical behaviour of the samples, initially the effect of scan rate was examined (an example of this evaluation is shown in Figure 4.29a for the C 1-4 sample). At low scan rates (1-5 mV/s), the curves exhibit a quasi-rectangular shape, which transitions into an elliptical form as the rate increases.

For clarity, Figure 4.29b presents a plot of the electrode's specific capacitance (calculated as the ratio between current and scan rate, per gram of electrode) versus voltage, allowing the transition from the quasi-rectangular profile at low scan rates to the elliptical form to be more easily seen.

Typically, rectangular shapes (in purple) correspond to an almost ideal supercapacitor behaviour, where at low scan rates no restrictions to ion diffusion and electrode polarisation take place [423]. However, with increasing scan rate, time for polarisation decreases, shifting towards the more elliptical profiles represented in pink, more representative of typical supercapacitors.

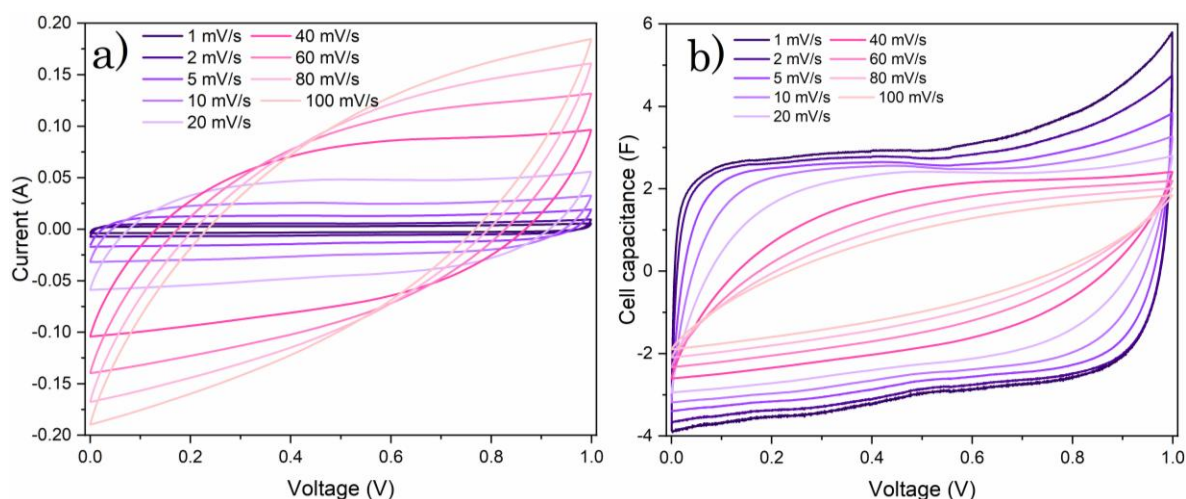


Figure 4.29: a) Cyclic voltammograms, and; b) Specific capacitance vs voltage of the C 1-4 electrode.

It is also observed that, irrespective of the scan rate, the obtained voltammograms do not exhibit any peaks that are associated with redox reactions, indicating that in this case, the process is purely electrostatic, with no pseudocapacitive contribution. This profile is expected in the devices containing C 1-4 and C 1-1.5, since they do not contain heteroatoms to provide pseudocapacitance. For the albumin and WS_2 -containing samples (voltammograms of these samples are presented in Annex 4), some redox peaks could be expected. The absence of these peaks can be attributed to the low concentration of heteroatoms (nitrogen for albumin and sulphur for WS_2), as explained in Section 4.4.1.2 (see Table 4.6).

For more detailed information on how the specific capacitance corresponding to each scan rate can be determined, please refer to Annex 5: Determination of specific capacitance through cyclic voltammetry experiments. From the results displayed in Figure 4.30 it is clear that higher scan rates lead to restrictions in ion diffusion (which in turn results in energy losses), and consequently, lower specific capacitances, with devices losing up to 80% of their original capacitance when scan rate increases to 100 mV/s.

It is also interesting to compare the capacitance values among all the prepared samples depending on the synthesis parameters—namely KOH ratio, albumin and

WS₂ presence. First of all, it can be observed from Figure 4.30 that the set of C 1-4 samples exhibits superior capacitance in comparison to their counterparts prepared with a 1.5 KOH ratio. The explanation for this is shown in Table 4.4. The electrochemical performance of these samples is strongly dependent on textural parameters, particularly pore size and pore volume. Since the ion size of the adopted electrolyte (H₂SO₄) is 0.426 nm [423], micropore volume plays a significant role in the final capacitance of the material. This means that samples with larger micropore volume are able to retain a higher amount of electrolyte ions, thereby displaying higher capacitances than those with lower micropore volume. Consequently, all C 1-4 carbons exhibit higher capacitances than their C 1-1.5 equivalents.

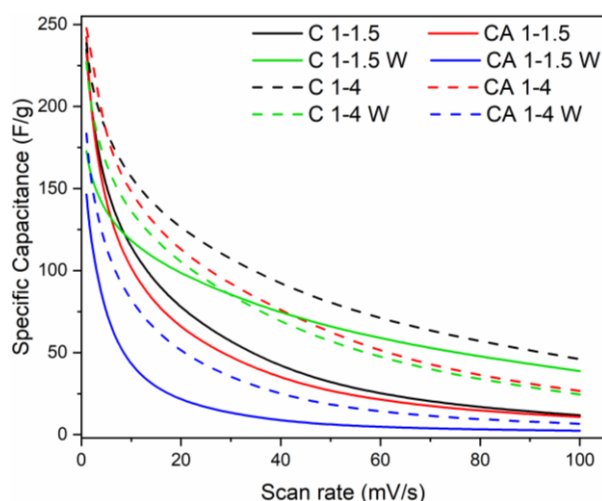


Figure 4.30: Capacitance variation of the prepared ACs and their derivatives with increasing scan rate from 1 to 100 mV/s.

However, not only micropore volume is fundamental to improved electrochemical performance. It must be also considered that a material will show enhanced capacitance when its pore sizes are close to the size of the electrolyte ion [423]. This is observed for the non-albumin doped samples (black and green lines) that exhibit slightly higher capacitances than their albumin-doped counterparts (red and blue lines, respectively). As pore size distribution plots outline in Figure 4.13, the addition of albumin results in a slight shift in the micropore peak (from 0.12 up to 1 nm). This minor increase in pore size can induce a decrease in capacitance, since the pores within the CA samples display a greater size difference to the SO₄²⁻ ion than the pores in the non-albumin-doped ACs.

Finally, the influence of WS₂ nanosheets on the electrochemical performance of the ACs can also be assessed. SEM analyses in Figure 4.15 demonstrate that the WS₂

nanosheets are not inserted into the carbon matrix, but deposited on its surface, blocking access to some of the pores, and therefore reducing the available pore volume, as seen in Table 4.4. The effect of this pore blockage is a reduction in the number of electrolyte ions that are able to polarize the electrode surface, therefore resulting in reduced capacitances for WS₂-doped ACs (green and blue lines) compared to non-WS₂ containing samples (black and red lines, respectively).

Although the effects of KOH activation and WS₂ nanosheets addition have been described, at scan rates above 10 mV/s and 30 mV/s, respectively, samples C 1-1.5 W and C 1-4 W (Figure 4.30) defy the tendency, displaying a capacitance higher than their undoped counterparts (C 1-1.5 & C 1-4). A likely explanation, based on post-mortem analysis (see Section 4.4.2.4), is that initially the pores are partially blocked, resulting in less accessible micropore volume. However, as the scan rate increases, the WS₂ nanosheets become displaced, enabling better access to the full pore structure compared to before.

Finally, it should be noted that the previous figure displays the capacitance of an individual electrode, but the capacitance of the total electrochemical cell can also be calculated. Since the measured device is a symmetrical cell with the two electrodes working as individual capacitors in series, the capacitance of the cell can be calculated as:

$$\frac{1}{C_{cell}} = \frac{1}{C_{electrode\ 1}} + \frac{1}{C_{electrode\ 2}} \quad \text{Equation 4.1}$$

As the electrochemical cell is symmetrical, the capacitance of each electrode is similar:

$$\frac{1}{C_{cell}} = \frac{1}{C_{electrode}} + \frac{1}{C_{electrode}} = \frac{2}{C_{electrode}} \rightarrow C_{cell} = C_{electrode} / 2$$

For the determination of specific capacitance, C_{sp}, it would be necessary to divide the capacitance by the mass of each electrode (for the C_{sp} of each electrode) or the mass of both electrodes (C_{sp} of the cell).

$$\frac{1}{C_{cell}} = \frac{2}{C_{electrode}} \rightarrow \frac{1}{C_{sp\ cell} * (2 * m_{electrode})} = \frac{2}{C_{sp\ electrode} * (m_{electrode})}$$

Therefore:

$$\frac{1}{C_{sp\ cell}} = \frac{4}{C_{sp\ electrode}} \rightarrow C_{sp\ cell} = \frac{C_{sp\ electrode}}{4} \quad \text{Equation 4.2}$$

Demonstrating that the specific capacitance of a symmetrical cell can be calculated by dividing the specific capacitance of a single electrode by 4.

4.4.2.2. Galvanostatic cycling

Galvanostatic charge-discharge testing was applied in order to determine the electrochemical parameters of the prepared electrodes, specifically capacitance, energy density and power density. Experimental data obtained from the charge/discharge cycles at low currents show linear plots for both the charge and discharge stages, verifying that, as observed during cyclic voltammetry, the process is purely electrostatic (no redox processes – indicative of pseudocapacitive behaviour). Furthermore, charge and discharge processes display similar times, showing good reversibility, and minimal ohmic drop (see Figure 4.31 a, black curve). Ohmic drop, also known as IR drop, is the sum of the internal resistances of all the components in the electrochemical cell that hinder the flow of electrons from one electrode to another [462].

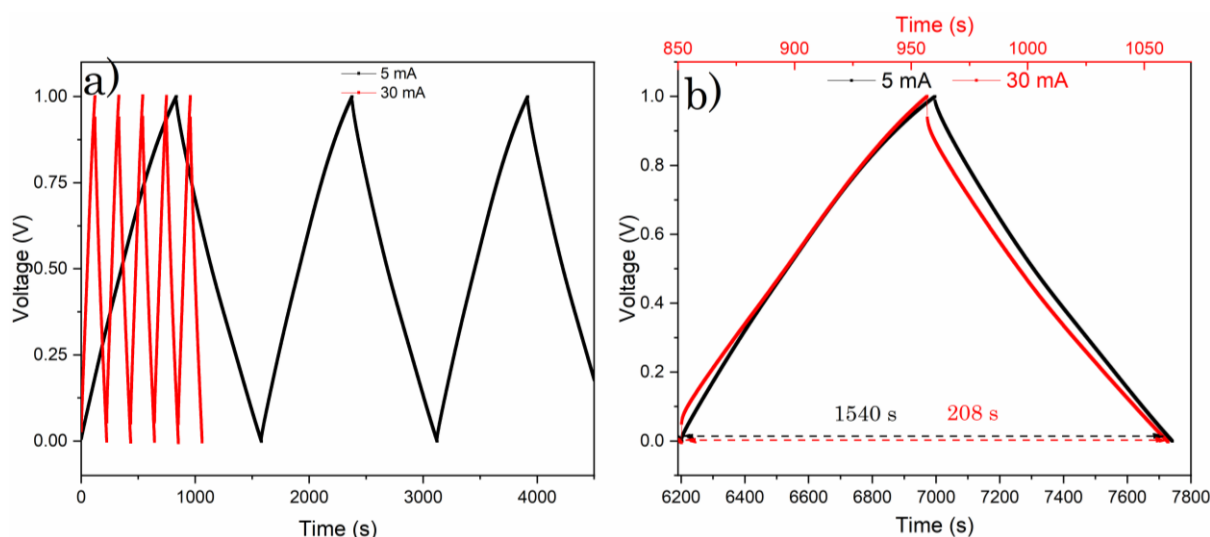


Figure 4.31: a) Galvanostatic charge-discharge cycles for the C 1-4 electrode sample at constant currents of 5 mA (black) and 30 mA (red); b) Galvanostatic curves at different currents of one full cycle taken from the 2nd charge-discharge cycle.

On the other hand, Figure 4.31a also shows the galvanostatic charge/discharge curves performed at higher currents (30 mA). From this plot it can be understood that, with increasing current, the time for surface polarization decreases, and consequently, the charge and discharge times, with increased voltage loss due to internal resistances (and subsequent loss in specific capacitance and energy density). Additional support for this observation is shown in Figure 4.31 b. Here, the cycles recorded at higher currents (red curves) occur over a noticeably shorter

time lapse than those at lower currents (black curves). While the black curve remains relatively symmetrical, the red curve shows visible signs of ohmic losses during both the charge and discharge steps.

An example for the calculation of all the experimental parameters (charge and discharge time, capacitance, stability, internal series resistance, power and energy density) is provided in Annex 6: Determination of electrochemical parameters through galvanostatic cycling. Furthermore, Figure 4.32a and Table A4 show the variation of these parameters with increasing current, confirming the previous explanation that, with greater current, capacitance and energy density decrease. On the other hand, power density increases with rising current, as power is inversely proportional to discharge time, which is reduced with increasing current.

After the determination of these parameters, it is possible to compare the maximum specific capacitance of the prepared electrodes (measured at a current of 1 mA), displayed in Figure 4.32b. Similar to the cyclic voltammetry results, sample C 1-4 shows the highest specific capacitance of 275 F/g — a value to the authors' knowledge that has not previously been achieved by other biomass-derived, HTC-treated electrodes in symmetrical supercapacitors (see Table 4.12).

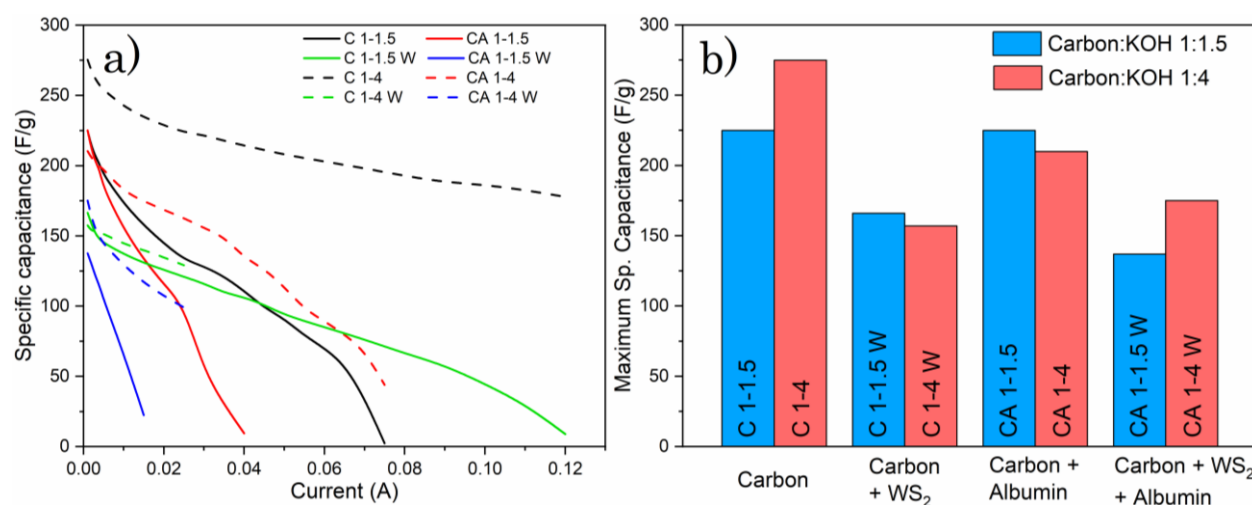


Figure 4.32: a) Specific capacitances of all ACs, calculated from galvanostatic tests; b) Maximum specific capacitances (measured at 1 mA) of all samples.

Moreover, when assessing the effect of albumin, analysis of Figure 4.32a and b show the same trend as in cyclic voltammetry tests, with the CA samples displaying a higher capacitance loss with increasing current compared to the non-albumin containing samples.

Additionally, all WS₂-doped samples display lower capacitance than their non-doped counterparts, confirming that nanosheet presence (or specifically, the

selected method for nanosheet addition) has a detrimental effect on the electrochemical performance due to a decline in textural properties. The other non-WS₂ doped ACs all exhibit excellent capacitances, exceeding 200 F/g at a current of 1 mA.

The stabilities of the prepared ACs obtained from Figure 4.32 a is shown in Table 4.11, where stability is defined as the ratio between the capacitance measured at the selected current and the maximum capacitance obtained at 1 mA:

Table 4.11: Specific capacitance retention (stability) of the prepared ACs at different currents.

Sample	Capacitance retention (%)			
	10 mA	25 mA	50 mA	100 mA
C 1-1.5	77%	59%	40%	- ^a
CA 1-1.5	69%	44%	-	-
C 1-1.5 W	82%	73%	56%	27%
CA 1-1.5 W	48%	-	-	-
C 1-4	88%	81%	76%	68%
CA 1-4	86%	77%	54%	-
C 1-4 W	92%	82%	-	-
CA 1-4 W	74%	57%	-	-

^a Means that the cell stopped working at this current.

From this table, C 1-4 exhibits the best capacitance retention across the measurement range. Only C 1-4 W matches or slightly exceeds its performance at low currents, while C 1-1.5 W is the only other sample that maintains capacitance retention over the full current range. Though, C 1-4 is the only AC that retains more than 50 % of its original capacitance at 100 mA—and impressively holds 65 % at 120 mA. At these current densities, the prepared electrode outperforms most commercial devices. It also exhibits excellent stability and opens the door to high-power, high-cycle-life applications where standard SCs fall short [463].

Table 4.12 compares the ACs developed in this thesis with other sustainable-source electrodes produced via HTC. It can be seen that C 1-4 outperforms the other materials, without the influence of nanofillers providing pseudocapacitance [33, 37, 464] or the use of more complex pore generation approaches, such as dual physical and chemical activation or the use of porogens [36]. Furthermore, its excellent textural properties (specifically BET area and micropore volume) and the adequate pore size in relation to the electrolyte ion size demonstrate again this material's suitability for electrochemical energy storage applications.

Table 4.12: Comparison of different biomass-derived, HTC processed ACs for use as electrodes for symmetrical supercapacitors.

Electrode	Electrolyte	Porosity	S_{BET} (m^2/g)	Max C_{sp} (F/g)
Cellulose (this study)	2M H_2SO_4	95% microporosity	1674	275
Chitosan [33]	1M H_2SO_4	36% microporosity	2124	274
Coconut shells [36]	0.5M H_2SO_4	Mesoporous structure	2440	246
Wood sawdust [35]	6M KOH	74% microporosity.	1185	244
<i>Enteromorpha prolifera</i> [37]	6M KOH	88% microporous.	1528	228
Cellulose [465]	1M TEABF ₄ /AN	87% microporosity.	2457	180
Starch [465]	1M TEABF ₄ /AN	87% microporosity.	2273	180
Jatropha [406]	1M KOH	Large micro and macropores.	747	175
Lignin [464]	6M KOH	Mainly microporous.	1337	130
Corn straws [466]	6M KOH	Mainly microporous.	1229	75

After the determination (and analysis) of the specific capacitance of the prepared materials, both power and energy density of the supercapacitor electrodes can also be determined, following the guidelines set out in Annex 6. A Ragone plot with these parameters is shown in Figure 4.33:

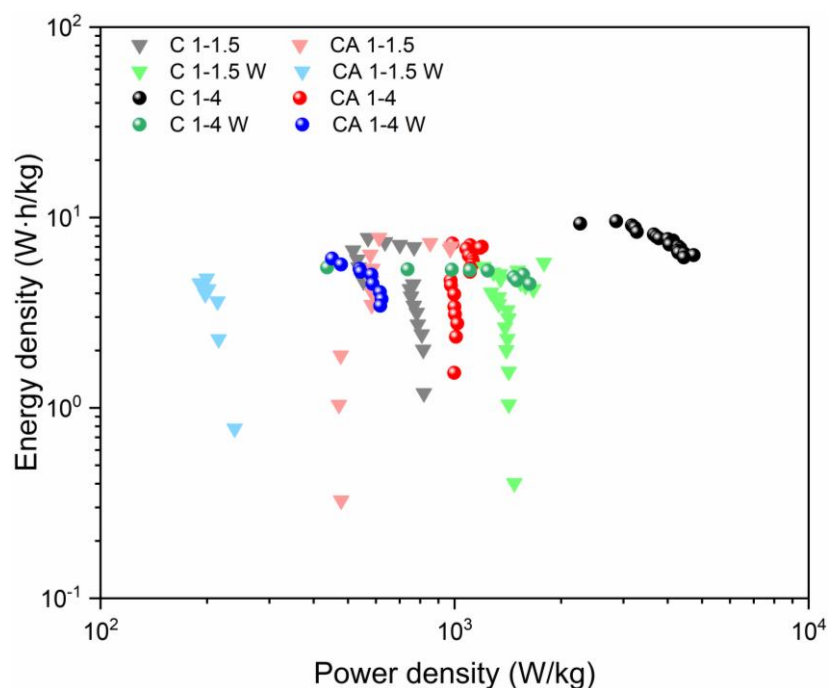


Figure 4.33: Ragone plot showing the energy density versus power density of the prepared ACs supercapacitors electrodes.

C 1-4 also displays the highest power and energy densities since these two parameters are directly related to specific capacitance, reaching maximum power densities close to 5000 W/kg and energy densities around 10 W h/kg. Comparing the obtained energy and power density values of these samples with typical values for electric double layer capacitors (see Figure 1.5), our developed materials stand in the same range of power density (10^3 - 10^5 W/kg) but present energy densities between one and two orders of magnitude higher (1-10 W/h kg compared to 10^{-1} in typical EDLCs [400, 467-469]).

4.4.2.3. Electrical impedance spectroscopy

Alternating current EIS was performed over a frequency range of 10^{-3} to 10^6 Hz to characterize the electrochemical cells' behaviour and to determine the impedance of each sample.

A comparison of the different parts of the Nyquist plots in Figure 4.34 reveals that all samples cross the X axis in the same point, implying that the influence of bulk resistance is the same for all of the carbons. This result is expected as the bulk resistance is the sum of internal resistances offered by electrolyte and cell components, which are the same for all electrochemical cells. Furthermore, the slopes at lower frequencies that relate to ion diffusion restrictions are consistent throughout the whole set of samples.

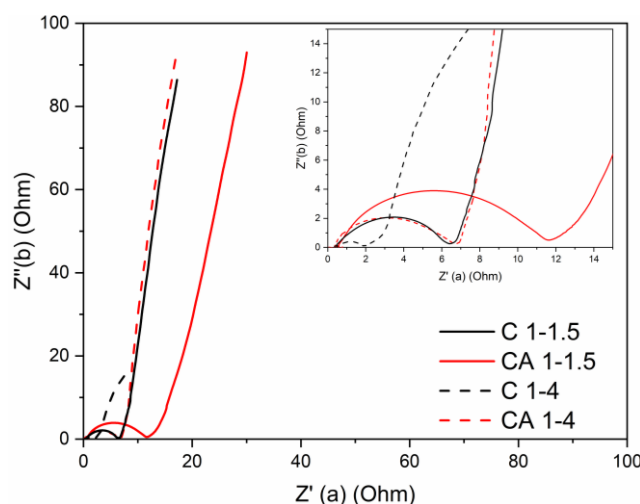


Figure 4.34: ESI Nyquist plots of the samples with highest capacitances (C 1-1.5, CA 1-1.5, C 1-4 and CA 1-4).

Nevertheless, analysis of the semicircles of the Nyquist plot (at impedance values of 0-40 Ω), that are associated with the charge transfer resistance (R_{CT}), are of special interest, with calculated values shown in Table 4.13. Consistent with

previous results, the sample that exhibits lowest charge transfer resistance is C 1-4, the carbon with highest capacitance, stability, power and energy density, confirming again that it has the best electrochemical performance. Furthermore, a comparison of the stability of the ACs (presented in Table 4.11 and Figure 4.32 a) shows the same trend for all materials, revealing a direct relationship between an electrode's low charge transfer resistance and its ability to function at higher currents. Low charge transfer resistance is also associated with higher electrochemical stabilities [307, 470], relating it to higher power and energy densities, as evidenced by previous studies [471].

Table 4.13: Charge transfer resistance values for all developed carbons.

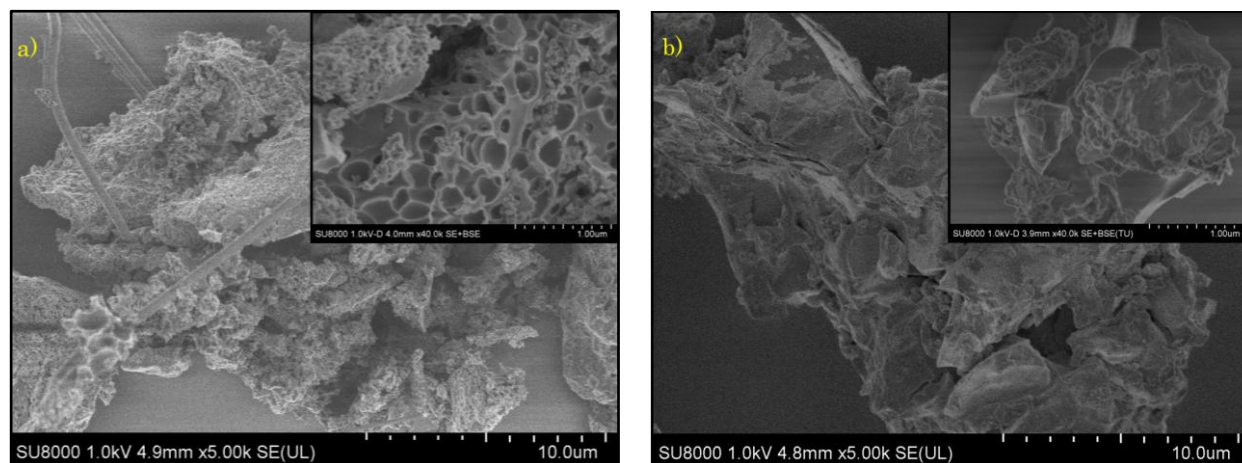
Sample	C 1-1.5	C 1-1.5 W	CA 1-1.5	CA 1-1.5 W
R_{CT} (Ω)	6.09	4.70	11.03	38.91
Sample	C 1-4	C 1-4 W	CA 1-4	CA 1-4 W
R_{CT} (Ω)	1.39	33.46	6.41	14.63

4.4.2.4. Post-mortem analysis.

As the C 1-4 set of samples shows increased electrochemical performance compared to the C 1-1.5 set, these four samples were analysed after supercapacitor testing to understand the effects of electrochemical cycling on the nature of the ACs. The electrochemical cells were disassembled, and the post-mortem ACs (AC-PM) were washed with water and acetone repeatedly to remove the electrolyte and dissolve the binder. Samples were subsequently dried at 50 °C under vacuum.

Scanning electron microscopy:

The macroscopic structure of the ACs-PM was tested by SEM, as seen in Figure 4.35. Micrographs show no changes in particle size, indicating that the electrochemical testing method does not alter the macroscopic structure of the ACs.



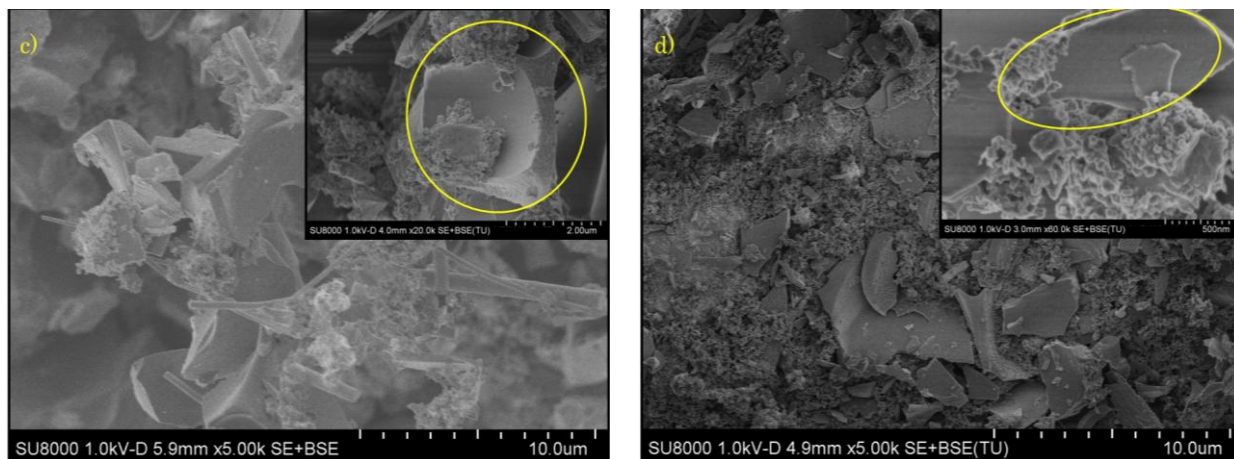


Figure 4.35: SEM micrographs of a) C 1-4, b) CA 1-4, c) C 1-4 W and d) CA 1-4 W after electrochemical testing.

Gas sorption porosimetry:

Afterwards, changes in the internal structure of the ACs-PM were evaluated using nitrogen sorption analysis at 77K, applying the same methodology and equipment as in previous measurements. Figure 4.36 presents a comparison of the adsorption isotherms of the carbons before and after electrochemical testing, as well as a detailed overview of the micropore contribution to the total pore volume of each sample.

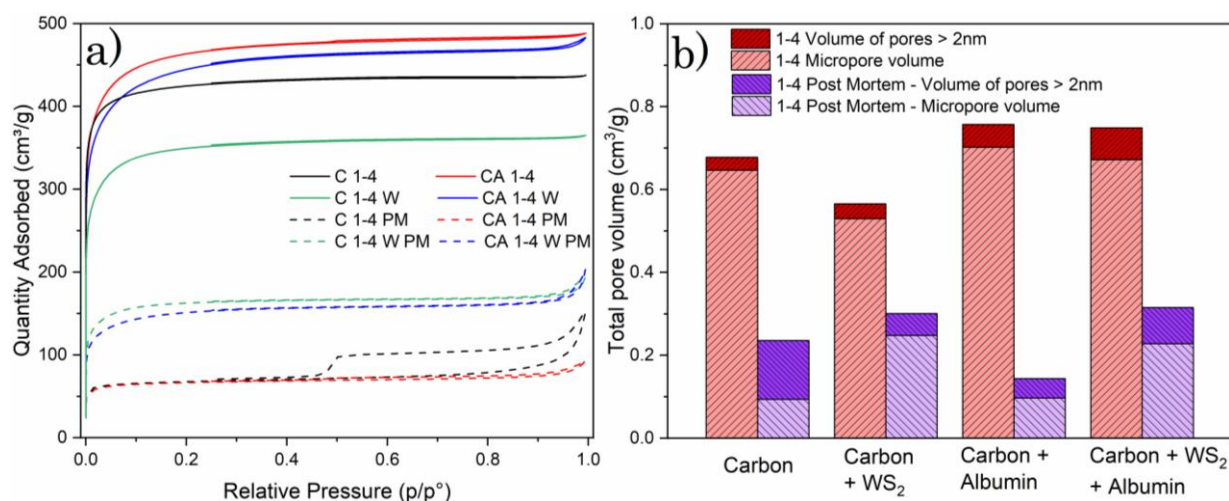


Figure 4.36: a) Nitrogen adsorption isotherms and b) micropore and total pore volume comparison of the C 1-4 set of samples before and after electrochemical treatment.

Furthermore, the textural properties of the carbonaceous electrodes were also determined and they are presented in Table 4.14, Figure 4.37 and Figure 4.38, showing the variation in each parameter with respect to the sample prior to electrochemical testing.

Table 4.14: Textural properties of the C 1-4 set of ACs after electrochemical testing.

Sample	BET area (m ² /g)	Micropore area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)
C 1-4 PM	264 (-84%) ^a	237 (-86%)	0.24 (-65%)	0.09 (-85%)
CA 1-4 PM	258 (-85%)	241 (-86%)	0.14 (-81%)	0.10 (-86%)
C 1-4 W PM	621 (-53%)	606 (-53%)	0.30 (-47%)	0.25 (-53%)
CA 1-4 W PM	565 (-66%)	540 (-66%)	0.32 (-58%)	0.23 (-66%)

^a Values in brackets indicate the change in properties regarding the original sample.

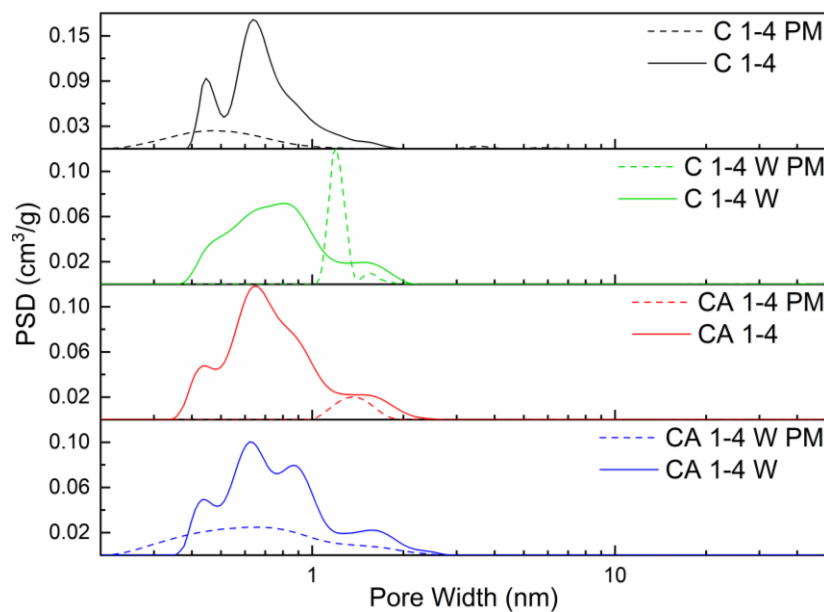


Figure 4.37: PSD of the C 1-4 set of samples before and after electrochemical treatment.

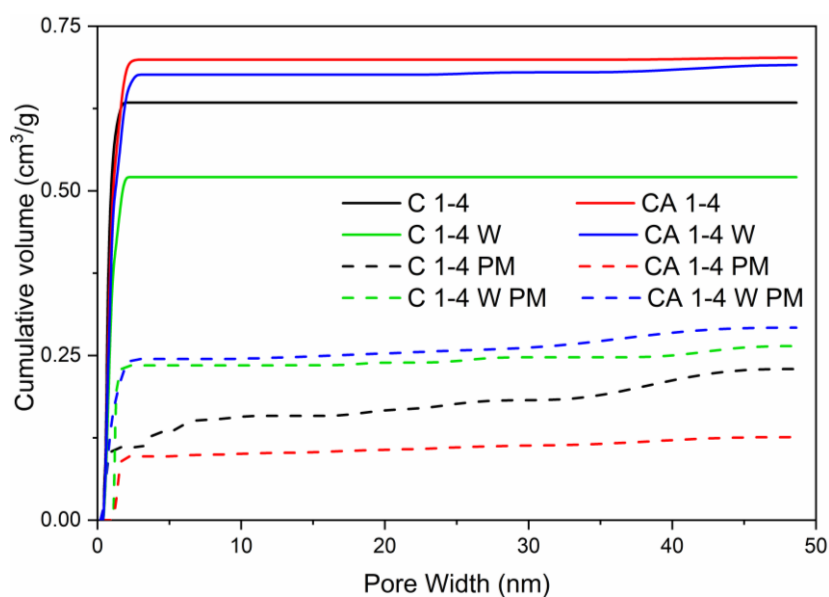


Figure 4.38: Cumulative pore volume of the C 1-4 set of samples before and after electrochemical treatment.

From these results, an evident decrease in the textural properties of the carbons can be observed, with a 50% to 86% reduction in both BET area and pore volume. Especially when observing the microporosity of the materials, it decreases significantly, indicating a destruction of the micropores in order to create pores of larger diameter. This case is especially evident in the case of C 1-4, which moves from 95% microporosity to only 40% after electrochemical testing. The rest of the samples experience a reduction from 90-94% to 67-82% in microporosity, losing a considerable fraction of their micropores, but less than the unmodified carbon. These results suggest that continued charge and discharge cycles result in a partial degradation of the electrodes' surface, destroying some micropores and widening others, which significantly reduces the electrodes' surface area and pore volume. Additionally, the marked decrease in micropore volume may also result from micropore blockage, possibly due to the accumulation of electrolyte ions within these pores.

Seeing these results, the influence of WS₂ nanosheets is evident, especially in the case of C 1-4 W. Table 4.14 shows that, while the non-WS₂-doped ACs lose 85-86% of their original micropore volume, C 1-4 W and CA 1-4 W lose only 53% and 66%, respectively. From this, it can be hypothesised that TMDCs appear to hinder pore destruction (and the subsequent mesopore formation), therefore explaining the higher stability of the WS₂-doped carbons against their non-doped counterparts. In fact, some articles already presented TMDCs as an effective nanofiller in order to improve the stability of carbon electrodes for supercapacitor applications [472, 473], attributing this phenomenon to a smoother mass diffusion and faster electron transfer within the electrode [474].

This conjecture is also supported by PSD analyses presented in Figure 4.37 and Figure 4.38, which: i) reveal an increasing pore volume at pore sizes >2nm only in PM samples and ii) display higher micropore (and total pore) volume for WS₂-doped samples. Also, the ACs PM display micropore peaks at higher pore widths than the original ACs, confirming the previous hypothesis of electrochemical testing destroying some of the micropores and widening others.

It is especially interesting to analyse the case of C 1-4 W, which presents the lowest reduction in textural properties. The explanation for this sample displaying lower micropore loss despite having similar microporosity than the rest of the ACs has been presented in Section 4.4.2.1. It is thought that the electrochemical treatment causes a displacement in the previously deposited nanosheets, therefore granting access to previously blocked micropores. This way, although the microporous

structure of C 1-4 W is destroyed in the same way as the other carbons, the access to new micropores helps to mitigate this micropore loss.

Raman spectroscopy:

Furthermore, in order to understand the changes in carbon functionality, Raman spectroscopy measurements were also carried out following the same methodology as in previous tests. The spectra deconvolution results are shown in Table 4.15.

Table 4.15: Raman deconvolution results.

Sample	Peak maxima (cm ⁻¹) ^a					D/G	
	D1	D2	D3	D4	G	Area	Height
C 1-4 PM	1352 (42%)	1608 (3%)	1499 (13%)	1266 (15%)	1593 (27%)	1.55	0.93
C 1-4 W PM	1351 (43%)	1611 (2%)	1508 (17%)	1227 (11%)	1592 (27%)	1.63	0.93
CA 1-4 PM	1353 (43%)	1607 (3%)	1530 (18%)	1257 (18%)	1594 (18%)	2.43	1.16
CA 1-4 W PM	1347 (44%)	1615 (1%)	1508 (17%)	1225 (11%)	1593 (11%)	1.75	0.98

From the results in this table, it can be seen that the carbons follow the same trend, where the D1 peak is still prominent, followed by the G peak, but with an important contribution from the D3 and 4 peaks. The physical meaning behind these values is that, after electrochemical treatment, the samples still present a marked disordered character, with D/G ratios ranging from 1.5 to 2.5, still indicative of turbostratic structures in the carbons.

Although the analysis from the results of this table provides important information, the most significant data comes from the comparison of Raman values of samples prior to and after electrochemical treatment (see Table 4.5). From this comparison, it can be observed that all the carbons experience a decrease in their D/G ratios (see Figure 4.39) indicating that, although they still remain turbostratic, the presence of graphitic structures holds greater significance. These values, together with the porosimetry results, indicate that there is a partial destruction of the carbons' surface due to electrochemical treatment. However, this surface destruction is more prominent for the non-graphitic regions, leading to a reduced D-peak contribution to the total area. This theory can be supported by analysing the variation of the D3 peak, which is related to the presence of

amorphous regions in the carbon, and displays a reduction of around 5-8% of the contribution to the total area. Although literature on post-mortem analysis of supercapacitor electrodes is minimal, previous studies ascertain that the reversibility (and thus, stability) of carbonaceous electrodes increases with structural order (e.g. graphitic content) [475], therefore confirming that the amorphous phase of the carbonaceous electrodes is less resistant to electrochemical degradation.

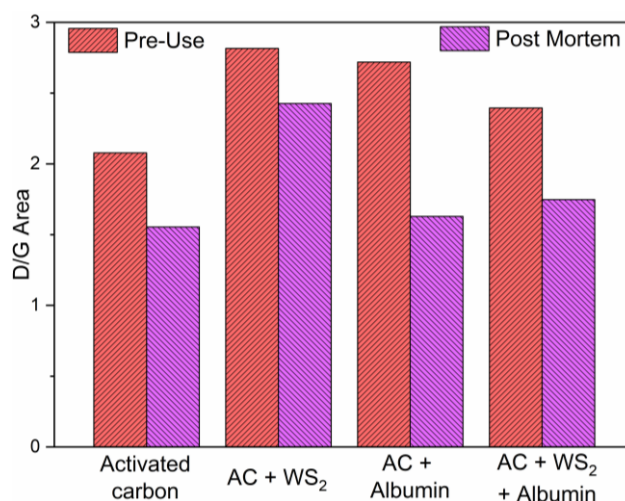


Figure 4.39: Variation of the D/G area ratio for the C 1-4 set of samples before and after electrochemical testing.

4.4.3. Electrocatalytic application for ORR

4.4.3.1. Rotating Ring Disk Electrode (RRDE)

To determine the catalytic properties of the developed ACs for the oxygen reduction reaction tests, a RRDE setup was used. In this setup, cyclic voltammetry was performed at the disk electrode while chronoamperometry was conducted at the ring electrode (details of the setup and procedure are provided in Section 3.2.14).

Before analysing the voltammograms recorded at the disk and ring, the collection efficiency of the equipment was first determined. Details of the theoretical and empirical calculation of this parameter are provided in Annex 7. After calculating the collection efficiency, the number of electrons transferred in the ORR and the amount of HO₂⁻ produced can be calculated. Annex 8 presents a calculation example of these parameters.

Figure 4.40 and Figure 4.41 show that, as expected, the glassy carbon (GC) electrode (without any catalyst) presents a poorer performance than any other

sample, with an HO_2^- production over 50%, in contrast to the “gold standard” commercial Pt/C catalyst, which produces only around 6% HO_2^- .

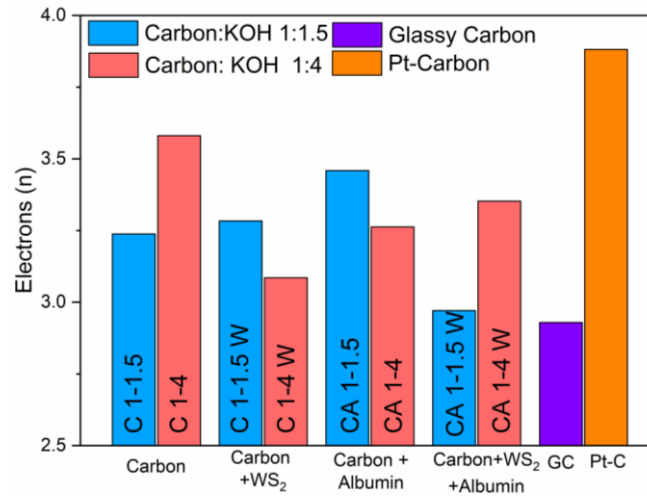


Figure 4.40: Number of electrons transferred by each catalyst in the oxygen reduction reaction.

The values in Figure 4.40 confirm that catalyst addition significantly directs the ORR towards the desired 4 electron pathway, as higher HO_2^- content is related to the 2-electron pathway. Equation 4.3 relates these two parameters:

$$n = 4 - 2 \cdot \frac{\% \text{HO}_2^-}{100} \quad \text{Equation 4.3}$$

This shows that an ideal 0% HO_2^- content implies an ORR happening completely through the 4-electron pathway ($n=4$), while increasing HO_2^- content can reduce the n value up to 2 electrons, which would correspond to an ORR completely driven via the 2-electron pathway, producing 100% HO_2^- .

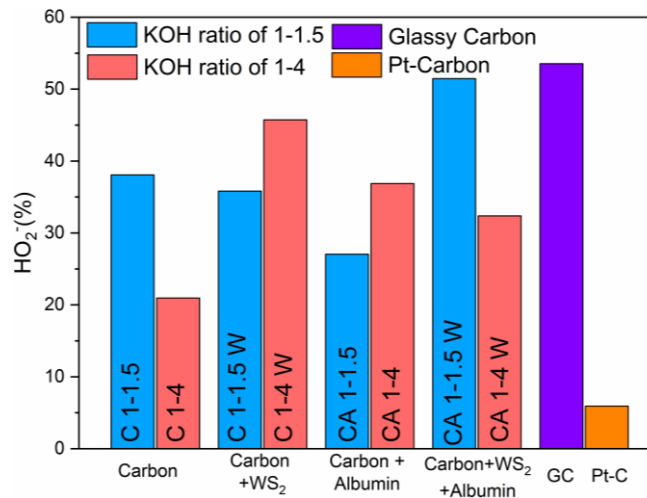


Figure 4.41: Amount of HO_2^- produced in presence of each catalyst during the oxygen reduction reaction.

When comparing the catalytic performances of the ACs, shown in Figure 4.40, the influence of textural properties remains a key factor, with C 1-1.5, C 1-4 W and CA 1-1.5 W (the samples with the lowest micropore volume, ranging from 0.26 to 0.53 cm³/g) presenting the poorest electrocatalytic performances, with 3.23, 3.09 and 2.97 electrons transferred, respectively (for comparison, the glassy carbon reference transfers 2.93 electrodes). Furthermore, C 1-1.5 W displays a micropore volume similar to that of the previous samples (0.43 cm³/g), but its high tungsten content (close to 4% w/w, substantially superior to that of any other WS₂ doped sample) leads to a minor increase in electrocatalytic active centres, which results in 3.28 electrons transferred.

Among the rest of the samples, C 1-4, CA 1-1.5 and CA 1-4 W exhibit the best electrocatalytic performances. C 1-4 presents an excellent combination of high micropore volume (0.65 cm³/g) and very low charge transfer resistance, R_{CT} , (1.4 Ω), resulting in the highest number of transferred electrons (3.58, not very far from the 3.87 electrons transferred by the standard Pt/C electrocatalyst), and consequently, the lowest HO₂⁻ generation, with only 20.9% w/w (see Figure 4.41). On the other hand, CA 1-1.5, although displaying similar micropore volume, presents higher R_{CT} (11 Ω), worsening its performance. However, its high conductivity (11.7 S/m, more than twice that of C 1-4) helps achieve a respectable 3.45 electrons transferred. CA 1-4 performs slightly worse than the two previous samples due to its higher R_{CT} and lower conductivity (14.6 Ω and 2 S/m, respectively) despite having similar micropore volume. However, the combination of heteroatom presence (1% of N and 0.8% S), along with good tungsten content (2.8% w/w) maintains a high number of electrons transferred (3.35).

The analysis of the electrocatalytic behaviour of the developed ACs, apart from assessing their suitability for ORR reactions, also helps elucidate which physicochemical properties have the largest impact on catalytic performance. From the presented results, it can be understood that the charge transfer resistance (R_{CT}) is a defining factor, as C 1-4, the sample with highest number of electrons, exhibits a resistance of only 2 Ω (approximately 6 times lower than that of the next best-performing sample). As previous studies have shown, R_{CT} is a key factor, since it promotes faster reaction kinetics and allows efficient use of all active sites [476, 477].

Besides R_{CT} , another critical factor is conductivity, which is also responsible for efficient electron transport, thereby enhancing ORR performance [478]. The importance of this parameter is evident as, from the most conductive samples (CA

1-1.5, C 1-1.5 and C 1-4), two of them exhibit n values > 3.4 . The only exception to this trend is C 1-1.5, which shows poorer performance due to its mesoporous nature. This result also highlights the importance of microporosity in enhancing electrocatalytic behaviour, as micropores provide strong adsorption forces for oxygen molecules, which promote bond splitting and ultimately direct the ORR towards the desired 4-electron pathway [479].

Finally, it is also important to recognise the influence of heteroatom content in ORR. Several studies have already proven that external atoms, concretely N and S, have a positive influence on the catalyst's performance as they reduce mass-transport limitations, and provide a high density of catalytic sites [480, 481]. Comparing the N and S concentration of the final ACs (see Table 4.6) it can be observed that the samples with higher heteroatom content (CA 1-4 W and C 1-1.5 W) exhibit higher values of 3.35 and 3.28 electrons, only surpassed by C 1-4 and CA 1-1.5. These results indicate that, while heteroatom doping is an efficient way to enhance ORR activity, high conductivity and low charge transfer resistance play a more decisive role in the overall electrocatalytic performance.

Moreover, Table 4.16 presents a summary of the obtained results, comparing the number of electrons transferred and amount of HO_2^- produced by each AC with those of the commercial Pt/C catalyst and a pristine glassy carbon electrode.

Table 4.16: Summary of electrocatalytic parameters of the developed ACs compared with the commercial Pt/C catalyst and glassy carbon pristine electrode.

Sample	Number of electrons (n)	HO_2^- content (%)	Sample	Number of electrons (n)	HO_2^- content (%)
C 1-1.5	3.24	38.1	C 1-4	3.58	20.9
CA 1-1.5	3.46	27.0	CA 1-4	3.26	36.9
C 1-1.5 W	3.28	35.8	C 1-4 W	3.09	45.7
CA 1-1.5 W	2.97	51.5	CA 1-4 W	3.35	32.4
GC	2.93	53.5	Pt-C	3.87	6.50

Notably, the electrocatalytic performance of C 1-4 compares very well to that of a commercial Pt-C catalyst (3.58 vs. 3.87 electrons), highlighting the potential of sustainable, abundant and cost-effective catalysts to compete with scarce and expensive noble metal use, with an efficiency reduction of only 7.5%. While other studies have already presented biomass-derived electrocatalysts with excellent n values close to 3.9, this study is the first, up to the author's knowledge, to achieve a value of $n \approx 3.6$ without the influence of heteroatoms or metals [482-485].

4.5. Conclusions

The results obtained from these experiments lead to the following findings:

- The followed synthesis procedure has proven that it is possible to obtain sustainably derived ACs through environmentally friendly processes with comparable or superior properties to those derived from fossil sources.
- Analysis of the carbon properties reveals that the amount of activating agent can substantially influence the textural properties of the developed ACs, increasing microporosity and surface area with increasing KOH ratio.
- SEM analyses reveal that WS₂ nanoparticle addition provokes a detrimental effect on the ACs, reducing the available pore volume and surface area due to WS₂ deposition blocking pores.
- Supercapacitor experiments reveal the influence of textural properties (especially micropores) in the electrochemical performance of the carbons. The sample with highest microporosity achieves the largest capacitance, energy and power density.
- Through post-mortem tests, WS₂ nanosheets appear to protect the carbonaceous structure from degradation after electrochemical testing, minimising the destruction or enlarging of micropores.
- In Oxygen Reduction Reaction experiments, for AC materials, micropore volume plays a key role in order to promote the 4-electron pathway. Furthermore, factors such as charge transfer resistance, conductivity and heteroatom content also influence the electrocatalytic properties of the materials.
- In both electrochemical and electrocatalytic applications, C 1-4 displays the best performance due to its unique combination of tailored textural properties and reduced charge transfer resistance.

5. Poly-L-lactic acid hybrid materials

5.1. Introduction

As previously discussed in Section 1.2, dye pollution remains a pressing environmental concern that requires fast, efficient and sustainable solutions. Among the diverse remediation approaches, adsorption stands out for its simplicity and cost-effectiveness. Activated carbons are among the most popular low-cost adsorbents, valued for their broad range of physicochemical properties, including chemical functionality, surface area and pore volume. In particular, producing ACs from biomass not only reduces the environmental impact of their manufacture but also yields materials with enhanced adsorption properties [486]. The appealing nature of these materials represents a solid alternative to other adsorbents; however, some disadvantages limit their use.

While ACs display high surface areas and great affinity for contaminants, their powdered form typically involves challenges in their handling and recovery, which can limit their use [487]. To overcome these limitations, scaffold-based systems have emerged as a solution. These structures provide a physical support for carbon materials, enabling the formation of 3D porous matrices that increase accessibility to active sites, enhancing adsorbent-adsorbate contact, to ultimately improve adsorption performance [488]. Scaffolds also contribute to improved mechanical properties and allow chemical functionalisation of the adsorbent system [489].

Various polymers have been explored as scaffolds, such as polyvinyl alcohol (PVA), polystyrene (PS), polyacrylonitrile (PAN) or polyurethane (PU) due to their combination of stability, hydrophilicity and adsorption capacity [490-493]. However, PLLA offers several compelling advantages, as it is naturally sourced and it exhibits comparable or superior mechanical properties to alternative petroleum based-polymers, particularly PS [494-496]. Furthermore, PLLA can be fully degraded in industrial facilities, unlike the mentioned conventional polymers, which can persist in soil and water for prolonged periods [497-500].

These attributes render PLLA as a promising alternative for developing sustainable and efficient scaffolds which, combined with sustainably sourced ACs, produce eco-friendly hybrid materials for adsorption applications.

5.2. Aim of this chapter

The following specific objectives have been set for this Chapter:

- Investigate different methodologies for incorporating AC and WS₂ nanosheets into the biopolymeric matrix.
- Assess the impact of WS₂ nanosheets on the chemical and mechanical properties of the PLLA scaffold.
- Evaluate of the adsorption performance of the prepared PLLA-AC morphologies towards both cationic and anionic dyes.
- Measure the adsorption capacity of the final AC-PLLA-WS₂ system in terms of adsorption load (mg/g), removal efficiency (%) and final dye concentration (mg/L).
- Elucidate the nature of the adsorption process by fitting the experimental data to various isothermal models (Freundlich, Langmuir, Temkin and Dubinin-Radushkevich).
- Analyse the kinetics of the adsorption process using first and second order kinetics.

5.3. Experimental procedure

5.3.1. Preparation of poly-L-lactic acid scaffold

As previously discussed, powdered activated carbon is difficult to recover from aqueous systems after use. To address this challenge, several PLLA–AC morphologies were fabricated and their performance evaluated. The goal was to develop a hybrid adsorbent that maximises the contact area between activated carbon and adsorbate while retaining sufficient interaction with the hydrophobic PLLA scaffold. Importantly, this would all have to be carried out without compromising adsorption performance. The investigated morphologies and methodologies are presented in the following section:

5.3.1.1. PLLA films

Initially, film morphologies were trialled because they offer straightforward handling and processing. To produce these films, both neat PLLA (as a control) and a PLLA–AC blend were first compounded by extrusion, then formed by hot pressing. Compounding took place in a Haake Minilab II counter-rotating twin-screw extruder at 190 °C and 100 rpm for 10 minutes, after which the extrudate was pressed into thin films under heat. These films were then cut into small pieces and placed in a mould (40 × 40 × 0.2 mm) sandwiched between two brass plates. The assembly was loaded into a Collin P-200-PM platen press at 190 °C, first under 10 bar for 2 minutes and then under 100 bar for an additional 2 minutes. Finally, the moulded films were cooled between water-cooled plates for 2 minutes.

For PLLA-AC films, different AC concentrations were added to the PLLA pellets and fed into the extruder, following the same methodology as before. The maximum concentration of AC was limited to 20% (yielding the material presented in Figure 5.1 a), as at higher concentrations the melt was too viscous to process on the extruder.

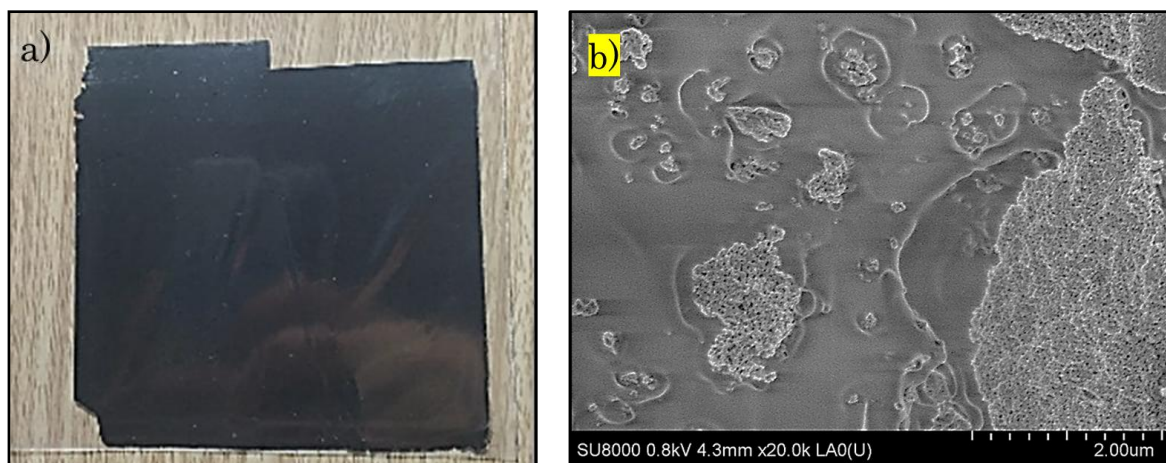


Figure 5.1: a) Pressed PLLA-AC (10% w/w) film, and b) SEM micrograph showing the cross-section of the cryofractured end of the same film.

To assess the adsorption capacity of the prepared films, preliminary tests were carried out using a 20 ppm Methylene Blue (MB) solution as adsorbate. MB, whose molecular structure is presented in Figure 5.2, is a commonly used dye due to its high molar absorptivity (ϵ_0 , a measure of how strongly a molecule absorbs light at a particular wavelength), making it suitable to evaluate the adsorption performance of a material.

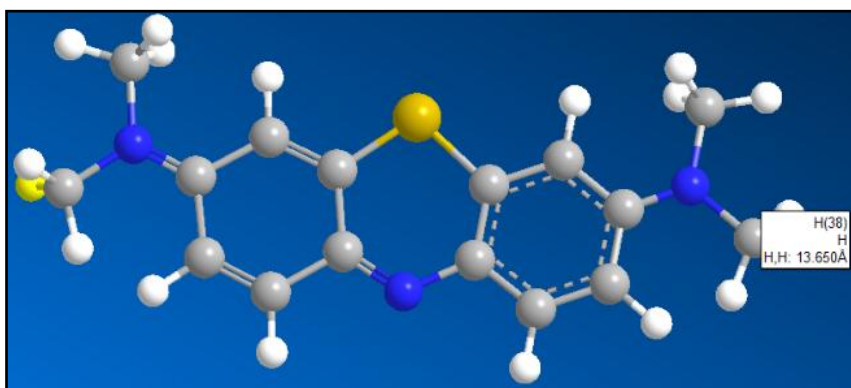


Figure 5.2: Molecular structure of Methylene Blue made using ChemDraw software.

Preliminary adsorption tests revealed minimal dye uptake, with a maximum removal of approximately 20% of the initial dye. Based on the SEM micrograph presented in Figure 5.1 b, it is hypothesized that the hydrophobic PLLA matrix acts as a barrier to the aqueous dye solution (contaminant), that is limiting accessibility to the AC and hindering effective contaminant removal.

5.3.1.2. PLLA beads

To enable higher AC loadings within the PLLA matrix, extrusion was discounted. PLLA was first dissolved in N-methyl-2-pyrrolidone (8% w/w), and then AC was

added to it at concentrations ranging from 0 to 50% w/w. Afterwards, a 5 mL aliquot of this mixture was added dropwise to a Petri dish containing stirring water to induce precipitation and bead formation. The resulting round-shaped materials are shown in Figure 5.3:



Figure 5.3: Prepared PLLA (left) and PLLA-AC (25% w/w) beads (right).

The formed beads were tested for contaminate removal following the same preliminary adsorption procedure as in Section 5.3.1.1. Dye removal efficiencies, even for the sample with the highest AC concentration, were found to be poor (below 10%), indicating that this morphology is not suitable. This is also likely due to the fact that the hydrophobic PLLA is forming a barrier to the AC, preventing dye adsorption. Therefore, different morphologies and processing strategies were explored.

5.3.1.3. PLLA pills

Previous tests involved combining PLLA and AC via melt blending or by dissolution followed by precipitation. In this trial, PLLA was cryomilled to fine powder, mixed with AC at concentration of 10% and 50% w/w, and then cold-pressed under between 5 and 10 tonnes into pills. This procedure is widely employed in the fabrication of supercapacitor electrodes (see Section 4.3.3) as it requires only a minimal amount of polymer binder relative to the adsorbent. Moreover, because the PLLA powder does not fully encapsulate the carbon particles, the intrinsic pore network of the AC remains readily accessible to aqueous solutions, enhancing mass transport compared with melt- or solvent-based approaches.

However, the formed pills proved unsuitable for dye adsorption independent of AC concentration, as the samples prepared at low loads (5 tonnes) dissolved upon contact with water. The pills prepared at 10 tonnes (shown in Figure 5.4) retained

their structural integrity, but demonstrated negligible adsorption capacity (less than 5%). The exact cause of failure for pellets pressed at 10 tonnes has not been fully investigated. However, upon handling and visual inspection, these pellets appeared highly compact with a very smooth surface. It is likely that the PLLA formed a continuous barrier—or directly occluded the pores of the AC—thereby inhibiting diffusion of the aqueous MB solution to the adsorbent.

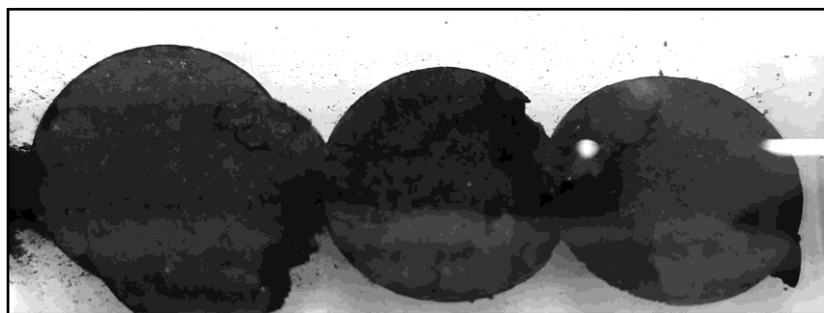


Figure 5.4: Final PLLA-AC (20% w/w) pills prepared at 10 tonnes.

5.3.1.4. PLLA fibres

Given the limited adsorption performance of the previously tested morphologies, a new strategy was developed to incorporate the AC into the polymer matrix in a way that preserves its porous structure and maximises the available contact area with MB molecules. To achieve this, PLLA-AC composite fibres were prepared via electrospinning, with WS₂ nanosheets added to enhance the mechanical properties of the resulting material.

As discussed in Section 1.3.2.2, electrospinning is a versatile technique for producing thin fibres with diameters ranging from the nanometre to the micrometre scale. The experimental setup and procedure are detailed in QR 2. Since electrospinning is a complex methodology that depends on a wide range of parameters, the development and optimisation of this method are discussed in the following section.



QR 2:
Electrospinning
process.

5.3.2. Development of the electrospinning method

5.3.2.1. Optimisation of electrospinning parameters through testing

To ensure successful fibre generation, several key electrospinning parameters were evaluated:

- **Solvent:** A range of solvents were studied based on their reported suitability for dissolving PLLA and facilitate electrospinning [291-293]. As explained in Section 1.3.2.2, an appropriate solvent must display a low boiling point and a medium-to-high dielectric constant, while also being able to effectively dissolve the polymer. The studied solvents were anisole, butanol, chloroform, cyrene (dihydrolevoglucosenone), dichloromethane (DCM), dimethylformamide (DMF), n-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), and 2-methyl-tetrahydrofuran (2-Me-THF). Table 5.1 summarises the thermal and electrical properties of the screened solvents. Although all these solvents were tested for electrospinning, **chloroform** was ultimately selected due to its efficiently solubilisation of PLLA, low boiling point (ideal for rapid solvent evaporation upon voltage application) and appropriate dielectric constant, yielding a continuous polymer fibre mat.

Table 5.1: Thermal and electrical properties of the selected electrospinning solvents.

Solvent	Anisole	Butanol	Chloroform	Cyrene	DCM
Boiling point (°C)	154	118	61	227	40
Dielectric constant	4.33	17.1	4.81	3.4	8.93
Solvent	DMF	NMP	THF	2-Me-THF	
Boiling point (°C)	152	204	66	80	
Dielectric constant	36.7	32.2	7.58	7.00	

- **Polymer concentration:** PLLA was dissolved in chloroform at concentrations ranging from **4% w/v to 12% w/v**, based on literature reports [501-504]. Experiments showed that higher concentrations were limited by solubility, and lower concentrations resulted in extremely thin and fragile fibres. Further optimisation of this parameter is discussed in Section 5.3.2.2 through SEM analyses.
- **Voltage:** Electrospinning was tested across a voltage range of 10-18 kV. It was found that a minimum voltage of **14 kV** is required to produce continuous and uniform PLLA fibres on the equipment.
- **Needle to collector distance:** Distances between 10-18 cm were evaluated. At longer distances (18 cm), a significant fraction of the material did not reach the collector, resulting in material loss. However, short distances (10 cm) did not allow sufficient time for solvent evaporation, leading to bead

formation rather than fibre generation. Optimal distances were found within the **10-16 cm** range, with SEM analyses used to determine the optimal distance.

- **Solution flow:** Flow rates below 1 mL/h resulted in the formation of small, short fibres instead of a continuous mat. However, rates above 3 mL/h led to the accumulation of material at the end of the needle, causing blockage and disrupting fibre formation. Based on these results, a flow of **1.5 mL/h** was chosen.
- **Electrospinning time:** Times ranging from 5 to 120 minutes were studied, and it was noted that a minimum duration of **15 minutes** is needed to produce an adequate PLLA mat. Moreover, the influence of electrospinning time on fibre morphology will be further discussed in the SEM analyses presented in Section 5.3.2.2.
- **Particle addition:** Both WS₂ nanosheets and AC were incorporated into the polymer matrix.
 - For WS₂ addition, literature research indicated that a **0.5% w/w** concentration (regarding the total solid) is enough to substantially enhance the mechanical and thermal properties [505, 506]. For this, mixtures of PLLA and WS₂ (0.5% w/w) were dissolved in chloroform (concentrations ranging from 4 to 12% w/v) and electrospun following the same electrospinning parameters as in neat PLLA. An example of the resulting WS₂-doped PLLA fibre (named PLLA-W from now) is shown in Figure 5.5.



Figure 5.5: Electrospun PLLA-W fibre mat after 30 minutes.

- In contrast, the incorporation of AC presented strong limitations, as experiments showed that only a 2% w/w AC concentration can be

added to PLLA solutions in order to successfully obtain PLLA-AC continuous fibres, which are shown in Figure 5.6 a. An increase in AC concentration led to needle blockage, which resulted in bead formation rather than fibres, as displayed in Figure 5.6 b:

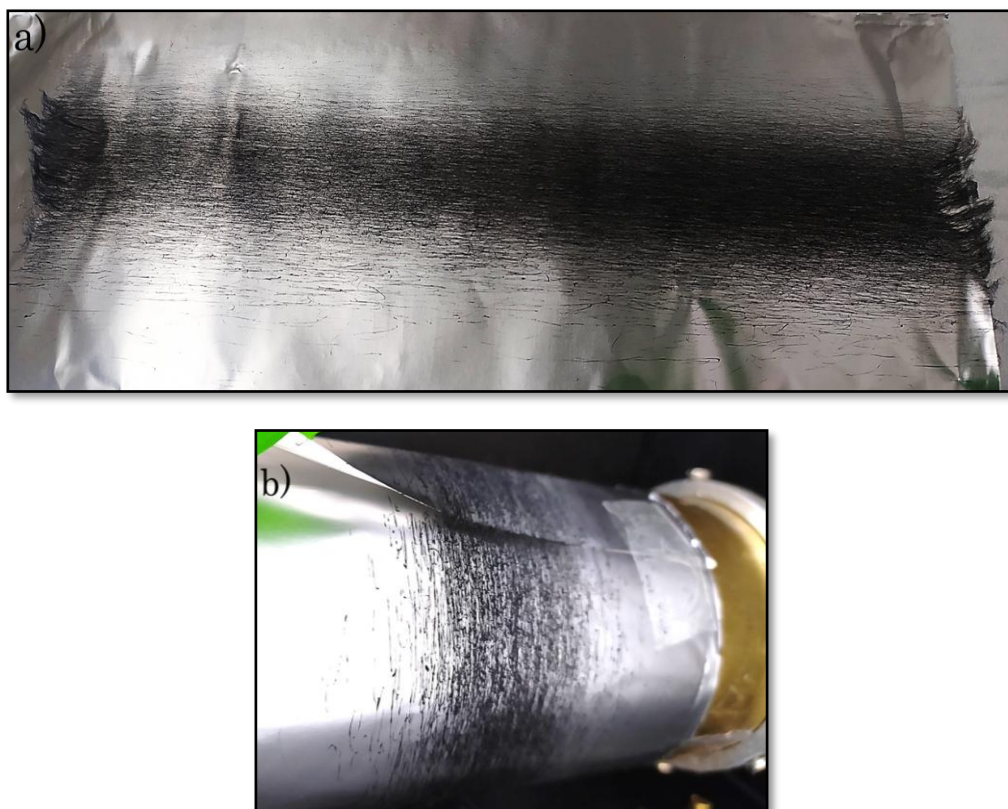


Figure 5.6: PLLA-AC electrospun material with an AC content of a) 2% w/w and b) 5% w/w.

Despite the semi-successful fibre formation at 2% w/w AC, this concentration was insufficient for efficient contaminant removal. Therefore, an alternative post-processing method was needed to achieve a higher AC loading.

The electrospun PLLA and PLLA-W fibres prepared using the investigated parameters are highly flexible, lightweight, with easily controllable diameter and an average mesh size depending on electrospinning time. This last two parameters are highly important as one increases the available surface area of the fibre, and hence, fibre contact with the contaminant, and the other permits good diffusion of the contaminant within the fibre mat. It was decided therefore to continue with this methodology, but to deposit the AC on the fibre instead of adding the carbon to the polymer solution.

This AC deposition was carried out by preparing an AC dispersion (10 g/L) in an ethanol-chloroform mixture (80:20 v/v). Chloroform was included in low concentrations to soften the polymer and facilitate good AC-fibre adhesion, while ethanol was chosen due to its miscibility with CHCl_3 and its sustainable nature. The dispersion was sonicated for 2 hours at 500 rpm, and subsequently it was spray coated over the fibre to obtain PLLA-AC or PLLA- WS_2 -AC hybrid materials. A demonstration of this procedure is available by scanning QR 3, and the final hybrid material (PLLA- WS_2 -AC) is presented in Figure 5.7:



QR 3: Spray coating.



Figure 5.7: Final PLLA-W-AC fibrous structure.

5.3.2.2. Optimisation of electrospinning parameters using SEM

To evaluate the influence of electrospinning parameters on the final fibre morphology, SEM was employed. Based on prior literature research and extensive testing, chloroform was identified as the optimal solvent, with a flow rate of 1.5 mL/h and an applied voltage of 14 kV. With these parameters fixed, further optimisation was conducted by systematically varying polymer concentration, distance to collector and electrospinning time (see Table 5.2), resulting in the evaluation of 80 different electrospinning conditions:

Table 5.2: Experimental electrospinning parameters.

Parameter	Value				
PLLA concentration (g PLLA/mL CHCl_3)	0.04 (4%)	0.06 (6%)	0.08 (8%)	0.1 (10%)	0.12 (12%)
Distance to collector (cm)	10	12	14	16	
Electrospinning time (min)	15	30	60	120	

Selected SEM micrographs of the resulting fibres are shown in Annex 9, which lead to the following conclusions and results presented in Table 5.3:

- **Polymer concentration:** At concentrations below 0.1 g/mL (10%), beads and beaded fibres are obtained, which are undesirable for adsorption applications. Nevertheless, at 0.12 g/mL, fibre diameters increase, potentially limiting diffusion and reducing adsorption performance. Literature supports that lower fibre diameters lead to increased adsorption capacities [507-509]. Consequently, an optimal concentration of **0.1 g/mL** was selected, balancing structural integrity and minimal fibre diameter.
- **Distance to collector:** Distances of 10 to 16 cm were evaluated. SEM micrographs showed significant bead presence when working at 10 cm. At 16 cm and 14 cm, defects and increased fibre diameters were observed. Therefore, it was decided that the optimal distance from needle to collector was **12 cm**, which produced uniform fibres with minimal bead presence.
- **Electrospinning time:** At times of 15 min, the number of fibres was very low, potentially reducing the mat integrity and adsorption capacity of the fibres. Conversely, times of 60 minutes or more led to a substantial increase in the number of fibres, and increasing fibre diameter, which could also impact final adsorption performance. For this, an electrospinning time of **30 minutes** was chosen as it provides adequate fibre number and diameter.

Table 5.3: Final optimised electrospinning parameters.

Parameter	Voltage	Solvent	Flow	PLLA concentration	Distance	Time
Result	14 kV	Chloroform	1.5 mL/h	0.1 g/mL	12 cm	30 min

5.4. Results and discussion

5.4.1. Fibre characterisation

5.4.1.1. Scanning electron microscopy

After determination of the most favourable electrospinning parameters, the final fibres were produced. The final set of samples consisted of 4 different combinations:

- PLLA fibres (neat polymer),
- PLLA-W fibres, with a 0.5% w/w concentration of the WS₂ nanosheets,
- PLLA-AC fibres, obtained by spray coating of PLLA fibres,
- PLLA-W-AC fibres, resulting from spray coating of PLLA-W fibres.

SEM micrographs of these samples are presented in Figure 5.8:

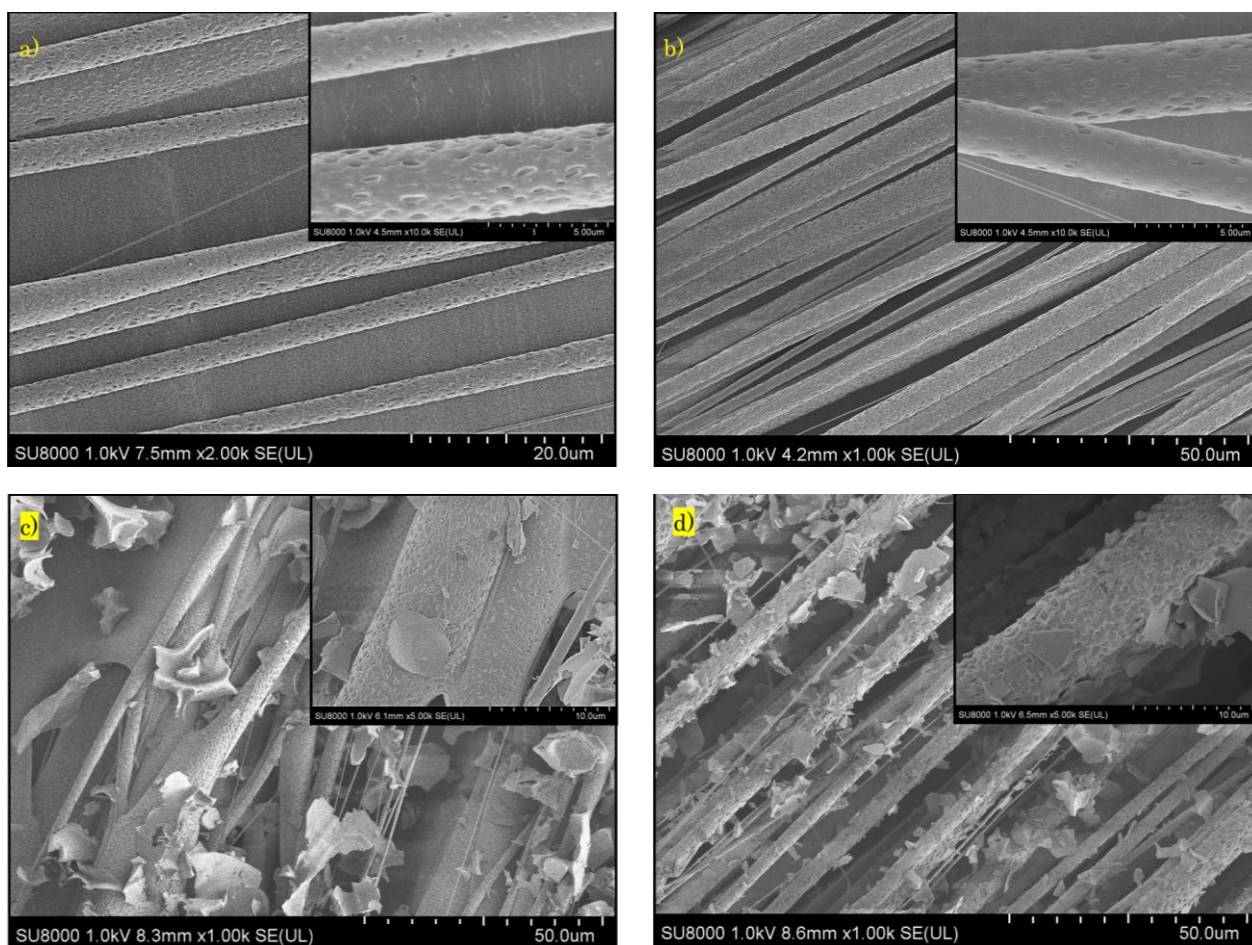


Figure 5.8: SEM micrographs of the a) PLLA; b) PLLA-W; c) PLLA-AC and d) PLLA-W-AC prepared electrospun fibres.

A notable feature across all samples from the SEM images (Figure 5.8) their inherent macroporosity. It is important to distinguish that the pore generation mechanism inside the fibres differs significantly from that of ACs. In fibres, porosity is mainly influenced by nature of the solvent(s) used and environmental conditions. The main mechanisms responsible for pore generation in electrospun fibres are summarised below:

- i) Breath figures: Pores of approximately 20-200 nm appear when a highly volatile solvent (non-miscible with water) is applied in a context of medium to high humidity as a result of water and solvent evaporation [510].
- ii) Vapor induced phase separation: Based on solvents with good water miscibility and low volatility, water vapour infiltration and subsequent evaporation leads to elliptical pores of approximately 50-300 nm [510].
- iii) Non-solvent induced phase separation: Through the combination of a highly volatile solvent with a low evaporative one, miscible with the first solvent but not dissolving the polymer, the result is elliptical pores of 20-100 nm diameter, the number of pores generated is typically but fewer in number compared to those created by the previously discussed mechanisms [510].
- iv) Thermally induced phase separation: In this mechanism, low volatile solvents are used, and pores are produced by a cooling process (usually in a nitrogen bath) that separates the polymer and the non-volatile solvent. Pores with different shapes and sizes between 2-50 nm are obtained.
- v) Selective removal: It is a post-treatment process that involves the use of a sacrificial substrate (typically a polymer) that is removed after electrospinning. Irregular pores between 5-30 nm are common in this mechanism [510].

Given the use of chloroform to produce fibres (a highly volatile solvent not miscible with water), the dominant pore formation mechanism in these samples is attributed to breath figures. This process is highly dependent on environmental humidity, as water vapour evaporation plays a significant role in pore generation (more humidity leads to more pores, resulting in porosity values close to 90%). The fast volatilisation of the solvent during electrospinning draws heat from the fibre surface, thereby reducing its surface temperature. In this moment, vapour from the humid environment condenses on the fibre surface in extremely small droplets of water. Afterwards, circular holes are produced in the fibre structure due to the vapourisation of water and the remaining solvent. From this point, the pore

morphology will highly depend on the nature of the polymer. If the polymer is hydrophilic (PVA, PEO), water droplets will mix with the polymer. Even after evaporation, the water-polymer interaction will create folds rather than pores. On the other hand, if working with a hydrophobic polymer (PLLA, PMMA, PS), the droplets will condense and leave round holes, which will be transformed into elliptical (or irregular) pores due to the electrostatic force being applied [510]. A schematic of the breath figures mechanism is presented in Figure 5.9:

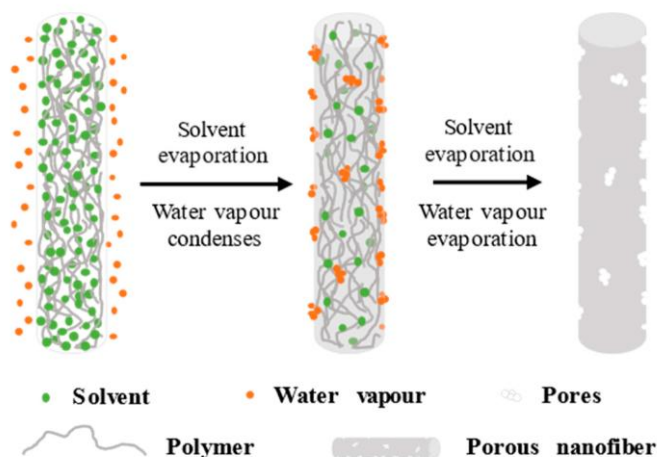


Figure 5.9: Breath figure mechanism of pore formation on the fibre surface [510].

Analysis of the images using ImageJ software reveals irregular pores with an average pore width of 170 nm (230 nm for the PLLA-W sample) and an average length of 520 nm (620 nm for PLLA-W). It is also observed that nanoparticle addition increases fibre diameter, as PLLA fibres exhibit a diameter of 2.83 μm , which increases to 3.19 μm in PLLA-W. This increase in fibre diameter can be attributed to higher WS_2 -PLLA solution viscosity compared to the pristine polymer, which in turn leads to a shorter and fatter jet during the electrospinning process, and, subsequently, a thicker fibre. This trend is consistent with other studies, which have observed that adding TiO_2 nanoparticles to PHBV increased its diameter by 17% [511], or PVA nanofibres increasing diameter with SiO_2 addition [512]).

Further evidence of WS_2 integration is provided in Figure 5.10, which shows that WS_2 nanosheets exhibit an average particle size below 100 nm—significantly smaller than the average fibre diameter. This fact, combined with the absence of visible WS_2 on the fibre surface, suggests that WS_2 nanosheets are embedded within the polymer matrix rather than deposited on its surface, as seen in the previous chapter with AC from cellulose.

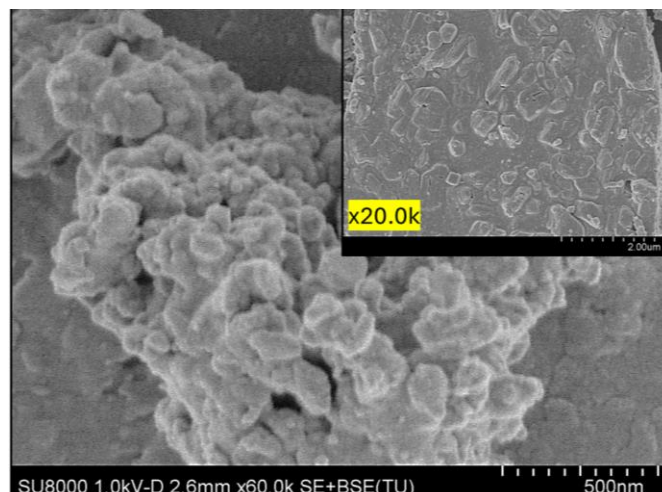
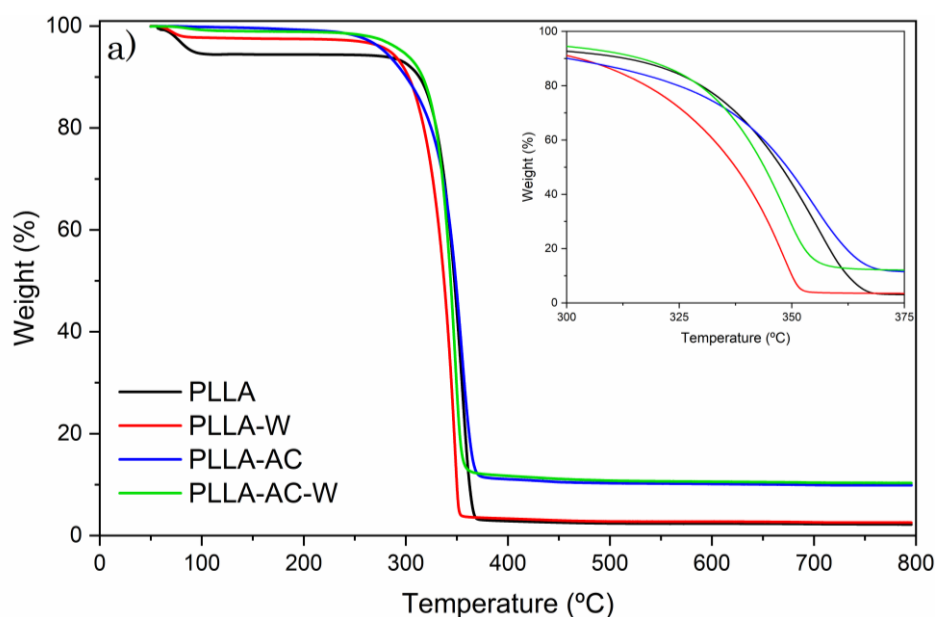


Figure 5.10: SEM micrographs of WS₂ nanosheets dispersed in ethanol at x20k (inserted image) and x60k resolution.

5.4.1.2. Thermogravimetric analysis

Thermogravimetric analyses were carried out to evaluate the thermal stability of the electrospun fibres and assess the effect of nanoparticle doping. Furthermore, the results from TGA allow a precise determination of the carbon content inside the fibres.

These experiments were performed using the same equipment and identical conditions to the ones presented in Section 4.4.1.3. Thermograms performed under a nitrogen atmosphere are presented in Figure 5.11a and the corresponding derivative is shown in Figure 5.11b:



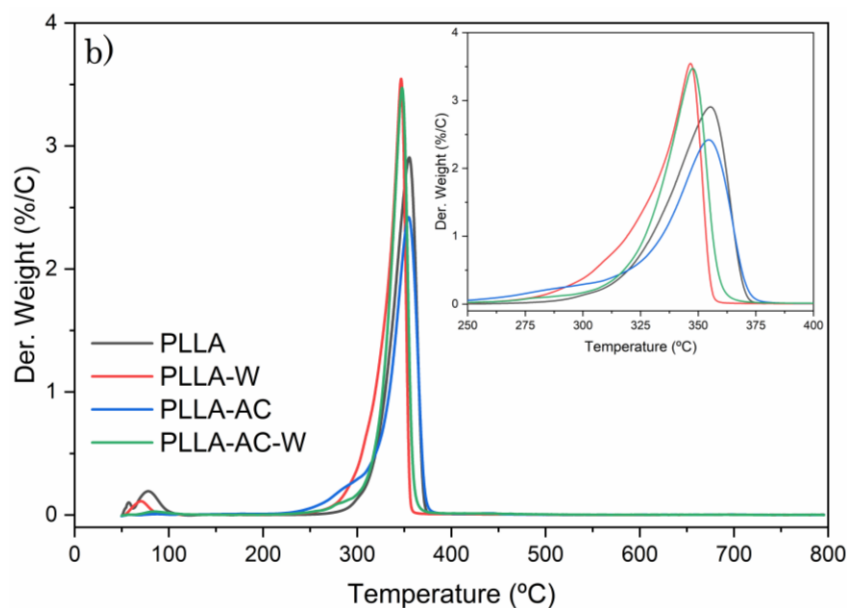


Figure 5.11: a) TGA and b) DTG curves of hybrid PLLA composites under N_2 atmosphere.

The thermograms show that the PLLA fibre exhibits a more pronounced initial mass loss after 100 °C compared to its modified counterparts, indicating a higher moisture content. This can be attributed to the more hydrophobic nature of both the AC and monolayer WS_2 nanosheets [513-515], reducing fibre water uptake and retention.

The thermograms also allowed the samples to be classified into two groups based on their residue content at 800°C. Fibres not containing AC exhibit residues below 2%, while AC-doped fibres (PLLA-AC and PLLA-W-AC, namely) display significantly higher residues of 9.9% and 10.3%, respectively. The difference between these values corresponds approximately to the AC concentration in the final material (9% w/w). Given that the target AC concentration was 10% w/w, these results suggest that approximately 10% of the sprayed material did not correctly bind to the fibre. Annex 10: Calculation of AC & WS_2 concentrations via TGA explains the procedure followed to determine these concentrations.

Further analysis of the DTG peaks indicates that the WS_2 -doped samples exhibited a maximum degradation peak approximately 6 to 10 °C earlier than those of the non- WS_2 -containing fibres. This shift, as previously discussed in Section 4.4.1.3, can be attributed to the catalytic effect of tungsten disulfide nanosheets, which promote thermal degradation of the polymer matrix. Moreover, the presence of WS_2 was confirmed from a 0.4% increase in the residual mass of the WS_2 -doped

fibres compared to their undoped counterparts. This result is consistent with the expected 0.5% w/w WS₂ concentration.

Additionally, TGAs were performed under an oxidative atmosphere (air), with the resulting thermograms shown in Figure 5.12. All samples present degradation peaks at the same temperatures, indicating similar degradation mechanisms.

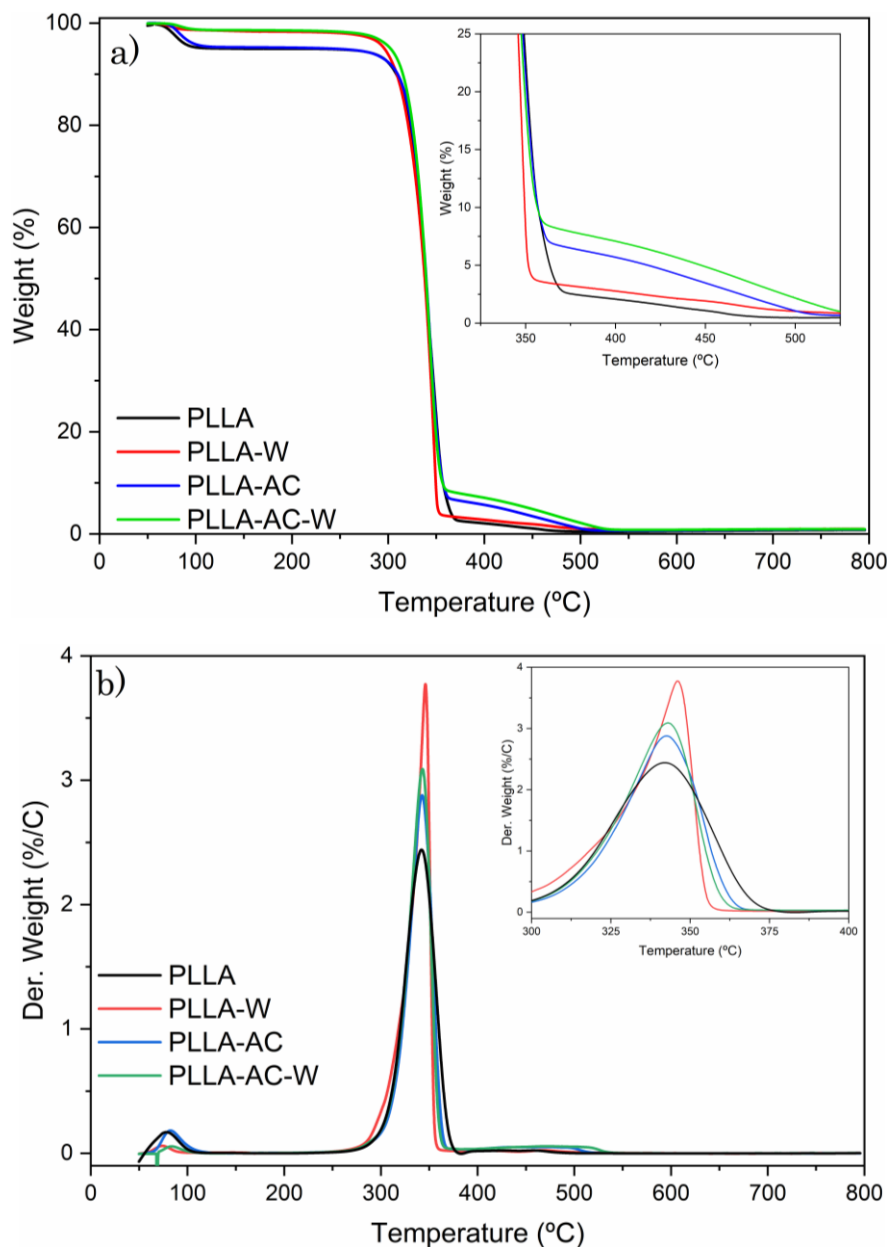


Figure 5.12: a) TGA and b) DTG curves of hybrid PLLA composites under air atmosphere.

It is also noteworthy that, after the main degradation process, which concludes around 350-375 °C, the residue of modified fibres is higher than in the original fibre. Concretely, PLLA-W exhibits a residue of 3.7%, PLLA-AC 7.0% and PLLA-W-AC 8.4%, compared to just 2.6% for the PLLA.

5.4.1.3. Differential scanning calorimetry

DSC was used to assess the crystallisation behaviour of the fibres. Tests were conducted dynamically, with a representative example shown in Figure 5.13, highlighting the thermodynamic transitions associated with the different heating/cooling process. These transitions include T_g (glass transition), melting and crystallisation (which can take place in the cooling process but also in the heating stage, especially in cases when the cooling rate is significantly elevated).

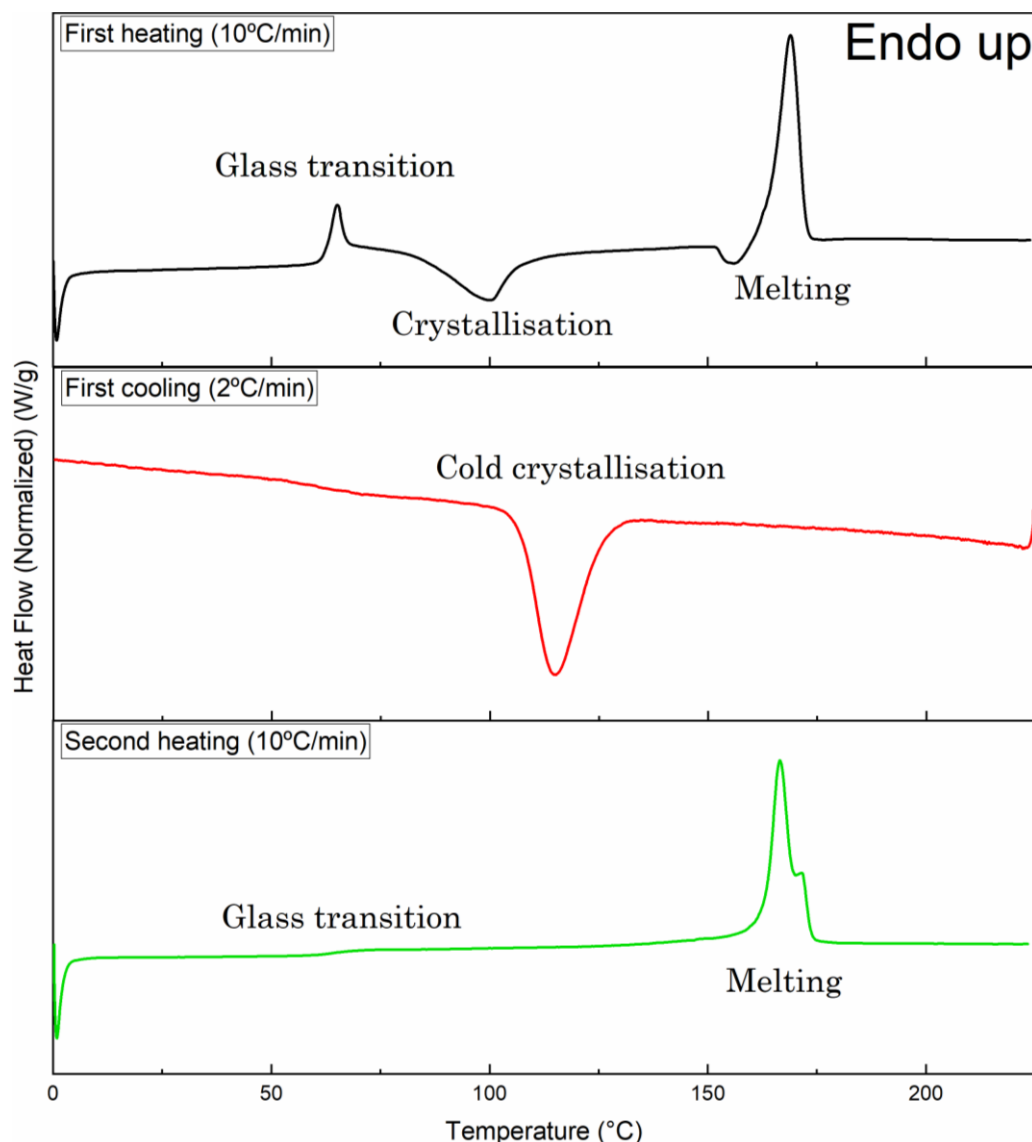


Figure 5.13: An example of DSC for the PLLA-AC-W composite fibre. The sample was heated and cooled according to the following program: heating (10°C/min for all runs), 5-minute isothermal, cooling (2°C/min for this run) and heating again (10°C/min, for all runs).

From an adsorption perspective, the degree of crystallinity of the different PLLA-based samples is a critical parameter, as it influences the hydrophobicity of the

polymer and the mobility of the polymeric chains (and therefore, the accessibility for external molecules) [516]. The degree of crystallinity of the PLLA hybrid materials was estimated using Equation 5.1:

$$(1 - \lambda) (\%) = \frac{\Delta H_c}{\Delta H_m^0_{PLLA}} \quad \text{Equation 5.1}$$

This equation allows the calculation of the degree of crystallinity $(1 - \lambda)$ as the ratio between the crystallisation enthalpy (ΔH_c) of the sample (considering the weight fraction of PLLA in each system) and the theoretical melting heat of 100% crystalline PLLA, ($\Delta H_m^0_{PLLA}$), with a reported value of 93 J/g [517]:

From this equation, along with DSC data presented in Table 5.4 the influence of the additives (WS_2 & AC) and cooling rate on the crystallinity of the fibres can be assessed. Furthermore, Figure 5.14 displays the cooling thermograms for the different fibre compositions:

Table 5.4: DSC results from the cooling and second heating processes of PLLA, PLLA-W and PLLA-W-AC.

Sample	Cooling rate (°C/min)	Crystallisation				Melting	
		Cooling		Heating		$T_{m,1}/T_{m,2}$ (°C)	$(1-\lambda)_m$ (%)
		T_c (°C)	$(1-\lambda)_c$ (%)	T_{cc} (°C)	$(1-\lambda)_{cc}$ (%)		
PLLA	1	101	8.3	125	3.8	158	16
	2	97	4.8	128	11	161	23
	5	98	1.7	131	21	168	34
	10	93	0.5	129	25	168	37
	20	-	-	128	31	167	37
PLLA-W	1	116	43	-	-	166/171	39
	2	104	27	-	-	165	35
	5	96	6.1	114	2.6	165/170	38
	10	92	1.4	114	23	165/171	38
	20	-	-	113	30	165/171	39
PLLA-W-AC	1	121	41	-	-	168	36
	2	115	40	-	-	167/172	38
	5	102	30	103	1.1	166/170	37
	10	95	5.5	108	20	170	39
	20	-	-	108	29	164/171	36

T_c : Crystallisation temperature; $(1-\lambda)_c$: Crystallisation degree; T_{cc} : Cold crystallisation temperature; $(1-\lambda)_{cc}$: Cold crystallisation degree; T_m : Melting temperature; $(1-\lambda)_m$: Melt-crystallisation degree.

The data indicates that crystallinity decreases with increasing cooling rate, independent of WS₂/AC presence, due to the reduced time available for polymer chains to reorganize into crystalline domains at higher cooling rates, consistent with previous reports [506]. Also, thermographs demonstrate that the crystallisation peaks broaden and shift to lower temperatures at higher cooling rates, further confirming that crystallisation occurs earlier with lower cooling rates [330, 332].

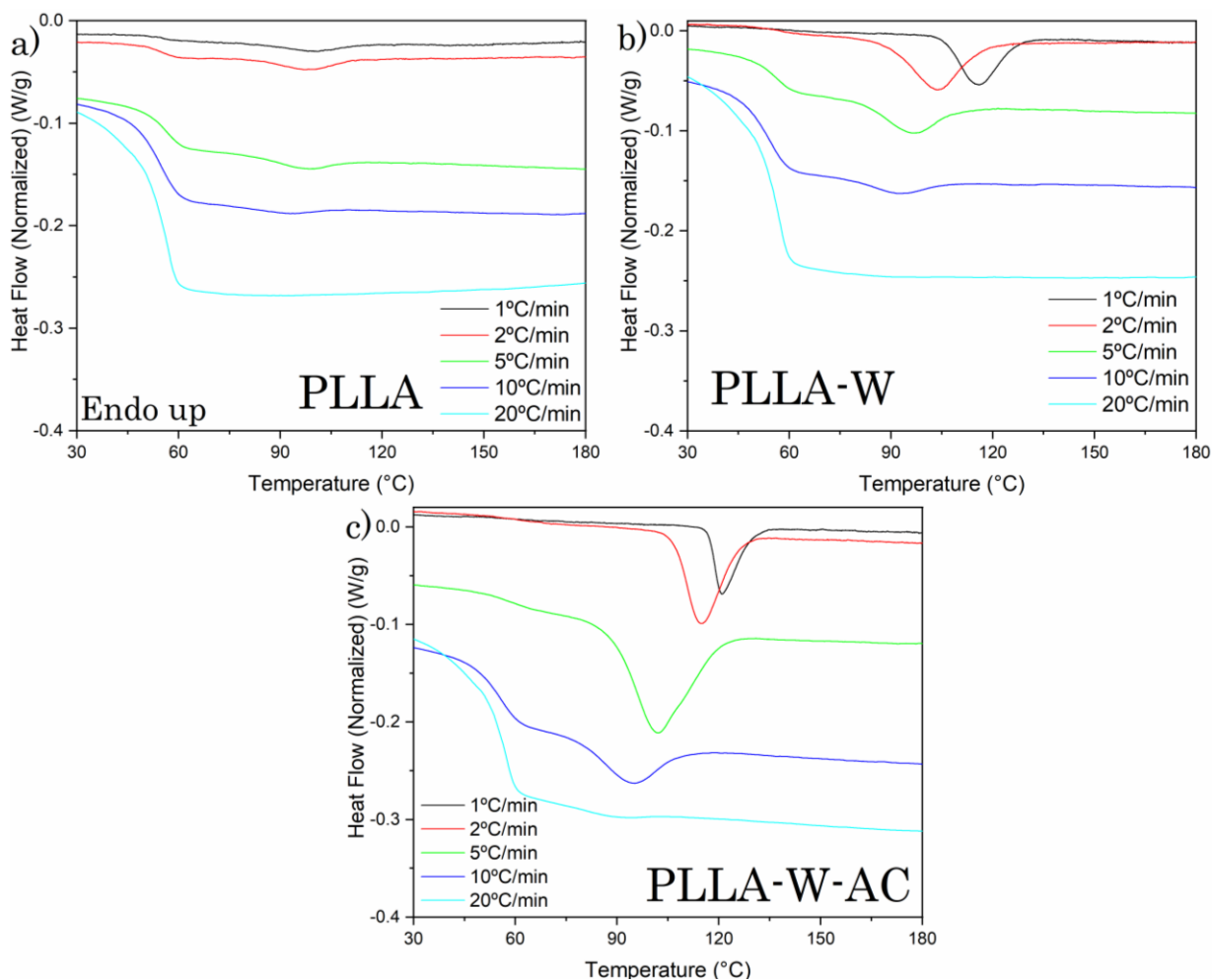


Figure 5.14: DSC cooling thermograms of a) PLLA, b) PLLA-W and c) PLLA-W-AC fibres.

From the presented data, the influence of WS₂ on the crystallisation process is evident. The thermographs for the WS₂-doped fibres exhibit wider crystallisation peaks, yielding higher enthalpy values after integration and, therefore, higher crystallinity. For more clarity Figure 5.15 shows the variation of crystallisation temperature (T_c) and degree of crystallinity $(1-\lambda)_c$ with cooling rate and particle loading. At lower cooling rates, WS₂ doped fibres begin crystallising at higher temperatures than neat PLLA, suggesting that nanosheet presence aids

crystallisation, acting as a nucleating agent (see Figure 5.15). This effect has also been observed in works on 1D-WS₂ nanotubes/PLLA blends [332, 505].

In the case of 2D-WS₂, it has been previously suggested that this morphology delays the crystallisation process [328], but recent studies prove that this assumption is highly dependent on WS₂ concentration. It has been observed that low (0.1% w/w) WS₂ concentrations retard crystallisation (and reduce crystallinity) but higher loadings (e.g. 1% w/w) can effectively promote the early formation of crystalline structures [330], as observed in this study.

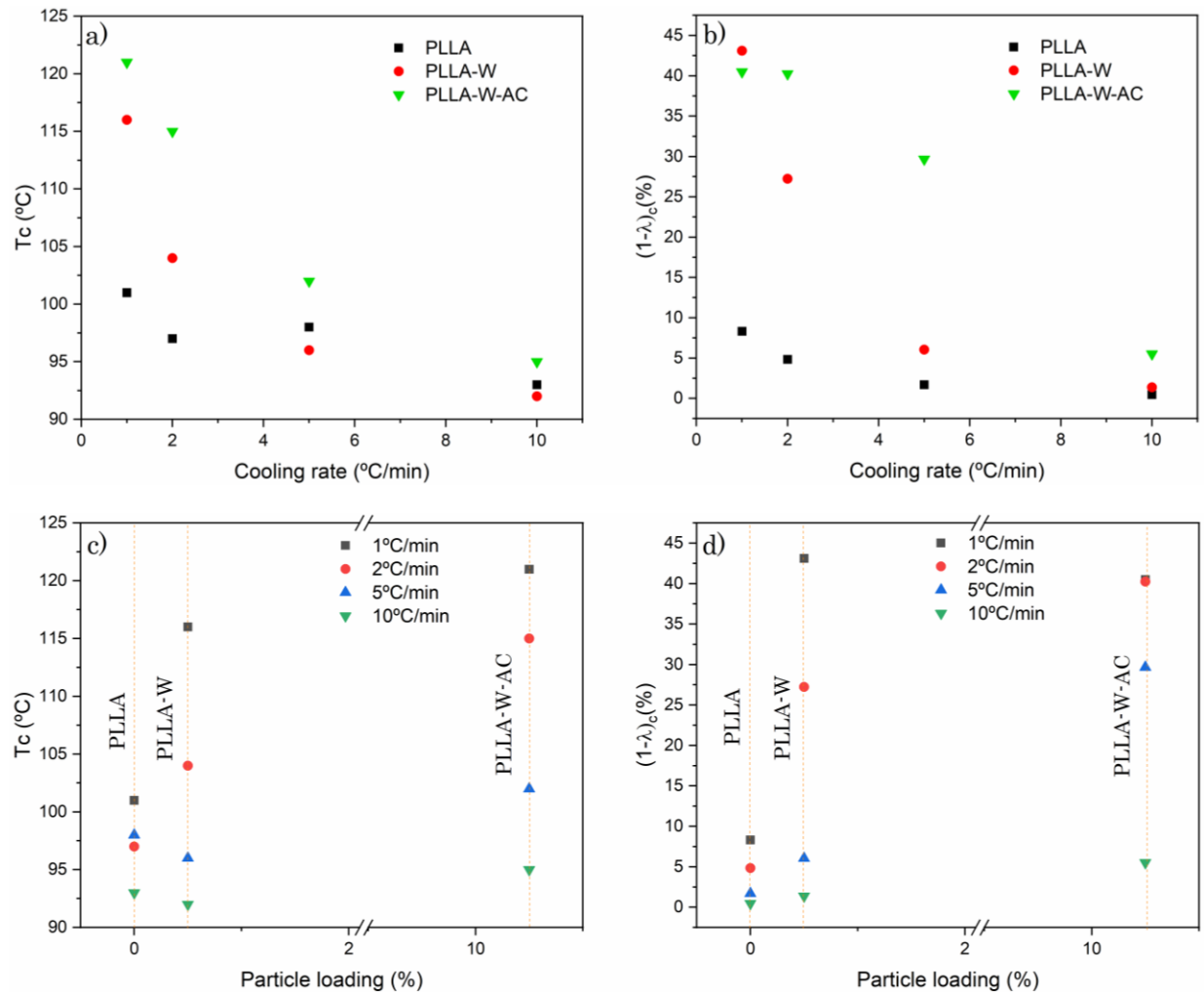


Figure 5.15: Variation of a,c) crystallisation temperature and b,d) crystallinity with cooling rate and particle loading, respectively.

Similarly, the presence of AC also promotes crystallisation. As observed in Figure 5.14, AC-containing fibres exhibit broader and higher-temperature crystallisation peaks compared to non-AC-containing samples, thus indicating a nucleating effect. While literature on this topic is less extensive, various studies have observed the nucleation activity of carbonaceous materials in polymeric fibres, such as carbon

black in PLLA [518], AC in PLA/PP blends [519], or carbon nanotubes in PLLA [520, 521], all of them increasing crystallinity.

Given the strong influence of 2D-WS₂ and AC on the crystallisation behaviour of PLLA, a quantitative estimation of their nucleation capacity was undertaken. To this end, the nucleation activity (ϕ) was determined using Dobrev and Gutzow's methodology [522, 523], as carefully explained in Annex 11.

The experimental values for ϕ were found to be 0.26 for PLLA-W and 0.21 for PLLA-W-AC. The comparison of the nucleating activity of the doped PLLA-W and PLLA-W-AC to neat PLLA ($\phi = 1$) indicates that both 2D-WS₂ and AC actively promote the nucleation of PLLA, with the combined WS₂+AC demonstrating the highest nucleating activity ($\phi = 0.21$). This result also correlates with the observed increase in crystallisation temperatures in the hybrid materials, as shown in Figure 5.15.

In addition, the activation energy of crystallisation (ΔE)-or effective energy barrier to crystallisation-was used to assess the ability of the chain segments to grow using Kissinger's model [524], as described in Annex 12. The obtained ΔE values for neat PLLA, PLLA-W, and PLLA-W-AC were calculated to be -310.4, -117.0 and -108.7 kJ/mol, respectively. The negative ΔE values indicate that the crystallisation rate increases with decreasing temperature, suggesting a spontaneous, barrierless process (the higher ΔE values, the greater difficulty in chain segment transport during crystallisation). The significantly higher ΔE values for the particle-doped samples compared to neat PLLA suggest that WS₂ and AC presence increases the activation energy and chain mobility does not appear to be a limiting factor, confirming that the nucleation activity of 2D-WS₂ and AC plays a key role in accelerating the crystallisation of PLLA.

Moreover, the effect of cooling rate on the melting behaviour of both PLLA and hybrid materials was assessed. As cooling rate increased from 1 to 20 °C/min, two different melting behaviours were identified, typically associated with melting-recrystallisation-remelting processes during heating [525, 526]. Figure 5.16 shows the DSC thermograms of neat and composite PLLA fibres heated at 10°C/min following melt crystallisation at varying cooling rates, while crystalline parameters derived from these measurements are summarised in Table 5.4.

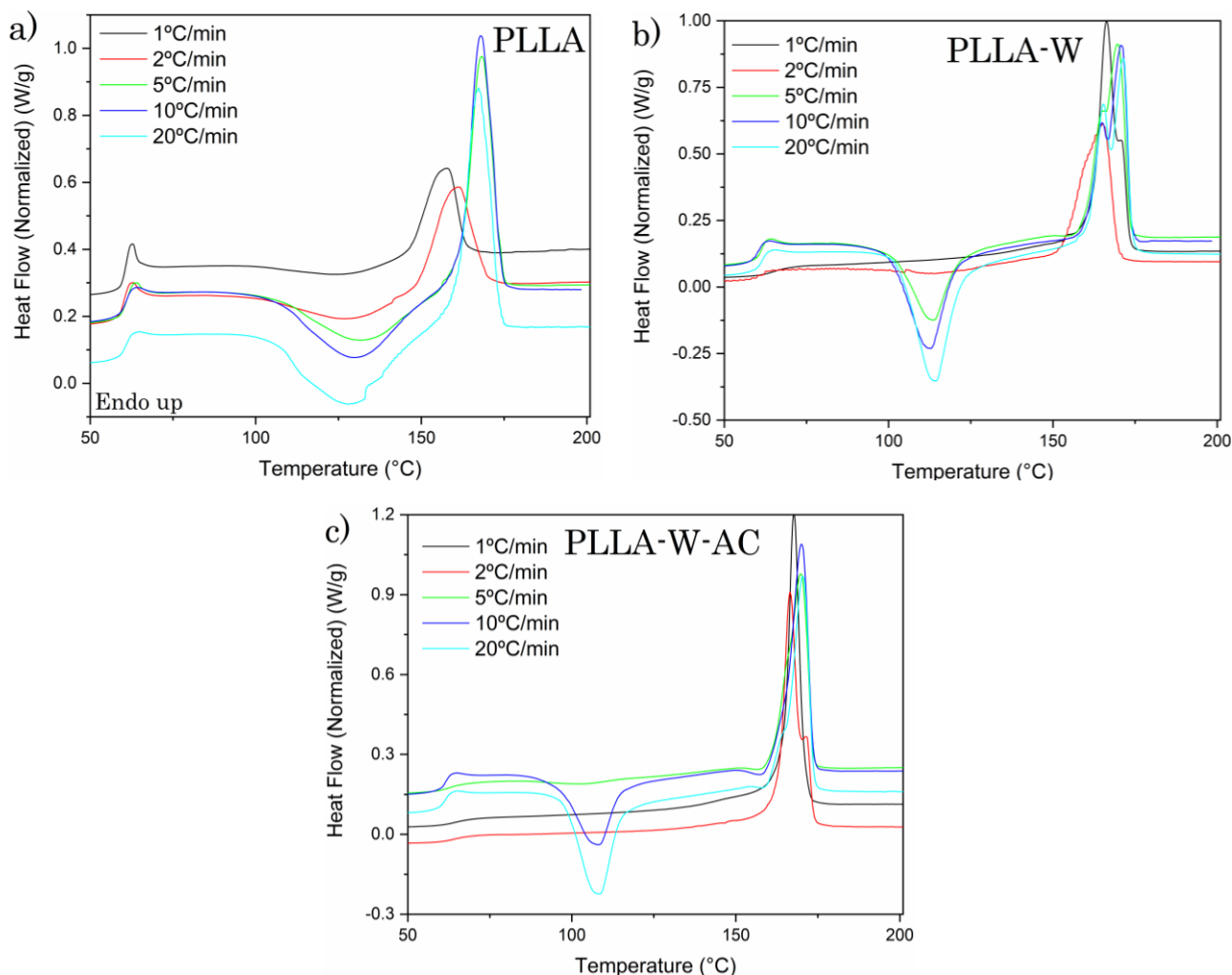


Figure 5.16: DSC heating thermograms of a) PLLA, b) PLLA-W and c) PLLA-W-AC hybrid composites after cooling from the melt at the indicated cooling rates.

During heating, all samples exhibited exothermic peaks corresponding to cold crystallisation, suggesting that melt-crystallisation was incomplete during the cooling phase. Notably, WS_2 presence led to a decrease in the cold crystallisation temperature, T_{cc} , ($T_{cc, PLLA} = 127.8^\circ\text{C}$ and $T_{cc, PLLA-W} = 114.1^\circ\text{C}$), confirming its ability to promote this process. This effect is more pronounced in the AC-containing fibres, which exhibit a T_{cc} of 108.2°C . These results confirm that both WS_2 and AC enhance cold crystallisation, which can also be verified by the average crystallinity data in displayed Table 5.4, with neat PLLA exhibiting an average $(1 - \lambda)_m$ value of 29.6%, a low value compared to the 37.8% and 37.5% of PLLA-W and PLLA-W-AC, respectively. This effect is more pronounced when working at low cooling rates, suggesting that under these conditions, nucleation is the rate limiting step, and addition of a heterogeneous nucleating agent will promote crystallisation. At faster cooling rates, crystal growth will be the rate limiting step, and the effect of the nucleating agent will be minimal [527].

5.4.1.4. Tensile tests.

The mechanical properties of the electrospun fibres were evaluated with particular attention to Young's modulus and tensile strength. The standard PLLA fibre, produced under optimised conditions (electrospinning time of 30 min, and a distance of 12 cm, with no added particles) was tested and used as the base reference. The effects of the needle distance to collector, electrospinning time and nanoparticle presence on the mechanical properties of the other prepared fibres were evaluated and compared to the reference PLLA sample.

To assess the influence of electrospinning time, a PLLA fibre fabricated with an electrospinning time of 60 minutes was also tested. Similarly, to evaluate the effect of needle-to-collector distance, a PLLA fibre prepared with a needle to collector distance of 16 cm was produced and analysed. Finally, to assess the impact of WS₂ and AC particles on the produced fibres, the final PLLA-W and PLLA-W-AC samples were also analysed.

The results of these measurements are summarised in Figure 5.17, revealing that increasing needle to collector distance results in a slight decrease in Young's modulus (approximately 5%) and a 65% decrease in tensile strength —dropping from 39.1 MPa to 13.5 MPa. Similarly, increasing electrospinning time from 30 to 60 minutes also results in decreased mechanical properties, reducing Young's modulus by approximately 37% and tensile strength by 66% (from 39.1 to 13.4 MPa). In both cases, fibre diameter increased, and it is known to reduce molecular orientation within the fibre, and increase internal defects, which in turn has a negative impact on the elastic modulus and tensile strength of the material [528].

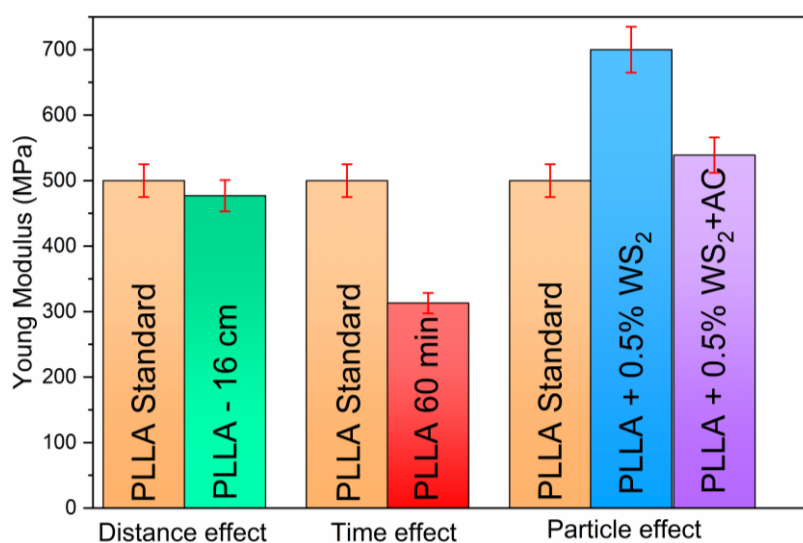


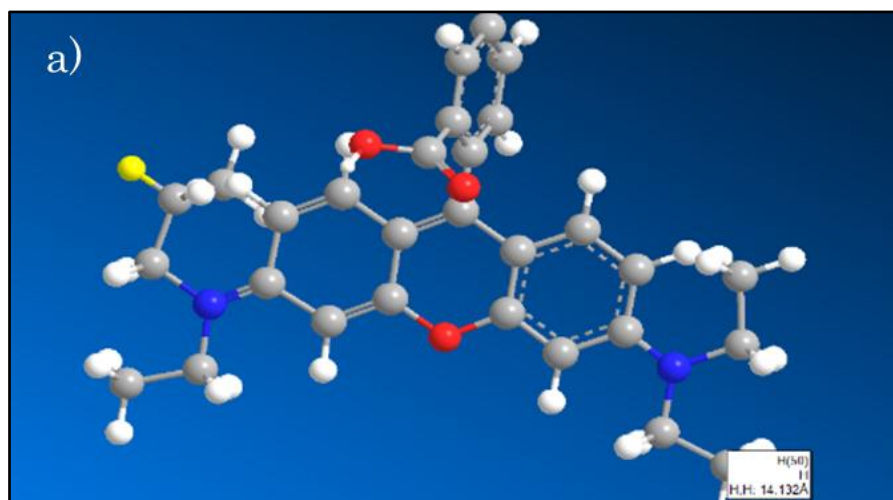
Figure 5.17: Young's modulus of the fibres produces with different parameters.

The influence of particle incorporation is also significant. It is known that the addition of TMDCs can improve mechanical properties. Blending of WS₂ nanotubes (1D) with PLLA was shown to increase Young's modulus by approximately 20% [333], and 17% for PHB composites [335]. Furthermore, the use of WS₂ with 2D morphologies has been shown to have an even greater impact on Young's modulus, with concentrations as low as 0.5 w/w 2D-WS₂ resulting in a 40% increase, from 500 MPa for neat PLLA to 700 MPa in the composite.

In contrast, AC presence has a detrimental effect on the mechanical properties of the fibre. The Young's modulus drops from 700 MPa for the PLLA-W to 539 MPa (23% reduction) for the PLLA-W-AC sample. This effect is consistent with previous studies, which have reported a 40% reduction in Young's modulus of polyamide-imide composites with only a 1% w/w AC loading [529], and for poly-caprolactone exhibiting a 13% drop with a 5% w/w AC concentration. These effects are attributed to the brittleness introduced by the large particle size of AC, which creates voids and reduces polymer/AC adhesion (see Figure 5.8c and d), therefore reducing its mechanical integrity [530].

5.4.2. Fibre application for dye adsorption

To investigate the adsorption behaviour of the prepared PLLA-W-AC nanostructured fibre mats, four dyes were selected and were divided into two main groups based on their ionic nature: cationic dyes (Methylene Blue, MB, and Rhodamine B, RB) and anionic dyes (Methyl Orange, MO, and Congo Red, CR). The AC used for adsorption (spray-coated over the PLLA-W fibre as explained in Section 5.3.2.1) was C 1-4, as it exhibited the most suitable textural properties (BET area, micropore volume and microporosity, as detailed in Table 4.4).



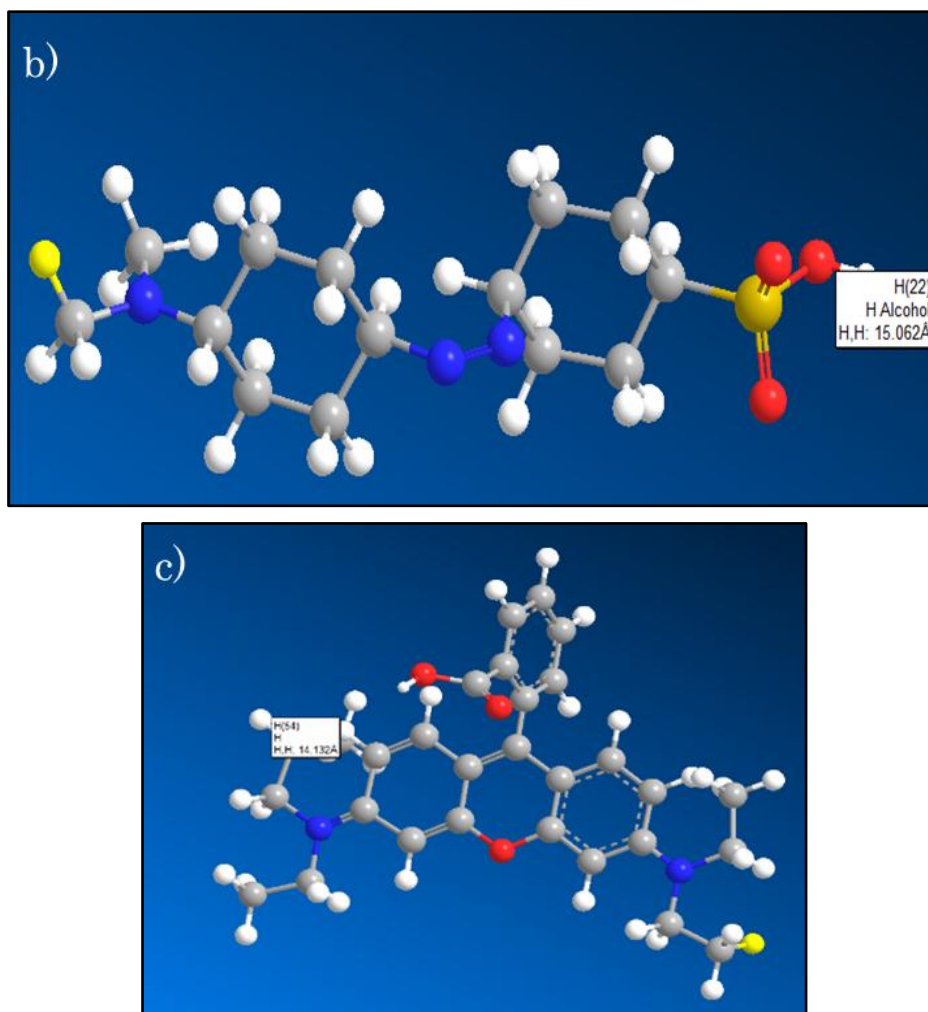


Figure 5.18: Molecular structure of a) Rhodamine B, b) Methyl Orange and c) Congo Red made using ChemDraw software.

For this purpose, dye solutions were prepared at concentrations ranging from 0.1 to 20 ppm and analysed using UV-Vis spectroscopy to generate calibration curves. These curves, along with the corresponding fitting equations for each dye can be found in Annex 13. Preliminary experiments using only the AC C 1-4 determined that 5 mg of adsorbent was sufficient to achieve maximum dye removal. Consequently, fibre mats with an average mass of 50 mg (10% w/w of C 1-4) were used in all adsorption tests.

5.4.2.1. Adsorption kinetics

Adsorption kinetics were carried out by placing the hybrid fibres into 50 mL of the prepared dye solutions (20 ppm) at 298 K under constant stirring at 500 rpm. Aliquots were taken at intervals ranging from 1 minute to 24 hours and analysed using UV-Vis spectroscopy to determine the dye concentrations at the specified times. Subsequently, the removal efficiency was calculated using Equation 5.2:

$$Removal (\%) = \frac{C_0 - C_t}{C_0} \cdot 100 \quad \text{Equation 5.2}$$

Where C_0 is the initial dye concentration (20 ppm) and C_t is the dye concentration measured at a given time t . With this data, dye removal can be calculated and plotted, as shown in Figure 5.19.

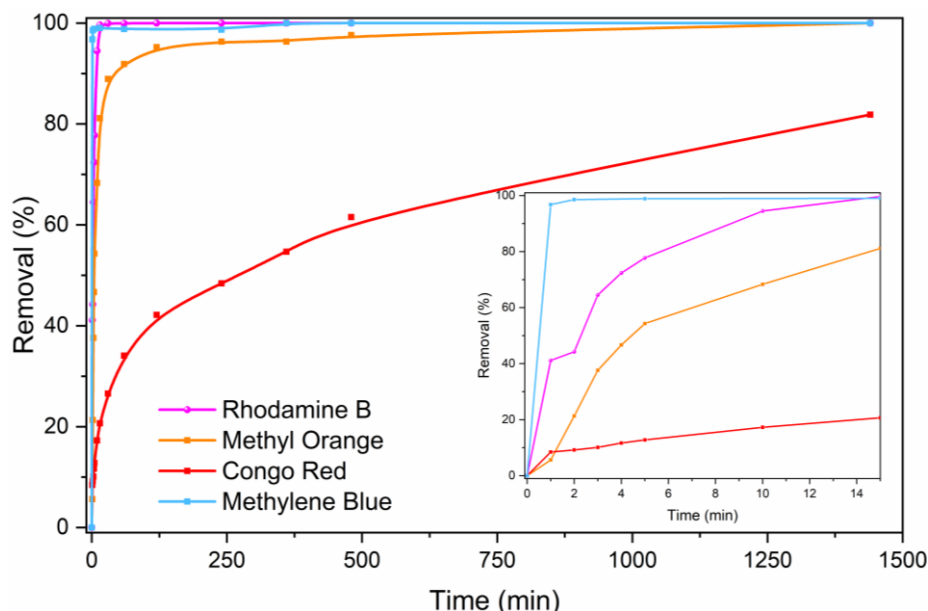


Figure 5.19: Dye removal at different times using PLLA-W-AC.

This plot shows that the tested fibres remove >99% of the MB and RB within 15 minutes and demonstrate exceptional affinity for the cationic dyes. However, the anionic dyes MO and CR exhibited slower kinetics, requiring approximately 120 minutes to reach 95% and 42% removal, respectively, with the latter after 24 hours only achieving a maximum of 80% removal.

These findings are consistent with previous studies, which have shown that AC exhibits greater affinity for cationic dyes (such as MB and RB) due to its negatively charged surface and hydrophobic interactions [531-533]. The electrostatic attraction between the negatively charged AC and positively charged dyes understandably enhances the adsorption of these types of compounds.

To further understand the adsorption mechanism, kinetic modelling was applied using four models: pseudo-first order, pseudo-second order, intraparticle diffusion and the Elovich model. Detailed calculation procedures for each model are provided in Annex 14. The kinetic parameters for each model and dye are summarised below (Table 5.5, Table 5.6, Table 5.7 & Table 5.8):

Table 5.5: Kinetic parameters for Congo Red adsorption using the PLLA-W-AC prepared samples.

Model	Parameters					R ²
Pseudo 1 st order	K ₁	2.59 · 10 ⁻³ min ⁻¹	Q _e	305 mg/g		0.941
Pseudo 2 nd order	K ₂	7.52 · 10 ⁻⁵ g/(mg min)	Q _e	280 mg/g		0.985
Intra-particle diffusion		K _i		9.75 mg/(g min ^{1/2})		0.949
Elovich	α	39.3 mg/(mg min)	β	2.21 · 10 ⁻² g/mg		0.946

Table 5.6: Kinetic parameters for Methyl Orange adsorption using the PLLA-W-AC prepared samples.

Model	Parameters					R ²
Pseudo 1 st order	K ₁	6.78 · 10 ⁻³ min ⁻¹	Q _e	115 mg/g		0.673
Pseudo 2 nd order	K ₂	3.99 · 10 ⁻⁴ g/(mg min)	Q _e	341 mg/g		0.999
Intra-particle diffusion		K _i		6.75 mg/(g min ^{1/2})		0.451
Elovich	α	409 mg/(mg min)	β	2.35 · 10 ⁻² g/mg		0.833

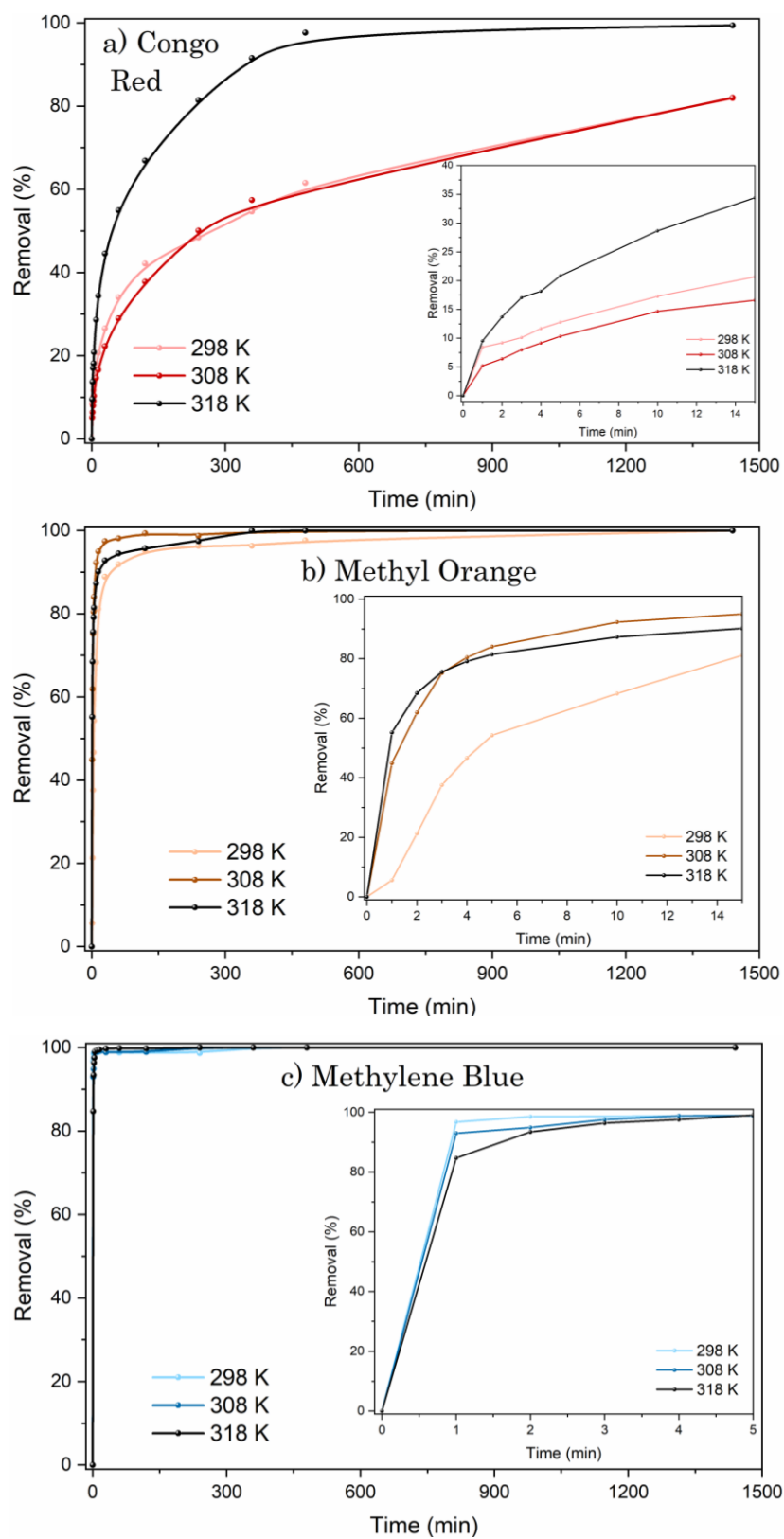
Table 5.7: Kinetic parameters for Methylene Blue adsorption using the PLLA-W-AC prepared samples.

Model	Parameters					R ²
Pseudo 1 st order	K ₁	2.28 · 10 ⁻³ min ⁻¹	Q _e	5.11 mg/g		0.259
Pseudo 2 nd order	K ₂	9.29 · 10 ⁻² g/(mg min)	Q _e	314 mg/g		1.00
Intra-particle diffusion		K _i		0.305 mg/(g min ^{1/2})		0.523
Elovich	α	-	β	-		-

Table 5.8: Kinetic parameters for Rhodamine B adsorption using the PLLA-W-AC prepared samples.

Model	Parameters					R ²
Pseudo 1 st order	K ₁	0.131 min ⁻¹	Q _e	76.4 mg/g		0.774
Pseudo 2 nd order	K ₂	2.49 · 10 ⁻³ g/(mg min)	Q _e	275 mg/g		0.999
Intra-particle diffusion		K _i		14.03 mg/(g min ^{1/2})		0.532
Elovich	α	13.9 mg/(mg min)	β	2.77 · 10 ⁻² g/mg		0.803

Among the models, the pseudo-second order kinetics provided the best fit for all dyes, with calculated adsorption capacities (Q_e) matching experimental values more accurately. This suggests that chemisorption is the rate limiting step [534]. In this process, the adsorption capacity is proportional to the number of active sites, and it is dependent on both the adsorbent concentration and its surface activity [535, 536].



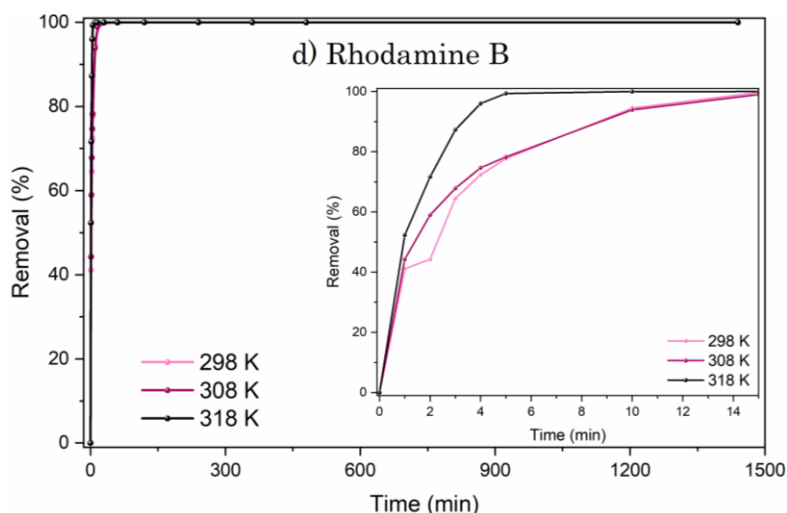


Figure 5.20: Removal kinetics of a) Congo Red; b) Methyl Orange; c) Methylene Blue and d) Rhodamine B at 298 K, 308 K and 318 K.

To assess the thermodynamic nature of the adsorption process, experiments were conducted at three temperatures: 298 K, 308 K and 318 K. From the results presented in Figure 5.20 it can be seen that, given the excellent performance of the hybrid adsorbent toward cationic dyes (MB and RB, Figure 5.20c and d, respectively), the effect of temperature cannot be easily evaluated, as >99% removal is achieved within extremely short time intervals for both dyes. However, in the case of Rhodamine B, a slight enhancement in adsorption rate was observed at higher temperatures. Specifically, at 318 K, where complete removal of the dye is obtained within 5 minutes, compared to 15 minutes at 298 K.

The influence of temperature for anionic dye adsorption is more evident. In the case of MO (Figure 5.20b), increasing the temperature from 298 K to 308 K improved removal efficiency from 88% to 97.5% at 30 minutes, with both achieving complete removal after 24 hours. For CR (Figure 5.20a), temperature has a substantial impact: removal increased from 35% (at 298 K) to 55% (at 318 K) at 30 minutes, and complete removal was only achieved after 24 hours for the sample maintained at the highest temperature, while those at lower temperatures only removed a maximum of 80% of the dye.

These results indicate that temperature improves adsorption performance, suggesting that these materials' adsorption is an endothermic process. The improved performance at higher temperatures can be due to several factors, such as an increased dye penetration, higher diffusion rates and increased ion mobility [537, 538]. However, due to the complex nature of adsorption, it is difficult to determine the dominant factor responsible for this adsorption enhancement.

5.4.2.2. Adsorption isotherms

To further investigate the adsorption mechanism and determine the maximum adsorption capacity of the fibres, adsorption isotherm studies were conducted. These experiments also provided information on the energetic values of the process and the nature of the adsorbent-adsorbate interactions [539].

Solutions with initial concentrations ranging from 50 to 200 ppm were prepared and the adsorbents were placed in these solutions and stirred until equilibrium was reached. The equilibrium concentrations were determined by UV-Vis and four models were applied to interpret the data: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. Annex 15 provides a calculation example for each model, and the corresponding fitting parameters are presented in Table 5.9, Table 5.10, Table 5.11 & Table 5.12.

Table 5.9: Isotherm fitting parameters for Congo Red adsorption using the prepared PLLA-W-AC samples.

Experimental Q_e at 200 mg/L				347 mg/g		
Model		Parameters			R^2	
Langmuir	K_L	0.121 L/mg	Q_m	245 mg/g	0.889	
Freundlich	K_F	49.1 mg/g	$1/n$	0.380	1.000	
Temkin	K_T	1.14 L/mg	B	47.1 J/mol	0.982	
Dubinin-Radushkevich	β	$2.52 \cdot 10^{-6} \text{ mol}^2/\text{kJ}^2$	Q_m	190 mg/g	0.881	

Table 5.10: Isotherm fitting parameters for Methyl Orange adsorption using the prepared PLLA-W-AC samples.

Experimental Q_e at 200 mg/L				424 mg/g		
Model		Parameters			R^2	
Langmuir	K_L	0.296 L/mg	Q_m	431 mg/g	0.998	
Freundlich	K_F	240 mg/g	$1/n$	0.121	0.951	
Temkin	K_T	153 L/mg	B	57.1 J/mol	0.961	
Dubinin-Radushkevich	β	$3.59 \cdot 10^{-6} \text{ mol}^2/\text{kJ}^2$	Q_m	414 mg/g	0.982	

Table 5.11: Isotherm fitting parameters for Methylene Blue adsorption using the prepared PLLA-W-AC samples.

Experimental Q_e at 200 mg/L				802 mg/g		
Model		Parameters			R^2	
Langmuir	K_L	4.75 L/mg	Q_m	665 mg/g	0.584	
Freundlich	K_F	356 mg/g	$1/n$	0.154	0.857	
Temkin	K_T	394 L/mg	B	37.8 J/mol	0.704	
Dubinin-Radushkevich	β	$2.16 \cdot 10^{-8} \text{ mol}^2/\text{kJ}^2$	Q_m	580 g/mg	0.759	

Table 5.12: Isotherm fitting parameters for Rhodamine B adsorption using the prepared PLLA-W-AC samples.

Experimental Q_e at 200 mg/L				454 mg/g	
Model	Parameters			R^2	
Langmuir	K_L	0.035 L/mg	Q_m	514 mg/g	0.481
Freundlich	K_F	74.6 mg/g	$1/n$	0.351	0.830
Temkin	K_T	0.428 L/mg	B	24.4 J/mol	0.746
Dubinin-Radushkevich	β	$1.47 \cdot 10^{-5} \text{ mol}^2/\text{kJ}^2$	Q_m	343 mg/g	0.581

Analysis of the fitting results reveals that the adsorption of cationic dyes is best described by the Freundlich isotherm, consistent with a heterogeneous adsorbent surface capable of a multilayer uptake of MB and RB [534]. In this process, multiple layers of adsorbed molecules form on the heterogeneous surface of the adsorbent, in contrast with the single layer of adsorbed molecules formed on a homogeneous surface during monolayer adsorption, as described by the Langmuir model. Consequently, samples exhibiting multilayer adsorption display higher adsorption capacities than those following monolayer adsorption, as a result of a greater number of layers of adsorbed molecules [540]. This result is consistent with the structural characteristics of ACs, which typically exhibit a negatively charged surface, turbostratic surface that favours the electrostatic attraction of cationic dyes, which typically occur at heterogeneous sites [541].

In contrast, the adsorption of the anionic dyes (MO and CR) can be described with both the Freundlich and Langmuir models, suggesting a multimodal adsorption mechanism. This assumption implies that some molecules may adsorb onto high-energy, homogeneous sites (as described by the Langmuir model), whereas others interact with lower-energy, heterogeneous sites, consistent with the Freundlich model. This mixed behaviour can be expected, as the structure of the carbon provides a heterogeneous character to the process, as previously explained. However, the anionic dyes are electrostatically repelled by the negatively charged AC surface. To overcome this repulsion, adsorption may take place on high-affinity, homogeneous sites, supporting the Langmuir fitting [542].

Interestingly, while cationic dyes exhibit higher maximum adsorption capacities (Q_{MAX} , measured at 200 ppm), Methyl Orange (an anionic dye) presents the highest equilibrium uptake (Q_e), measured at 20 ppm. This contrast suggests that at low dye concentrations, molecule size and diffusivity play a more decisive role in adsorption, while electrostatic interactions and π - π stacking become increasingly relevant at higher concentrations [543, 544].

Overall, the developed PLLA-WS₂-AC hybrid adsorbents demonstrate excellent adsorption performance toward cationic dyes (Methylene Blue and Rhodamine B), and notable efficiency for the tested anionic dyes (Methyl Orange and Congo Red). To contextualise these results, Table 5.13 compares the performance of the developed materials with those of other biomass-based adsorbents. This table underscores the outstanding performance of the developed materials, demonstrating adsorption capacities that are competitive with those of other biomass-derived adsorbents. In some cases, the adsorption capacity of these hybrid adsorbents can exceed an impressive Q_e of 800 mg/g. While there is extensive research on biomass-based adsorbents, many of them exhibit capacities of 100 mg/g or lower. This contrast highlights the high efficiency of the PLLA-W-AC fibres, achieved with only sustainable precursors and environmentally friendly processes.

Table 5.13: Biomass-derived adsorbents and their performance compared to the developed materials presented.

Dye	Precursor	$Q_{\max}(\text{mg/g})^a$
Congo Red	Sucrose [545]	780
	PLLA-W-AC hybrid composite (this work)	347
	Ashitaba (plant waste) [546]	345
	Orange peel [547]	155
	Algae biomass [548]	91.9
Methyl Orange	Bamboo fibres [549]	592
	PLLA-W-AC hybrid composite (this work)	424
	Bamboo waste [550]	344
	Pomelo peel [551]	163
	Pinecone [552]	109
Methylene Blue	PLLA-W-AC hybrid composite (this work)	802
	Pinewood [553]	556
	Cashew nut shell [554]	476
	Ashitaba (plant waste) [546]	315
	Walnut shell [546]	289
Rhodamine B	Locust bean husk [555]	1111
	PLLA-W-AC hybrid composite (this work)	454
	Bagasse pith [556]	264
	<i>Calophyllum inophyllum</i> seeds [557]	169.5
	Bamboo shoot shell [558]	85.8

^a Measured at room temperature.

5.5. Conclusions

The experimental findings of this study lead to the following conclusions:

- Electrospun fibres are the most effective morphology for developing a hybrid PLLA-WS₂-AC material with high dye adsorption efficiency.
- The overall crystallisation rate, final crystallinity and subsequent melting behaviour of PLLA are significantly influenced by the incorporation of both 2D-WS₂ and AC, and variation of cooling rate.
- 2D-WS₂ act as an efficient nucleating agent, improving the melt and cold-crystallisation behaviour of PLLA. This effect is maximised in the presence of AC.
- The incorporation of WS₂ significantly improves the fibres' mechanical properties, increasing Young's modulus by 37% with only a 0.5% w/w nanofiller loading.
- The hybrid fibres demonstrated rapid and complete adsorption of Methylene blue and Rhodamine B, demonstrating the strong affinity of AC for cationic dyes. Furthermore, kinetic analysis reveals a 2nd order process, suggesting a chemically controlled adsorption process for all dyes.
- Temperature increase significantly enhances the adsorption performance of the cationic dyes (especially Congo Red), revealing the endothermic nature of the adsorption process.
- Isotherm analysis revealed that cationic dye adsorption is best described by the Freundlich model, suggesting a heterogeneous surface and multilayer adsorption. In contrast, anionic dyes exhibited characteristics of both Langmuir and Freundlich models, indicating a combination of homogeneous and heterogeneous adsorption mechanisms.

6. General conclusions and future work

6.1. General conclusions of the thesis

The primary objective of this thesis was to develop functional and sustainable materials capable of serving as electrodes for supercapacitors, electrocatalysts for ORR and adsorbents for water remediation (see Chapter 2). The findings presented in Chapters 4 and 5 demonstrate that this goal has been successfully achieved, yielding excellent results.

Activated carbon for energy applications (Chapter 4):

First, a cellulose-based activated carbon was synthesised using environmentally friendly methodologies. It was found that the use of HTC as a pre-treatment enhanced the thermal stability of the materials, resulting in carbonaceous structures with >75% carbon content. Furthermore, the incorporation of albumin increased the nitrogen content of the carbon—primarily in the form of pyrrolic and quaternary groups. However, this increase was not sufficient to induce a pseudocapacitive effect in the carbonaceous electrodes.

Physicochemical analyses revealed that WS₂ nanosheets were deposited onto the carbon surface, blocking the pores and consequently decreasing electrochemical performance. XPS also revealed that sulphur atoms were predominantly in the form of sulphate groups, indicating an oxidised form of the nanosheets that led to decreased conductivity.

Electrochemical tests demonstrated that **C 1-4 exhibited the greatest performance across the whole set of samples, displaying the highest capacitance, exceeding 275 F/g, with power densities close to 5000 W/kg**. These outstanding results were attributed to its superior textural properties, including a surface area exceeding 1600 m²/g and a micropore volume of 0.65 cm³/g, with a pore size matching to the electrolyte ion. The combination of these features resulted in a material with minimal charge transfer resistance ($R_{CT}=1.4\ \Omega$), allowing efficient passage of electrons and, therefore, displaying excellent electrochemical performance.

Additionally, post-mortem characterisation—an uncommon but highly informative approach in electrochemical studies, provided insights into the physicochemical

modifications taking place after testing. It was discovered that the continued charge-discharge cycles led to a partial degradation of the electrodes' surface, destroying some micropores and widening others to create mesopores (with a significant reduction in the electrodes' surface and pore volume). Interestingly, PSD analysis showed that WS₂-doped carbons exhibited lower pore volume loss than their non-doped counterparts, suggesting that TMDC presence blocks the pores, and as such, are less affected by electrochemical testing.

Studies on the electrocatalytic behaviour of these ACs revealed a strong correlation between micropore volume and performance. The samples with lower R_{CT}, higher conductivity and greater heteroatom content were the most effective to promote the 4-electron pathway. The best-performing material (**C 1-4**) displayed a catalytic activity comparable to that of a commercial Pt-C catalyst, **transferring 3.58 electrons**—only 7% less than the 3.87 electrons transferred by the commercial catalyst.

Biopolymeric fibres for wastewater remediation (Chapter 5):

Various PLLA-AC morphologies were developed, but only electrospun fibres proved effective for dye adsorption. The influence of key electrospinning parameters was evaluated (polymer concentration, electrospinning time, needle-to-collector distance) using SEM. However, the direct incorporation of AC could not be achieved due to needle blockage. In order to address this issue, polymer-TMDC solutions were first electrospun and an AC solution was spray-coated on the fibre.

The presence of nanoparticles significantly influenced the mechanical properties of the final material, as evidenced by a **37% increase in Young's modulus** with the addition of just 0.5% w/w WS₂. DSC analyses also revealed that TMDC incorporation increased crystallinity and promoted earlier crystallisation compared to non-WS₂-containing fibres.

Finally, adsorption analyses of anionic and cationic dyes yielded remarkable results. Cationic dyes were completely removed in less than 15 minutes. This process occurs via a combination of chemisorption and physisorption through a multilayer mechanism. In contrast, anionic dye adsorption displayed lower efficiency, likely due to an intermediate adsorption behaviour between monolayer and multilayer mechanisms, as evidenced by the Freundlich and Langmuir isotherm fittings. In any case, the hybrid adsorbent showed **excellent adsorption capacities (exceeding 250 mg/g for each dye)**, with improved performance, especially for the anionic dyes at increased temperatures.

6.2. Limitations of the work and future research

Although this research has yielded very good results, several limitations have been encountered concerning both the experimental processes and their applications. This section outlines the key limitations and proposes potential solutions.

Activated carbon for energy applications (Chapter 4):

In the development of carbonaceous materials, two main challenges were identified. The first issue is related to the use of KOH to control the developed porosity. Despite its effectiveness, a fraction of mesoporosity remains in the final carbon, which, although helps electrolyte diffusion, has a lower impact than the micropores on the overall performance of the material. To address this, two main solutions are proposed: activation via molten KOH, which recent experiments have shown to produce more microporous materials than dissolved KOH, or physical activation using CO₂ or water steam, both of which are known to effectively create microporous structures [172].

One of the greater limitations in the synthesis of cellulose-based carbon is the insertion of WS₂ nanoparticles. These nanofillers fail to successfully penetrate the carbon matrix, which affects the textural properties of the final material. However, recent research has shown that these nanomaterials can be prepared through hydrothermal processing [559]. Therefore, it is proposed that a new hydrothermal carbonisation methodology could be applied simultaneously to both the carbon and WS₂ precursors to create a hybrid structure that provides an effective insertion of the TMDCs into the carbonaceous structure.

Regarding the supercapacitor application, while these nanomaterials yield excellent capacitance results, improvements in both energy and power density can still be made. Given that energy density is directly related to the square of the applied voltage, it can be understood that the use of an ionic liquid as electrolyte can significantly increase the energy density, even at the expense of slightly reducing capacitance.

Biopolymeric fibres for wastewater remediation (Chapter 5):

The synthesis of the biopolymeric matrix by electrospinning encountered some limitations. First, given the environmentally friendly nature of this project, the use of chloroform for electrospinning is a major drawback. A thorough investigation was carried out to identify the optimal solvent, but green solvents failed to match the results obtained with chloroform. Certain green solvents, such as butanol

(118°C) or anisole (154°C), present good dielectric constants for electrospinning, but elevated boiling points. If research on these solvents is conducted and this issue is addressed by modifying the electrospinning parameters, a fully green synthesis of PLLA-WS₂ fibres would be within reach.

Furthermore, an important limitation encountered while dealing with polymeric fibres is the incorporation of activated carbon. Due to its large particle size, AC concentration on fibres is limited to 2%. Thus, new methodologies were explored in order to add AC after electrospinning (spray coating). Nevertheless, AC particles could effectively be inserted into the polymeric matrix if a method to reduce the particle size while maintaining the porous structure was developed, which remains an ongoing challenge.

The application of these bionanomaterials for dye removal yielded impressive results, suggesting new promising directions in this field. It was demonstrated that the adsorbent displays greater chemical affinity for the cationic dyes compared to anionic dyes. Consequently, chemical functionalisation of the hybrid material could be explored in order to improve the affinity for Congo Red and Methyl Orange. Moreover, the reusability and desorption of these materials have yet to be assessed. This represents an important area for further research. In fact, understanding the regeneration capacity and adsorptive behaviour of these materials would be particularly insightful, as it could open the door to novel applications, such as drug delivery systems.

Additionally, the success of this work encourages further research on the use of these materials for the removal of other environmentally harmful components, such as Persistent Organic Pollutants (POPs), Endocrine Disrupting Chemicals (EDCs) and Pharmaceuticals and Personal Care Products (PPCPs).

In conclusion, this study successfully combined sustainable precursors with environmentally friendly methodologies to develop fully functional bionanomaterials. These composites displayed outstanding performance across all the studied applications, matching or exceeding the capacities of previously developed biomass-derived materials. These findings highlight the potential of sustainably derived materials for energy and environmental applications, leading the way toward a better future, and setting the standard for further advancements in sustainable technology and green chemistry.

References

- [1] IEA, "World Energy Outlook 2023," 20. [Online]. Available: <https://www.iea.org/reports/world-energy-outlook-2023>
- [2] "Global Energy Statistical Yearbook 2020," 2020.
- [3] (2021). *Global Energy review 2021, Assessing the effects of economic recoveries on global energy demand and CO2 emissions in 2021*.
- [4] "Electricity Prices in Europe – Who Pays the Most?" <https://strom-report.com/electricity-prices-europe/> (accessed 01-06-2024).
- [5] J. C. Christophe Blot, François Geerolf, "The direct and indirect impacts of the war on inflation," Economic Governance and EMU Scrutiny Unit (EGOV), 2023.
- [6] U.N.F.C.C.C. "The Paris Agreement." <https://unfccc.int/process-and-meetings/the-paris-agreement> (accessed 2025).
- [7] IPCC, "Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change," *IPCC*, p. 151, 2014.
- [8] S. Fuss *et al.*, "Betting on negative emissions," *Nature Climate Change*, vol. 4, no. 10, pp. 850-853, 2014/10/01 2014.
- [9] IEA. "World Energy Investment 2024." <https://www.iea.org/reports/world-energy-investment-2024> (accessed 2025).
- [10] IEA, "World Energy Outlook 2024," 2024. [Online]. Available: <https://www.iea.org/reports/world-energy-outlook-2024>
- [11] H. Chen, T. N. Cong, W. Yang, C. Tan, Y. Li, and Y. Ding, "Progress in electrical energy storage system: A critical review," *Progress in Natural Science*, vol. 19, no. 3, pp. 291-312, 2009/03/10/ 2009.
- [12] J. Mitali, S. Dhinakaran, and A. A. Mohamad, "Energy storage systems: a review," *Energy Storage and Saving*, vol. 1, no. 3, pp. 166-216, 2022/09/01/ 2022.
- [13] S. Koohi-Fayegh and M. A. Rosen, "A review of energy storage types, applications and recent developments," *Journal of Energy Storage*, vol. 27, p. 101047, 2020/02/01/ 2020.
- [14] M. S. Guney and Y. Tepe, "Classification and assessment of energy storage systems," *Renewable and Sustainable Energy Reviews*, vol. 75, pp. 1187-1197, 2017/08/01/ 2017.
- [15] P. García-Hernández, "Síntesis y caracterización de materiales híbridos a base de óxido de grafeno/polímeros intrínsecamente conductores para su empleo en supercondensadores," 2013.
- [16] D. Pacheco Catalán, "Síntesis de polímeros electroconductores para la aplicación en dispositivos energéticos no convencionales (Tesis Doctoral)," Universidad de Mérida, 2009.
- [17] Renewable Power 2023 [Online] Available: <https://www.iea.org/reports/renewables-2023>

- [18] S. Insights. "Global Pumped Hydroelectric Energy Storage Market Size, Share, and COVID-19 Impact Analysis, By Source, By End User, and By Region, Analysis and Forecast 2023 - 2033." <https://www.sphericalinsights.com/reports/pumped-hydroelectric-energy-storage-market> (accessed 22-11-2024).
- [19] P. Research. "Supercapacitors Market Size, Share, and Trends 2024 to 2034." <https://www.precedenceresearch.com/supercapacitors-market#:~:text=How%20much%20is%20the%20CAGR,forecast%20period%202024%20to%202034.> (accessed 22-11-2024).
- [20] P. Research. "Fuel Cell Market Size Share, and Trends 2024 to 2034." <https://www.precedenceresearch.com/fuel-cell-market> (accessed 22-11-2024).
- [21] Y. Shao *et al.*, "Design and Mechanisms of Asymmetric Supercapacitors," *Chemical Reviews*, vol. 118, no. 18, pp. 9233-9280, 2018/09/26 2018.
- [22] J. H. Chang, "Modeling of an Electrochemical Cell," Electrical and Computer Engineering, University of Toronto, 2010.
- [23] H. Becker, "United States Patent Office low voltage electrolytic capacitor," 1954.
- [24] D. L. Boos, "Electrolytic capacitor having carbon paste electrodes," ed: Google Patents, 1970.
- [25] J. Garche and P. T. Moseley, *Electrochemical Energy Storage for Renewable Sources and Grid Balancing*. Oxford, NETHERLANDS: Elsevier, 2014.
- [26] S. Trasatti and G. Buzzanca, "Ruthenium dioxide: A new interesting electrode material. Solid state structure and electrochemical behaviour," *Journal of electroanalytical chemistry and interfacial electrochemistry*, vol. 29, no. 2, pp. A1-A5, 1971.
- [27] A. Dutta, S. Mitra, M. Basak, and T. Banerjee, "A comprehensive review on batteries and supercapacitors: Development and challenges since their inception," *Energy Storage*, vol. 5, no. 1, p. e339, 2023.
- [28] M. Yaseen *et al.*, "A Review of Supercapacitors: Materials Design, Modification, and Applications," *Energies*, vol. 14, no. 22, p. 7779, 2021.
- [29] K. C. S. Lakshmi and B. Vedhanarayanan, "High-Performance Supercapacitors: A Comprehensive Review on Paradigm Shift of Conventional Energy Storage Devices," *Batteries*, vol. 9, no. 4, p. 202, 2023.
- [30] P. Kurzweil, "Chapter 19 - Electrochemical Double-layer Capacitors," in *Electrochemical Energy Storage for Renewable Sources and Grid Balancing*, P. T. Moseley and J. Garche Eds. Amsterdam: Elsevier, 2015, pp. 345-407.
- [31] B. O. K. Park, C. D. Lokhande, H. S. Park, K. D. Jung, and O. H. S. Joo, "Electrodeposited ruthenium oxide (RuO₂) films for electrochemical supercapacitors," *Journal of Materials Science*, Article vol. 39, no. 13, pp. 4313-4317, 2004.
- [32] M. Boota and Y. Gogotsi, "MXene—Conducting Polymer Asymmetric Pseudocapacitors," *Advanced Energy Materials*, Article vol. 9, no. 7, 2019, Art no. 1802917.
- [33] X. Tong *et al.*, "Tailoring the physicochemical properties of chitosan-derived N-doped carbon by controlling hydrothermal carbonization time for high-performance supercapacitor application," *Carbohydrate Polymers*, vol. 207, pp. 764-774, 2019/03/01/ 2019.

- [34] C. Liu, K. Wang, Y. Du, Y. Shan, P. Duan, and N. Ramzan, "Hydrothermal Carbonization of Cellulose with Ammonium Sulfate and Thiourea for the Production of Supercapacitor Carbon," *Polymers*, vol. 15, no. 23, p. 4478, 2023.
- [35] L. Yang, Y. Feng, M. Cao, and J. Yao, "Two-step preparation of hierarchical porous carbon from KOH-activated wood sawdust for supercapacitor," *Materials Chemistry and Physics*, Article vol. 238, 2019, Art no. 121956.
- [36] A. Jain, C. Xu, S. Jayaraman, R. Balasubramanian, J. Y. Lee, and M. P. Srinivasan, "Mesoporous activated carbons with enhanced porosity by optimal hydrothermal pre-treatment of biomass for supercapacitor applications," *Microporous and Mesoporous Materials*, vol. 218, pp. 55-61, 2015/12/01/ 2015.
- [37] M. Ren *et al.*, "High Performance N-Doped Carbon Electrodes Obtained via Hydrothermal Carbonization of Macroalgae for Supercapacitor Applications," *ChemElectroChem*, vol. 5, no. 18, pp. 2686-2693, 2018/09/12 2018.
- [38] J. Chang *et al.*, "Activated porous carbon prepared from paulownia flower for high performance supercapacitor electrodes," *Electrochimica Acta*, Article vol. 157, pp. 290-298, 2015.
- [39] W. Du *et al.*, "Designing synthesis of porous biomass carbon from wheat straw and the functionalizing application in flexible, all-solid-state supercapacitors," *Journal of Alloys and Compounds*, vol. 797, pp. 1031-1040, 2019/08/15/ 2019.
- [40] J. Li, "Preparation of Ginger Straw based Porous Carbon using One- step Pyrolysis Process as Electrode Material for Supercapacitor," *International Journal of Electrochemical Science*, pp. 10289-10305, 11/01 2019.
- [41] S. Zhang, J. Liu, P. Huang, H. Wang, C. Cao, and W. Song, "Carbonaceous aerogel and CoNiAl-LDH@CA nanocomposites derived from biomass for high performance pseudo-supercapacitor," *Science Bulletin*, Article vol. 62, no. 12, pp. 841-845, 2017.
- [42] L. Lyu *et al.*, "Yeast-derived N-doped carbon microsphere/polyaniline composites as high performance pseudocapacitive electrodes," *Electrochimica Acta*, Article vol. 291, pp. 256-266, 2018.
- [43] L. Fan, Z. Tu, and S. H. Chan, "Recent development of hydrogen and fuel cell technologies: A review," *Energy Reports*, vol. 7, pp. 8421-8446, 2021/11/01/ 2021.
- [44] H. Ibrahim, A. Ilinca, and J. Perron, "Energy storage systems—Characteristics and comparisons," *Renewable and Sustainable Energy Reviews*, vol. 12, no. 5, pp. 1221-1250, 2008/06/01/ 2008.
- [45] T. Ralph *et al.*, "Low cost electrodes for proton exchange membrane fuel cells: Performance in single cells and Ballard stacks," *Journal of the Electrochemical Society*, vol. 144, no. 11, p. 3845, 1997.
- [46] N. Sazali, W. N. Wan Salleh, A. S. Jamaludin, and M. N. Mhd Razali, "New Perspectives on Fuel Cell Technology: A Brief Review," *Membranes*, vol. 10, no. 5, p. 99, 2020.
- [47] M. Qiang, "Hydrogen: Green Energy in the 21st Century," ed: Beijing, 2005.

- [48] S. Trasatti, "Water electrolysis: who first?," *Journal of Electroanalytical Chemistry*, vol. 476, no. 1, pp. 90-91, 1999/10/21/ 1999.
- [49] A. Ursúa, L. M. Gandía, and P. Sanchis, "Hydrogen production from water electrolysis: Current status and future trends," in *Proceedings of the IEEE*, 2012, vol. 100, 2 ed., pp. 410-426, doi: 10.1109/JPROC.2011.2156750. [Online]. Available: <https://www.scopus.com/inward/record.uri?eid=2-s2.0-84856233112&doi=10.1109%2fJPROC.2011.2156750&partnerID=40&md5=d65b8aed58012de39328fb3bea684f77>
- [50] V. Schröder, B. Emonts, H. Janßen, and H. P. Schulze, "Explosion limits of hydrogen/oxygen mixtures at initial pressures up to 200 bar," *Chemical Engineering and Technology*, Article vol. 27, no. 8, pp. 847-851, 2004.
- [51] M. Carmo, D. L. Fritz, J. Mergel, and D. Stolten, "A comprehensive review on PEM water electrolysis," *International Journal of Hydrogen Energy*, vol. 38, no. 12, pp. 4901-4934, 2013/04/22/ 2013.
- [52] J. Russell, L. Nuttall, and A. Fickett, "Hydrogen generation by solid polymer electrolyte water electrolysis," *Am. Chem. Soc. Div. Fuel Chem. Prepr*, vol. 18, pp. 24-40, 1973.
- [53] W. T. Grubb, "Batteries with Solid Ion Exchange Electrolytes," *Journal of the Electrochemical Society*, Article vol. 106, no. 4, pp. 275-278, 1959.
- [54] F. Barbir, "PEM electrolysis for production of hydrogen from renewable energy sources," *Solar Energy*, Article vol. 78, no. 5, pp. 661-669, 2005.
- [55] P. Millet *et al.*, "PEM water electrolyzers: From electrocatalysis to stack development," *International Journal of Hydrogen Energy*, Article vol. 35, no. 10, pp. 5043-5052, 2010.
- [56] P. Millet, R. Ngameni, S. A. Grigoriev, and V. N. Fateev, "Scientific and engineering issues related to PEM technology: Water electrolyzers, fuel cells and unitized regenerative systems," *International Journal of Hydrogen Energy*, Article vol. 36, no. 6, pp. 4156-4163, 2011.
- [57] W. Dönitz and E. Erdle, "High-temperature electrolysis of water vapor: status of development and perspectives for application," *International Journal of Hydrogen Energy*, Article vol. 10, no. 5, pp. 291-295, 1985.
- [58] M. A. Laguna-Bercero, "Recent advances in high temperature electrolysis using solid oxide fuel cells: A review," *Journal of Power Sources*, Review vol. 203, pp. 4-16, 2012.
- [59] E. Wallnöfer-Ogris, F. Poimer, R. Köll, M.-G. Macherhammer, and A. Trattner, "Main degradation mechanisms of polymer electrolyte membrane fuel cell stacks – Mechanisms, influencing factors, consequences, and mitigation strategies," *International Journal of Hydrogen Energy*, vol. 50, pp. 1159-1182, 2024/01/02/ 2024.
- [60] X. Wang *et al.*, "Review of Metal Catalysts for Oxygen Reduction Reaction: From Nanoscale Engineering to Atomic Design," *Chem*, vol. 5, no. 6, pp. 1486-1511, 2019/06/13/ 2019.
- [61] S.-H. Zhang, Y. Zhao, Z.-Y. Yang, Z.-F. He, and H. Wu, "The 1.35Ga diabase sills from the northern North China Craton: Implications for breakup of the Columbia (Nuna) supercontinent," *Earth and Planetary Science Letters*, vol. 288, no. 3, pp. 588-600, 2009/11/15/ 2009.

-
- [62] M. E. Scofield, H. Liu, and S. S. Wong, "A concise guide to sustainable PEMFCs: recent advances in improving both oxygen reduction catalysts and proton exchange membranes," *Chemical Society Reviews*, vol. 44, no. 16, pp. 5836-5860, 2015.
- [63] S. Samad *et al.*, "Carbon and non-carbon support materials for platinum-based catalysts in fuel cells," *International Journal of Hydrogen Energy*, Review vol. 43, no. 16, pp. 7823-7854, 2018.
- [64] M. S. Garapati and R. Sundara, "Highly efficient and ORR active platinum-scandium alloy-partially exfoliated carbon nanotubes electrocatalyst for Proton Exchange Membrane Fuel Cell," *International Journal of Hydrogen Energy*, Article vol. 44, no. 21, pp. 10951-10963, 2019.
- [65] J. Gu, G.-M. Zhang, R. Yao, T. Yu, M.-F. Han, and R.-S. Huang, "High Oxygen Reduction Activity of Pt-Ni Alloy Catalyst for Proton Exchange Membrane Fuel Cells," *Catalysts*, vol. 12, no. 3, p. 250, 2022.
- [66] A. Ostroverkh *et al.*, "Efficient Pt-C MEA for PEMFC with Low Platinum Content Prepared by Magnetron Sputtering," *Fuel Cells*, Article vol. 18, no. 1, pp. 51-56, 2018.
- [67] C. Wang and J. S. Spendelow, "Recent developments in Pt-Co catalysts for proton-exchange membrane fuel cells," *Current Opinion in Electrochemistry*, vol. 28, p. 100715, 2021/08/01/ 2021.
- [68] S. Li *et al.*, "Tuning oxygen vacancy in SnO₂ inhibits Pt migration and agglomeration towards high-performing fuel cells," *Applied Catalysis B: Environmental*, vol. 320, p. 122017, 2023/01/01/ 2023.
- [69] Q. Wang *et al.*, "Phenylenediamine-based FeN_x/C catalyst with high activity for oxygen reduction in acid medium and its active-site probing," *Journal of the American Chemical Society*, Article vol. 136, no. 31, pp. 10882-10885, 2014.
- [70] J. Ding, P. Wang, S. Ji, H. Wang, V. Linkov, and R. Wang, "N-doped mesoporous FeN_x/carbon as ORR and OER bifunctional electrocatalyst for rechargeable zinc-air batteries," *Electrochimica Acta*, Article vol. 296, pp. 653-661, 2019.
- [71] L. Majidi *et al.*, "Highly Active Rhenium-, Ruthenium-, and Iridium-Based Dichalcogenide Electrocatalysts for Oxygen Reduction and Oxygen Evolution Reactions in Aprotic Media," *Chemistry of Materials*, vol. 32, no. 7, pp. 2764-2773, 2020/04/14 2020.
- [72] H. Huang, X. Feng, C. Du, S. Wu, and W. Song, "Incorporated oxygen in MoS₂ ultrathin nanosheets for efficient ORR catalysis," *Journal of Materials Chemistry A*, 10.1039/C5TA01600B vol. 3, no. 31, pp. 16050-16056, 2015.
- [73] H. Singh, M. Marley-Hines, S. Chakravarty, and M. Nath, "Multi-walled carbon nanotube supported manganese selenide as a highly active bifunctional OER and ORR electrocatalyst," *Journal of Materials Chemistry A*, Article vol. 10, no. 12, pp. 6772-6784, 2022.
- [74] A. P. Tiwari, D. Kim, Y. Kim, and H. Lee, "Bifunctional Oxygen Electrocatalysis through Chemical Bonding of Transition Metal Chalcogenides on Conductive Carbons," *Advanced Energy Materials*, vol. 7, no. 14, p. 1602217, 2017.

- [75] H.-j. Huang, T. Yang, F.-y. Lai, and G.-q. Wu, "Co-pyrolysis of sewage sludge and sawdust/rice straw for the production of biochar," *Journal of Analytical and Applied Pyrolysis*, vol. 125, pp. 61-68, 2017/05/01/ 2017.
- [76] J. Lin *et al.*, "Environmental impacts and remediation of dye-containing wastewater," *Nature Reviews Earth & Environment*, vol. 4, no. 11, pp. 785-803, 2023/11/01 2023.
- [77] V. Katheresan, J. Kansedo, and S. Y. Lau, "Efficiency of various recent wastewater dye removal methods: A review," *Journal of Environmental Chemical Engineering*, vol. 6, no. 4, pp. 4676-4697, 2018/08/01/ 2018.
- [78] T. A. Nguyen and R.-S. Juang, "Treatment of waters and wastewaters containing sulfur dyes: A review," *Chemical Engineering Journal*, vol. 219, pp. 109-117, 2013/03/01/ 2013.
- [79] R. Al-Tohamy *et al.*, "A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety," *Ecotoxicology and Environmental Safety*, vol. 231, p. 113160, 2022/02/01/ 2022.
- [80] C. Novotný *et al.*, "Comparative use of bacterial, algal and protozoan tests to study toxicity of azo- and anthraquinone dyes," (in eng), *Chemosphere*, vol. 63, no. 9, pp. 1436-42, Jun 2006.
- [81] A. Tkaczyk, K. Mitrowska, and A. Posyniak, "Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review," (in eng), *Sci Total Environ*, vol. 717, p. 137222, May 15 2020.
- [82] T. A. Khattab, M. Rehan, and T. Hamouda, "Smart textile framework: Photochromic and fluorescent cellulosic fabric printed by strontium aluminate pigment," *Carbohydrate Polymers*, vol. 195, pp. 143-152, 2018/09/01/ 2018.
- [83] S.-L. Lim, W.-L. Chu, and S.-M. Phang, "Use of *Chlorella vulgaris* for bioremediation of textile wastewater," *Bioresource Technology*, vol. 101, no. 19, pp. 7314-7322, 2010/10/01/ 2010.
- [84] F. O. Topaç, E. Dindar, S. Uçaroğlu, and H. S. Başkaya, "Effect of a sulfonated azo dye and sulfanilic acid on nitrogen transformation processes in soil," *Journal of Hazardous Materials*, vol. 170, no. 2, pp. 1006-1013, 2009/10/30/ 2009.
- [85] I. Haq, A. Raj, and Markandeya, "Biodegradation of Azure-B dye by *Serratia liquefaciens* and its validation by phytotoxicity, genotoxicity and cytotoxicity studies," *Chemosphere*, vol. 196, pp. 58-68, 2018/04/01/ 2018.
- [86] A. Sharma *et al.*, "Photosynthetic Response of Plants Under Different Abiotic Stresses: A Review," *Journal of Plant Growth Regulation*, vol. 39, no. 2, pp. 509-531, 2020/06/01 2020.
- [87] B. d. C. Ventura-Camargo, P. P. Maltempi, and M. A. Marin-Morales, "The use of the cytogenetic to identify mechanisms of action of an azo dye in *Allium cepa* meristematic cells," *J Environ Anal Toxicol*, vol. 1, no. 3, pp. 1-12, 2011.
- [88] Y. Sun, Y. Gu, and Q. Zha, "A novel surface imprinted resin for the selective removal of metal-complexed dyes from aqueous solution in batch

- experiments: ACB GGN as a representative contaminant," *Chemosphere*, vol. 280, p. 130611, 2021/10/01/ 2021.
- [89] O. A. Amer, S. S. Ali, M. Azab, W. A. El-Shouny, J. Sun, and Y. A. G. Mahmoud, "Exploring new marine bacterial species, *Alcaligenes faecalis* Alca F2018 valued for bioconversion of shrimp chitin to chitosan for concomitant biotechnological applications," *International Journal of Biological Macromolecules*, vol. 196, pp. 35-45, 2022/01/31/ 2022.
- [90] K. Sharma, P. Sharma, S. K. Dhiman, P. Chadha, and H. S. Saini, "Biochemical, genotoxic, histological and ultrastructural effects on liver and gills of fresh water fish *Channa punctatus* exposed to textile industry intermediate 2 ABS," *Chemosphere*, vol. 287, p. 132103, 2022/01/01/ 2022.
- [91] M. Piątkowska, P. Jedziniak, M. Olejnik, J. Żmudzki, and A. Posyniak, "Absence of evidence or evidence of absence? A transfer and depletion study of Sudan I in eggs," *Food Chemistry*, vol. 239, pp. 598-602, 2018/01/15/ 2018.
- [92] V. K. Balakrishnan, S. Shirin, A. M. Aman, S. R. de Solla, J. Mathieu-Denoncourt, and V. S. Langlois, "Genotoxic and carcinogenic products arising from reductive transformations of the azo dye, Disperse Yellow 7," *Chemosphere*, vol. 146, pp. 206-215, 2016/03/01/ 2016.
- [93] Y. Will, J. E. McDuffie, A. J. Olaharski, and B. D. Jeffy, *Drug discovery toxicology: From target assessment to translational biomarkers*. John Wiley & Sons, 2016.
- [94] F. M. D. Chequer *et al.*, "The azo dyes Disperse Red 1 and Disperse Orange 1 increase the micronuclei frequencies in human lymphocytes and in HepG2 cells," *Mutation Research/Genetic Toxicology and Environmental Mutagenesis*, vol. 676, no. 1, pp. 83-86, 2009/05/31/ 2009.
- [95] K. Lacasse and W. Baumann, *Textile Chemicals: Environmental data and facts*. Springer Science & Business Media, 2012.
- [96] B. Louhichi, F. Gaied, K. Mansouri, and M. R. Jeday, "Treatment of textile industry effluents by Electro-Coagulation and Electro-Fenton processes using solar energy: A comparative study," *Chemical Engineering Journal*, vol. 427, p. 131735, 2022/01/01/ 2022.
- [97] R. G. Saratale, S. Sivapathan, G. D. Saratale, J. R. Banu, and D.-S. Kim, "Hydroxamic acid mediated heterogeneous Fenton-like catalysts for the efficient removal of Acid Red 88, textile wastewater and their phytotoxicity studies," *Ecotoxicology and Environmental Safety*, vol. 167, pp. 385-395, 2019/01/15/ 2019.
- [98] H. Zhao, P. Cao, L. Lu, F. Li, C. H. Pang, and T. Wu, "Co-regulation of dispersion, exposure and defect sites on CeO₂ (111) surface for catalytic oxidation of Hg⁰," *Journal of Hazardous Materials*, vol. 424, p. 126566, 2022/02/15/ 2022.
- [99] M. A. M. Al-Alwani, N. A. Ludin, A. B. Mohamad, A. A. H. Kadhum, and A. Mukhlus, "Application of dyes extracted from *Alternanthera dentata* leaves and *Musa acuminata* bracts as natural sensitizers for dye-sensitized solar cells," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 192, pp. 487-498, 2018/03/05/ 2018.
- [100] F. Li, S. C. Srivatsa, and S. Bhattacharya, "A review on catalytic pyrolysis of microalgae to high-quality bio-oil with low oxygenous and nitrogenous

- compounds," *Renewable and Sustainable Energy Reviews*, vol. 108, pp. 481-497, 2019/07/01/ 2019.
- [101] E. Noman, B. A. Talip, A. Al-Gheethi, R. Mohamed, and H. Nagao, "Decolourisation of dyes in greywater by mycoremediation and mycosorption process of fungi from peatland; primary study," *Materials Today: Proceedings*, vol. 31, pp. 23-30, 2020/01/01/ 2020.
- [102] S. S. Mohanty and A. Kumar, "Enhanced degradation of anthraquinone dyes by microbial monoculture and developed consortium through the production of specific enzymes," *Scientific reports*, vol. 11, no. 1, p. 7678, 2021.
- [103] Y. Pan *et al.*, "Removal of azo dye in an up-flow membrane-less bioelectrochemical system integrated with bio-contact oxidation reactor," *Chemical Engineering Journal*, vol. 326, pp. 454-461, 2017/10/15/ 2017.
- [104] N. A. Khan, B. N. Bhadra, and S. H. Jhung, "Heteropoly acid-loaded ionic liquid@metal-organic frameworks: Effective and reusable adsorbents for the desulfurization of a liquid model fuel," *Chemical Engineering Journal*, vol. 334, pp. 2215-2221, 2018/02/15/ 2018.
- [105] F. Li, L. Katz, and Z. Hu, "Adsorption of major nitrogen-containing components in microalgal bio-oil by activated carbon: equilibrium, kinetics, and ideal adsorbed solution theory (IAST) model," *ACS sustainable chemistry & engineering*, vol. 7, no. 19, pp. 16529-16538, 2019.
- [106] N. Z. Al-Mutairi, "Coagulant toxicity and effectiveness in a slaughterhouse wastewater treatment plant," *Ecotoxicology and Environmental Safety*, vol. 65, no. 1, pp. 74-83, 2006/09/01/ 2006.
- [107] S. Samsami, M. Mohamadizani, M.-H. Sarrafzadeh, E. R. Rene, and M. Firoozbahr, "Recent advances in the treatment of dye-containing wastewater from textile industries: Overview and perspectives," *Process Safety and Environmental Protection*, vol. 143, pp. 138-163, 2020/11/01/ 2020.
- [108] K. G. Akpomie and J. Conradie, "Advances in application of cotton-based adsorbents for heavy metals trapping, surface modifications and future perspectives," *Ecotoxicology and Environmental Safety*, vol. 201, p. 110825, 2020/09/15/ 2020.
- [109] A. Metecan, A. Cihanoğlu, and S. Alsoy Altinkaya, "A positively charged loose nanofiltration membrane fabricated through complexing of alginate and polyethyleneimine with metal ions on the polyamideimide support for dye desalination," *Chemical Engineering Journal*, vol. 416, p. 128946, 2021/07/15/ 2021.
- [110] I. G. Werten and Khoiruddin, "Reverse osmosis applications: Prospect and challenges," *Desalination*, vol. 391, pp. 112-125, 2016/08/01/ 2016.
- [111] M. Behera, J. Nayak, S. Banerjee, S. Chakraborty, and S. K. Tripathy, "A review on the treatment of textile industry waste effluents towards the development of efficient mitigation strategy: An integrated system design approach," *Journal of Environmental Chemical Engineering*, vol. 9, no. 4, p. 105277, 2021/08/01/ 2021.
- [112] Y. Shi, Q. Chang, T. Zhang, G. Song, Y. Sun, and G. Ding, "A review on selective dye adsorption by different mechanisms," *Journal of*

- Environmental Chemical Engineering*, vol. 10, no. 6, p. 108639, 2022/12/01/ 2022.
- [113] L. Liu *et al.*, "Rapid decolorization of anthraquinone and triphenylmethane dye using chloroperoxidase: Catalytic mechanism, analysis of products and degradation route," *Chemical Engineering Journal*, vol. 244, pp. 9-18, 2014/05/15/ 2014.
- [114] M. Solís, A. Solís, H. I. Pérez, N. Manjarrez, and M. Flores, "Microbial decolouration of azo dyes: A review," *Process Biochemistry*, vol. 47, no. 12, pp. 1723-1748, 2012/12/01/ 2012.
- [115] A. Ahmad *et al.*, "Recent advances in new generation dye removal technologies: novel search for approaches to reprocess wastewater," *RSC Advances*, 10.1039/C4RA16959J vol. 5, no. 39, pp. 30801-30818, 2015.
- [116] S. A. Ganiyu *et al.*, "Boron-doped activated carbon as efficient and selective adsorbent for ultra-deep desulfurization of 4,6-dimethyldibenzothiophene," *Chemical Engineering Journal*, Article vol. 321, pp. 651-661, 2017.
- [117] G. Crini, "Non-conventional low-cost adsorbents for dye removal: A review," *Bioresource Technology*, Review vol. 97, no. 9, pp. 1061-1085, 2006.
- [118] M. Rafatullah, O. Sulaiman, R. Hashim, and A. Ahmad, "Adsorption of methylene blue on low-cost adsorbents: A review," *Journal of Hazardous Materials*, Review vol. 177, no. 1-3, pp. 70-80, 2010.
- [119] K. Mojsov, D. Andronikov, A. Janevski, A. Kuzelov, and S. Gaber, "The application of enzymes for the removal of dyes from textile effluents," *Advanced technologies*, vol. 5, no. 1, pp. 36-41, 2016.
- [120] S. De Gisi, G. Lofrano, M. Grassi, and M. Notarnicola, "Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review," *Sustainable Materials and Technologies*, Review vol. 9, pp. 10-40, 2016.
- [121] R. Kumar, J. Rashid, and M. A. Barakat, "Synthesis and characterization of a starch- AlOOH-FeS_2 nanocomposite for the adsorption of congo red dye from aqueous solution," *RSC Advances*, 10.1039/C4RA05183A vol. 4, no. 72, pp. 38334-38340, 2014.
- [122] G. Mezohegyi, F. P. van der Zee, J. Font, A. Fortuny, and A. Fabregat, "Towards advanced aqueous dye removal processes: A short review on the versatile role of activated carbon," *Journal of Environmental Management*, Review vol. 102, pp. 148-164, 2012.
- [123] M. Zhao *et al.*, "Algae Biomass Hydrogels for Enhanced Removal of Heavy Metal Ions," *Gels*, vol. 11, no. 3, p. 150, 2025.
- [124] N. Murshid *et al.*, "Metal Oxide Hydrogel Composites for Remediation of Dye-Contaminated Wastewater: Principal Component Analysis," *Gels*, vol. 8, no. 11, p. 702, 2022.
- [125] O. Mouhtady, E. Obeid, M. Abu-samha, K. Younes, and N. Murshid, "Evaluation of the Adsorption Efficiency of Graphene Oxide Hydrogels in Wastewater Dye Removal: Application of Principal Component Analysis," *Gels*, vol. 8, no. 7, p. 447, 2022.
- [126] V. K. Gupta and Suhas, "Application of low-cost adsorbents for dye removal-a review," (in eng), *J Environ Manage*, vol. 90, no. 8, pp. 2313-42, Jun 2009.

- [127] A. A. Adeyemo, I. O. Adeoye, and O. S. Bello, "Adsorption of dyes using different types of clay: a review," *Applied Water Science*, Review vol. 7, no. 2, pp. 543-568, 2017.
- [128] R. Fabryanty *et al.*, "Removal of crystal violet dye by adsorption using bentonite – alginate composite," *Journal of Environmental Chemical Engineering*, Article vol. 5, no. 6, pp. 5677-5687, 2017.
- [129] M. S. Salman *et al.*, "Chitosan-coated cotton fiber composite for efficient toxic dye encapsulation from aqueous media," *Applied Surface Science*, Article vol. 622, 2023, Art no. 157008.
- [130] A. Azari, R. Nabizadeh, S. Nasser, A. H. Mahvi, and A. R. Mesdaghinia, "Comprehensive systematic review and meta-analysis of dyes adsorption by carbon-based adsorbent materials: Classification and analysis of last decade studies," *Chemosphere*, Review vol. 250, 2020, Art no. 126238.
- [131] J. M. Dias, M. C. Alvim-Ferraz, M. F. Almeida, J. Rivera-Utrilla, and M. Sánchez-Polo, "Waste materials for activated carbon preparation and its use in aqueous-phase treatment: a review," (in eng), *J Environ Manage*, vol. 85, no. 4, pp. 833-46, Dec 2007.
- [132] A. E. Burakov *et al.*, "Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review," *Ecotoxicology and Environmental Safety*, Review vol. 148, pp. 702-712, 2018.
- [133] G. Tan, W. Sun, Y. Xu, H. Wang, and N. Xu, "Sorption of mercury (II) and atrazine by biochar, modified biochars and biochar based activated carbon in aqueous solution," *Bioresource Technology*, Article vol. 211, pp. 727-735, 2016.
- [134] X. F. Tan *et al.*, "Biochar as potential sustainable precursors for activated carbon production: Multiple applications in environmental protection and energy storage," *Bioresource Technology*, Review vol. 227, pp. 359-372, 2017.
- [135] G. H. Brundtland, "Our Common Future: Report of the World Commission on Environment and Development.," UN, Geneva, 1987. [Online]. Available: <http://www.un-documents.net/ocf-ov.htm>
- [136] Y. M. Bar-On, R. Phillips, and R. Milo, "The biomass distribution on Earth," (in English), *Proc. Natl. Acad. Sci. U. S. A.*, Article vol. 115, no. 25, pp. 6506-6511, Jun 2018.
- [137] S. García-Condado *et al.*, "Assessing lignocellulosic biomass production from crop residues in the European Union: Modelling, analysis of the current scenario and drivers of interannual variability," *GCB Bioenergy*, vol. 11, no. 6, pp. 809-831, 2019.
- [138] A. Kazmi and P. S. Shuttleworth, *The Economic Utilisation of Food Co-Products*. The Royal Society of Chemistry, 2013.
- [139] T. Huber, J. Müssig, O. Curnow, S. Pang, S. Bickerton, and M. P. Staiger, "A critical review of all-cellulose composites," *Journal of Materials Science*, vol. 47, pp. 1171-1186, 2012.
- [140] A. Payen, "Seances Acad," *Sci., a*, vol. 7, p. 1052, 1838.

-
- [141] S. J. Eichhorn *et al.*, "Review: Current international research into cellulosic fibres and composites," *Journal of Materials Science*, vol. 36, no. 9, pp. 2107-2131, 2001/05/01 2001.
- [142] D. Klemm, B. Heublein, H.-P. Fink, and A. Bohn, "Cellulose: Fascinating Biopolymer and Sustainable Raw Material," *Angewandte Chemie International Edition*, vol. 44, no. 22, pp. 3358-3393, 2005.
- [143] M. K. B. Bakri, M. R. Rahman, and F. I. Chowdhury, "Chapter 1 - Sources of cellulose," in *Fundamentals and Recent Advances in Nanocomposites Based on Polymers and Nanocellulose*, M. R. Rahman Ed.: Elsevier, 2022, pp. 1-18.
- [144] B. Tiryaki, E. Yagmur, A. Banford, and Z. Aktas, "Comparison of activated carbon produced from natural biomass and equivalent chemical compositions," *Journal of analytical and applied pyrolysis*, vol. 105, pp. 276-283, 2014.
- [145] J. Figueiredo, M. Ismael, C. Anjo, and A. Duarte, "Cellulose and derivatives from wood and fibers as renewable sources of raw-materials," *Carbohydrates in sustainable development I*, pp. 117-128, 2010.
- [146] W. M. A. W. Daud and W. S. W. Ali, "Comparison on pore development of activated carbon produced from palm shell and coconut shell," *Bioresource technology*, vol. 93, no. 1, pp. 63-69, 2004.
- [147] G. Lv and S. Wu, "Analytical pyrolysis studies of corn stalk and its three main components by TG-MS and Py-GC/MS," *Journal of Analytical and Applied Pyrolysis*, vol. 97, pp. 11-18, 2012.
- [148] A. Abdolali, W. Guo, H. Ngo, S. Chen, N. Nguyen, and K. Tung, "Typical lignocellulosic wastes and by-products for biosorption process in water and wastewater treatment: a critical review," *Bioresource technology*, vol. 160, pp. 57-66, 2014.
- [149] A. R. Reed and P. T. Williams, "Thermal processing of biomass natural fibre wastes by pyrolysis," *International Journal of Energy Research*, vol. 28, no. 2, pp. 131-145, 2004.
- [150] K. Perepelkin, "Renewable Plant Resources and Processed Products in Chemical Fibre Production," *Fibre Chemistry*, vol. 36, no. 3, 2004.
- [151] F. Esa, S. M. Tasirin, and N. A. Rahman, "Overview of Bacterial Cellulose Production and Application," *Agriculture and Agricultural Science Procedia*, vol. 2, pp. 113-119, 2014/01/01/ 2014.
- [152] V. K. Nathan, "Chapter 8 - Application of extremozymes in the paper and pulp industries," in *Extremozymes and Their Industrial Applications*, N. K. Arora, S. Agnihotri, and J. Mishra Eds.: Academic Press, 2022, pp. 231-247.
- [153] D. Klemm, B. Philipp, T. Heinze, U. Heinze, and W. Wagenknecht, *Comprehensive cellulose chemistry. Volume 1: Fundamentals and analytical methods*. 1998.
- [154] Suhas, V. K. Gupta, P. J. M. Carrott, R. Singh, M. Chaudhary, and S. Kushwaha, "Cellulose: A review as natural, modified and activated carbon adsorbent," *Bioresource Technology*, vol. 216, pp. 1066-1076, 2016/09/01/ 2016.

- [155] O. S. Manoukian *et al.*, "Biomaterials for Tissue Engineering and Regenerative Medicine," in *Encyclopedia of Biomedical Engineering*, R. Narayan Ed. Oxford: Elsevier, 2019, pp. 462-482.
- [156] Z. Wu, Z. Cheng, and W. Ma, "Adsorption of Pb (II) from glucose solution on thiol-functionalized cellulosic biomass," *Bioresource technology*, vol. 104, pp. 807-809, 2012.
- [157] Z. He, H. Song, Y. Cui, W. Zhu, K. Du, and S. Yao, "Porous spherical cellulose carrier modified with polyethyleneimine and its adsorption for Cr (III) and Fe (III) from aqueous solutions," *Chinese Journal of Chemical Engineering*, vol. 22, no. 9, pp. 984-990, 2014.
- [158] D. W. O'Connell, C. Birkinshaw, and T. F. O'Dwyer, "Heavy metal adsorbents prepared from the modification of cellulose: A review," *Bioresource technology*, vol. 99, no. 15, pp. 6709-6724, 2008.
- [159] O. K. Júnior, L. V. A. Gurgel, R. P. de Freitas, and L. F. Gil, "Adsorption of Cu (II), Cd (II), and Pb (II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse chemically modified with EDTA dianhydride (EDTAD)," *Carbohydrate Polymers*, vol. 77, no. 3, pp. 643-650, 2009.
- [160] Y. Zhou, Y. Min, H. Qiao, Q. Huang, E. Wang, and T. Ma, "Improved removal of malachite green from aqueous solution using chemically modified cellulose by anhydride," *International journal of biological macromolecules*, vol. 74, pp. 271-277, 2015.
- [161] L. Wang and J. Li, "Adsorption of CI Reactive Red 228 dye from aqueous solution by modified cellulose from flax shive: Kinetics, equilibrium, and thermodynamics," *Industrial Crops and products*, vol. 42, pp. 153-158, 2013.
- [162] J. Chen, R. Zhu, N. Sheng, C. Zhu, and Z. Rao, "Preparation of cellulose-derived biomass porous carbon and its supercapacitor performance," *Huagong Xuebao/CIESC Journal*, Article vol. 73, no. 9, pp. 4194-4206, 2022.
- [163] C. Long, D. Qi, T. Wei, J. Yan, L. Jiang, and Z. Fan, "Nitrogen-doped carbon networks for high energy density supercapacitors derived from polyaniline coated bacterial cellulose," *Advanced Functional Materials*, Article vol. 24, no. 25, pp. 3953-3961, 2014.
- [164] X. Wang, D. Kong, B. Wang, Y. Song, and L. Zhi, "Activated pyrolysed bacterial cellulose as electrodes for supercapacitors," *Science China Chemistry*, Article vol. 59, no. 6, pp. 713-718, 2016.
- [165] J. Ai *et al.*, "Corncob cellulose-derived hierarchical porous carbon for high performance supercapacitors," *Journal of Power Sources*, Article vol. 484, 2021, Art no. 229221.
- [166] T. Li *et al.*, "Controllable production of liquid and solid biofuels by doping-free, microwave-assisted, pressurised pyrolysis of hemicellulose," *Energy Conversion and Management*, vol. 144, pp. 104-113, 2017/07/15/ 2017.
- [167] Z. Xu *et al.*, "The Role of Hydrothermal Carbonization in Sustainable Sodium-Ion Battery Anodes," *Advanced Energy Materials*, vol. 12, no. 18, p. 2200208, 2022.
- [168] L. L. Baxter *et al.*, "The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences," *Fuel Processing Technology*, vol. 54, no. 1, pp. 47-78, 1998/03/01/ 1998.

- [169] T. Wang, Y. Zhai, Y. Zhu, C. Li, and G. Zeng, "A review of the hydrothermal carbonization of biomass waste for hydrochar formation: Process conditions, fundamentals, and physicochemical properties," *Renewable and Sustainable Energy Reviews*, vol. 90, pp. 223-247, 2018/07/01/ 2018.
- [170] E. Bevan, J. Fu, and Y. Zheng, "Challenges and opportunities of hydrothermal carbonisation in the UK; case study in Chirnside," *RSC Advances*, 10.1039/D0RA04607H vol. 10, no. 52, pp. 31586-31610, 2020.
- [171] H. S. Kambo and A. Dutta, "A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications," *Renewable and Sustainable Energy Reviews*, vol. 45, pp. 359-378, 2015/05/01/ 2015.
- [172] M. Prieto, H. Yue, N. Brun, G. J. Ellis, M. Naffakh, and P. S. Shuttleworth, "Hydrothermal Carbonization of Biomass for Electrochemical Energy Storage: Parameters, Mechanisms, Electrochemical Performance, and the Incorporation of Transition Metal Dichalcogenide Nanoparticles," *Polymers*, vol. 16, no. 18, p. 2633, 2024.
- [173] J. Fang, L. Zhan, Y. S. Ok, and B. Gao, "Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass," *Journal of Industrial and Engineering Chemistry*, vol. 57, pp. 15-21, 2018/01/25/ 2018.
- [174] L. R. Bento, A. J. R. Castro, A. B. Moreira, O. P. Ferreira, M. C. Bisinoti, and C. A. Melo, "Release of nutrients and organic carbon in different soil types from hydrochar obtained using sugarcane bagasse and vinasse," *Geoderma*, vol. 334, pp. 24-32, 2019/01/15/ 2019.
- [175] M. Sevilla, J. A. Maciá-Agulló, and A. B. Fuertes, "Hydrothermal carbonization of biomass as a route for the sequestration of CO₂: Chemical and structural properties of the carbonized products," *Biomass and Bioenergy*, Article vol. 35, no. 7, pp. 3152-3159, 2011.
- [176] Y. Sun, G. Yang, C. Wen, L. Zhang, and Y. S. Wang, "Preparation of carbon sphere from lactose by hydrothermal reaction and its performance in gas separation," *Environmental Progress and Sustainable Energy*, Article vol. 33, no. 2, pp. 581-587, 2014.
- [177] S. Román, J. M. Valente Nabais, B. Ledesma, J. F. González, C. Laginhas, and M. M. Titirici, "Production of low-cost adsorbents with tunable surface chemistry by conjunction of hydrothermal carbonization and activation processes," *Microporous and Mesoporous Materials*, Article vol. 165, pp. 127-133, 2013.
- [178] T. Tan, L. Yan, Y. Lian, and X. Qi, "Adsorption of reactive brilliant red K-2BP on amino-functionalized carbon materials prepared from hydrothermal carbonization of glucose," *Chinese Journal of Environmental Engineering*, Article vol. 8, no. 10, pp. 4122-4128, 2014.
- [179] K. Mochidzuki, N. Sato, and A. Sakoda, "Production and characterization of carbonaceous adsorbents from biomass wastes by aqueous phase carbonization," *Adsorption*, Conference Paper vol. 11, no. 1 SUPPL., pp. 669-673, 2005.
- [180] T. M. A. Babeker and Q. Chen, "Heavy Metal Removal from Wastewater by Adsorption with Hydrochar Derived from Biomass: Current Applications

- and Research Trends," *Current Pollution Reports*, vol. 7, no. 1, pp. 54-71, 2021/03/01 2021.
- [181] A. Loczechin *et al.*, "Functional Carbon Quantum Dots as Medical Countermeasures to Human Coronavirus," *ACS Applied Materials & Interfaces*, vol. 11, no. 46, pp. 42964-42974, 2019/11/20 2019.
- [182] S. Kang, X. Li, J. Fan, and J. Chang, "Characterization of Hydrochars Produced by Hydrothermal Carbonization of Lignin, Cellulose, d-Xylose, and Wood Meal," *Industrial & Engineering Chemistry Research*, vol. 51, no. 26, pp. 9023-9031, 2012/07/04 2012.
- [183] D. Kim, S. Park, and K. Y. Park, "Upgrading the fuel properties of sludge and low rank coal mixed fuel through hydrothermal carbonization," *Energy*, Article vol. 141, pp. 598-602, 2017.
- [184] D. Kim, K. Lee, and K. Y. Park, "Hydrothermal carbonization of anaerobically digested sludge for solid fuel production and energy recovery," *Fuel*, Article vol. 130, pp. 120-125, 2014.
- [185] D. Kim, K. Lee, and K. Y. Park, "Upgrading the characteristics of biochar from cellulose, lignin, and xylan for solid biofuel production from biomass by hydrothermal carbonization," *Journal of Industrial and Engineering Chemistry*, vol. 42, pp. 95-100, 2016/10/25/ 2016.
- [186] F. Mbarki *et al.*, "Hydrothermal pre-treatment, an efficient tool to improve activated carbon performances," *Industrial Crops and Products*, vol. 140, p. 111717, 2019/11/15/ 2019.
- [187] M. Sevilla and A. B. Fuertes, "Sustainable porous carbons with a superior performance for CO₂ capture," *Energy & Environmental Science*, 10.1039/C0EE00784F vol. 4, no. 5, pp. 1765-1771, 2011.
- [188] Y. Li *et al.*, "Microwave assisted hydrothermal preparation of rice straw hydrochars for adsorption of organics and heavy metals," *Bioresource Technology*, vol. 273, pp. 136-143, 2019/02/01/ 2019.
- [189] F. Bergius, *Die Anwendung hoher drucke bei chemischen Vorgängen und eine nechbildung des Entstehungsprozesses der Steinkohle*. W. Knapp, 1913.
- [190] E. Berl and A. Schmidt, "Über die Entstehung der Kohlen. II. Die Inkohlung von Cellulose und Lignin in neutralem Medium," *Justus Liebigs Annalen der Chemie*, vol. 493, no. 1, pp. 97-123, 1932.
- [191] A. Kruse and N. Dahmen, "Water – A magic solvent for biomass conversion," *The Journal of Supercritical Fluids*, vol. 96, pp. 36-45, 2015/01/01/ 2015.
- [192] J. Zhang and J. Chen, "Selective Transfer Hydrogenation of Biomass-Based Furfural and 5-Hydroxymethylfurfural over Hydrotalcite-Derived Copper Catalysts Using Methanol as a Hydrogen Donor," *ACS Sustainable Chemistry & Engineering*, vol. 5, no. 7, pp. 5982-5993, 2017/07/03 2017.
- [193] X. Cao *et al.*, "Hydrothermal conversion of xylose, glucose, and cellulose under the catalysis of transition metal sulfates," *Carbohydrate Polymers*, vol. 118, pp. 44-51, 2015/03/15/ 2015.
- [194] T. M. Aida, N. Shiraishi, M. Kubo, M. Watanabe, and R. L. Smith, "Reaction kinetics of d-xylose in sub- and supercritical water," *The Journal of Supercritical Fluids*, vol. 55, no. 1, pp. 208-216, 2010/11/01/ 2010.

- [195] D. Jung, P. Körner, and A. Kruse, "Kinetic study on the impact of acidity and acid concentration on the formation of 5-hydroxymethylfurfural (HMF), humins, and levulinic acid in the hydrothermal conversion of fructose," *Biomass Conversion and Biorefinery*, vol. 11, 08/01 2021.
- [196] M. M. Titirici, *Hydrothermal Carbonisation: a Sustainable Alternative to Versatile Carbon Materials*. 2012.
- [197] G. Yang, E. A. Pidko, and E. J. M. Hensen, "Mechanism of Brønsted acid-catalyzed conversion of carbohydrates," *Journal of Catalysis*, vol. 295, pp. 122-132, 2012/11/01/ 2012.
- [198] J. Horvat, B. Klaić, B. Metelko, and V. Šunjić, "Mechanism of levulinic acid formation," *Tetrahedron Letters*, vol. 26, no. 17, pp. 2111-2114, 1985/01/01/ 1985.
- [199] I. V. Sumerskii, S. M. Krutov, and M. Y. Zarubin, "Humin-like substances formed under the conditions of industrial hydrolysis of wood," *Russian Journal of Applied Chemistry*, vol. 83, no. 2, pp. 320-327, 2010/02/01 2010.
- [200] A. Funke and F. Ziegler, "Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering," vol. 4, no. 2, pp. 160-177, 2010.
- [201] D. Knežević, W. van Swaaij, and S. Kersten, "Hydrothermal Conversion Of Biomass. II. Conversion Of Wood, Pyrolysis Oil, And Glucose In Hot Compressed Water," *Industrial & Engineering Chemistry Research*, vol. 49, no. 1, pp. 104-112, 2010/01/06 2010.
- [202] J. Lee, K. Lee, D. Sohn, Y. M. Kim, and K. Y. Park, "Hydrothermal carbonization of lipid extracted algae for hydrochar production and feasibility of using hydrochar as a solid fuel," *Energy*, vol. 153, pp. 913-920, 2018/06/15/ 2018.
- [203] W. Yang, H. Wang, M. Zhang, J. Zhu, J. Zhou, and S. Wu, "Fuel properties and combustion kinetics of hydrochar prepared by hydrothermal carbonization of bamboo," *Bioresource Technology*, vol. 205, pp. 199-204, 2016/04/01/ 2016.
- [204] W. Yang, T. Shimanouchi, and Y. Kimura, "Characterization of the Residue and Liquid Products Produced from Husks of Nuts from *Carya cathayensis* Sarg by Hydrothermal Carbonization," *ACS Sustainable Chemistry & Engineering*, vol. 3, no. 4, pp. 591-598, 2015/04/06 2015.
- [205] J. Cai, B. Li, C. Chen, J. Wang, M. Zhao, and K. Zhang, "Hydrothermal carbonization of tobacco stalk for fuel application," *Bioresource Technology*, vol. 220, pp. 305-311, 2016/11/01/ 2016.
- [206] W. Yang *et al.*, "Elevating the fuel properties of *Humulus lupulus*, *Plumeria alba* and *Calophyllum inophyllum* L. through wet torrefaction," *Fuel*, vol. 146, pp. 88-94, 2015/04/15/ 2015.
- [207] M. Sevilla and A. B. Fuertes, "The production of carbon materials by hydrothermal carbonization of cellulose," *Carbon*, vol. 47, p. 2281, 09/01 2009.
- [208] Y. Gao, X.-H. Wang, H.-P. Yang, and H.-P. Chen, "Characterization of products from hydrothermal treatments of cellulose," *Energy*, vol. 42, no. 1, pp. 457-465, 2012/06/01/ 2012.

- [209] W. Yang, I. Shimizu, T. Ono, and Y. Kimura, "Preparation of Biodegradable Foam from Walnut Shells Treated by Subcritical Water," *Journal of Chemical Technology and Biotechnology*, vol. 90, 01/01 2015.
- [210] K. Krysanova, A. Krylova, V. Zaichenko, V. Lavrenov, and V. Khaskhachikh, "Influence of the parameters of the hydrothermal carbonization of the biomass on the biocoal obtained from peat," *E3S Web Conf.*, vol. 114, p. 07003, 2019.
- [211] H. Kim, S. Han, E. Song, and S. Park, "Estimation of the characteristics with hydrothermal carbonisation temperature on poultry slaughterhouse wastes," *Waste Management & Research*, vol. 36, p. 0734242X1877208, 05/18 2018.
- [212] K. Y. Park, K. Lee, and D. Kim, "Characterized hydrochar of algal biomass for producing solid fuel through hydrothermal carbonization," *Bioresource Technology*, vol. 258, pp. 119-124, 2018/06/01/ 2018.
- [213] C. Falco, N. Baccile, and M.-M. Titirici, "Morphological and structural differences between glucose, cellulose and lignocellulosic biomass derived hydrothermal carbons," *Green Chemistry*, 10.1039/C1GC15742F vol. 13, no. 11, pp. 3273-3281, 2011.
- [214] Y. Gao *et al.*, "Effect of residence time on chemical and structural properties of hydrochar obtained by hydrothermal carbonization of water hyacinth," *Energy*, vol. 58, pp. 376-383, 09/01 2013.
- [215] L. Zhang, S. Liu, B. Wang, Q. Wang, G. Yang, and J. Chen, "Effect of Residence Time on Hydrothermal Carbonization of Corn Cob Residual," *BioResources*, vol. 10, 05/13 2015.
- [216] Z. Al-Kaabi, R. Pradhan, N. Thevathasan, A. Gordon, Y. W. Chiang, and A. Dutta, "Bio-carbon production by oxidation and hydrothermal carbonization of paper recycling black liquor," *Journal of Cleaner Production*, vol. 213, pp. 332-341, 2019/03/10/ 2019.
- [217] S. Nizamuddin *et al.*, "An overview of effect of process parameters on hydrothermal carbonization of biomass," *Renewable and Sustainable Energy Reviews*, vol. 73, pp. 1289-1299, 2017/06/01/ 2017.
- [218] M. T. Reza *et al.*, "Review Article: Hydrothermal Carbonization of Biomass for Energy and Crop Production," *Applied Bioenergy*, vol. 1, 02/01 2014.
- [219] M. Siskin and A. R. Katritzky, "Reactivity of Organic Compounds in Superheated Water: General Background," *Chemical Reviews*, vol. 101, no. 4, pp. 825-836, 2001/04/01 2001.
- [220] M. T. Reza, E. Rottler, L. Herklotz, and B. Wirth, "Hydrothermal carbonization (HTC) of wheat straw: Influence of feedwater pH prepared by acetic acid and potassium hydroxide," *Bioresource Technology*, vol. 182, pp. 336-344, 2015/04/01/ 2015.
- [221] X. Liu *et al.*, "Hydrothermal carbonization of sewage sludge: Effect of feed-water pH on hydrochar's physicochemical properties, organic component and thermal behavior," *Journal of Hazardous Materials*, vol. 388, p. 122084, 2020/04/15/ 2020.
- [222] T. Wang *et al.*, "Feedwater pH affects phosphorus transformation during hydrothermal carbonization of sewage sludge," *Bioresource Technology*, vol. 245, pp. 182-187, 2017/12/01/ 2017.

-
- [223] T. Wang *et al.*, "Acetic Acid and Sodium Hydroxide-Aided Hydrothermal Carbonization of Woody Biomass for Enhanced Pelletization and Fuel Properties," *Energy & Fuels*, vol. 31, no. 11, pp. 12200-12208, 2017/11/16 2017.
- [224] X. Liang and J. Yang, "Synthesis of a Novel Carbon Based Strong Acid Catalyst Through Hydrothermal Carbonization," *Catalysis Letters*, vol. 132, no. 3, p. 460, 2009/07/28 2009.
- [225] O. S. Djandja *et al.*, "Catalytic hydrothermal carbonization of wet organic solid waste: A review," *Science of The Total Environment*, vol. 873, p. 162119, 2023/05/15/ 2023.
- [226] B. Ledesma Cano, M. Alonso Sánchez, J. M. Díaz Rasero, S. Román Suero, and S. Nogales Delgado, "Basic Principles of HTC," in *Introduction to Hydrocarbonization: Principles and Applications*, B. Ledesma Cano, M. Alonso Sánchez, J. M. Díaz Rasero, S. Román Suero, and S. Nogales Delgado Eds. Cham: Springer Nature Switzerland, 2024, pp. 15-27.
- [227] S. Karagöz, T. Bhaskar, A. Muto, and Y. Sakata, "Catalytic hydrothermal treatment of pine wood biomass: effect of RbOH and CsOH on product distribution," vol. 80, no. 10, pp. 1097-1102, 2005.
- [228] W. A. Rasaq, C. O. R. Okpala, C. A. Igwegbe, and A. Białowiec, "Catalyst-Enhancing Hydrothermal Carbonization of Biomass for Hydrochar and Liquid Fuel Production-A Review," (in eng), *Materials (Basel)*, vol. 17, no. 11, May 27 2024.
- [229] L. Moreno-Garcia, Y. Gariépy, S. Barnabé, and G. S. V. Raghavan, "Effect of environmental factors on the biomass and lipid production of microalgae grown in wastewaters," *Algal Research*, vol. 41, p. 101521, 2019/08/01/ 2019.
- [230] T. McClure, J.-C. Cocuron, V. Osmark, L. K. McHale, and A. P. Alonso, "Impact of Environment on the Biomass Composition of Soybean (*Glycine max*) seeds," *Journal of Agricultural and Food Chemistry*, vol. 65, no. 32, pp. 6753-6761, 2017/08/16 2017.
- [231] C. Zhong and X. Wei, "A comparative experimental study on the liquefaction of wood," *Energy*, vol. 29, no. 11, pp. 1731-1741, 2004/09/01/ 2004.
- [232] M. H. Thomsen, A. Thygesen, and A. B. Thomsen, "Hydrothermal treatment of wheat straw at pilot plant scale using a three-step reactor system aiming at high hemicellulose recovery, high cellulose digestibility and low lignin hydrolysis," *Bioresource Technology*, vol. 99, no. 10, pp. 4221-4228, 2008/07/01/ 2008.
- [233] C. Sánchez, "Lignocellulosic residues: Biodegradation and bioconversion by fungi," *Biotechnology Advances*, vol. 27, no. 2, pp. 185-194, 2009/03/01/ 2009.
- [234] P. Kumar, D. M. Barrett, M. J. Delwiche, and P. Stroeve, "Methods for Pretreatment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofuel Production," *Industrial & Engineering Chemistry Research*, vol. 48, no. 8, pp. 3713-3729, 2009/04/15 2009.
- [235] M. Tayyab, "Bioethanol production from lignocellulosic biomass by environment-friendly pretreatment methods: A review," *Applied Ecology and Environmental Research*, vol. 16, pp. 225-249, 2018.

- [236] X. Cui, J. J. L. Lee, and W. N. Chen, "Eco-friendly and biodegradable cellulose hydrogels produced from low cost okara: towards non-toxic flexible electronics," *Scientific Reports*, vol. 9, no. 1, p. 18166, 2019/12/03 2019.
- [237] M. Liu, S. Tong, Z. Tong, Y. Guan, and Y. Sun, "A strong, biodegradable and transparent cellulose-based bioplastic stemmed from waste paper," *Journal of Applied Polymer Science*, vol. 140, no. 13, p. e53671, 2023.
- [238] A. Mikhailidi, I. Volf, D. Belosinschi, B.-M. Tofanica, and E. Ungureanu, "Cellulose-Based Metallogels—Part 1: Raw Materials and Preparation," *Gels*, vol. 9, no. 5, p. 390, 2023.
- [239] H. Haykiri-Acma, S. Yaman, and S. Kucukbayrak, "Effect of heating rate on the pyrolysis yields of rapeseed," *Renewable Energy*, vol. 31, no. 6, pp. 803-810, 2006/05/01/ 2006.
- [240] B. Zhang, M. von Keitz, and K. Valentas, "Thermal Effects on Hydrothermal Biomass Liquefaction," *Applied Biochemistry and Biotechnology*, vol. 147, no. 1, pp. 143-150, 2008/03/01 2008.
- [241] A. V. Bridgwater, D. Meier, and D. Radlein, "An overview of fast pyrolysis of biomass," *Organic Geochemistry*, vol. 30, no. 12, pp. 1479-1493, 1999/12/01/ 1999.
- [242] J. Akhtar and N. A. S. Amin, "A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass," *Renewable and Sustainable Energy Reviews*, vol. 15, no. 3, pp. 1615-1624, 2011/04/01/ 2011.
- [243] S. Ahmed, A. Ahmed, D. B. Basha, S. Hussain, I. Uddin, and M. A. Gondal, "Critical review on recent developments in conducting polymer nanocomposites for supercapacitors," *Synthetic Metals*, vol. 295, p. 117326, 2023/05/01/ 2023.
- [244] C. Zhan, G. Yu, Y. Lu, L. Wang, E. Wujcik, and S. Wei, "Conductive polymer nanocomposites: a critical review of modern advanced devices," *Journal of Materials Chemistry C*, 10.1039/C6TC04269D vol. 5, no. 7, pp. 1569-1585, 2017.
- [245] E. Colusso and A. Martucci, "An overview of biopolymer-based nanocomposites for optics and electronics," *Journal of Materials Chemistry C*, 10.1039/D1TC00607J vol. 9, no. 17, pp. 5578-5593, 2021.
- [246] H. Kolya and C.-W. Kang, "Next-Generation Water Treatment: Exploring the Potential of Biopolymer-Based Nanocomposites in Adsorption and Membrane Filtration," *Polymers*, vol. 15, no. 16, p. 3421, 2023.
- [247] O. Agboola *et al.*, "A Review on Polymer Nanocomposites and Their Effective Applications in Membranes and Adsorbents for Water Treatment and Gas Separation," *Membranes*, vol. 11, no. 2, p. 139, 2021.
- [248] G. L. Wilkes, B. Orler, and H.-H. Huang, "Ceramers: Hybrid materials incorporating polymeric/oligomeric species into inorganic glasses utilizing a sol-gel approach," in *American Chemical Society, Polymer Preprints, Division of Polymer Chemistry*, 1985, vol. 26, 2 ed., pp. 300-302.
- [249] J. Wen and G. L. Wilkes, "Organic/inorganic hybrid network materials by the sol-gel approach," *Chemistry of Materials*, Review vol. 8, no. 8, pp. 1667-1681, 1996.

- [250] V. Siracusa, P. Rocculi, S. Romani, and M. Dalla Rosa, "Biodegradable polymers for food packaging: a review," *Trends in food science & technology*, vol. 19, no. 12, pp. 634-643, 2008.
- [251] A. Mohanty, M. a. Misra, and G. Hinrichsen, "Biofibres, biodegradable polymers and biocomposites: An overview," *Macromolecular materials and Engineering*, vol. 276, no. 1, pp. 1-24, 2000.
- [252] P. Bordes, E. Pollet, and L. Avérous, "Nano-biocomposites: biodegradable polyester/nanoclay systems," *Progress in Polymer Science*, vol. 34, no. 2, pp. 125-155, 2009.
- [253] M. J. Getahun, B. B. Kassie, and T. S. Alemu, "Recent advances in biopolymer synthesis, properties, & commercial applications: a review," *Process Biochemistry*, vol. 145, pp. 261-287, 2024/10/01/ 2024.
- [254] "European Bioplastics: Bioplastics market development update 2024." <https://www.european-bioplastics.org/market/> (accessed 2025).
- [255] M. Singhvi, D. Joshi, M. Adsul, A. Varma, and D. Gokhale, "D-(-)-Lactic acid production from cellobiose and cellulose by *Lactobacillus lactis* mutant RM2-2 4," *Green Chemistry*, vol. 12, no. 6, pp. 1106-1109, 2010.
- [256] M. G. Adsul, A. J. Varma, and D. V. Gokhale, "Lactic acid production from waste sugarcane bagasse derived cellulose," *Green Chemistry*, vol. 9, no. 1, pp. 58-62, 2007.
- [257] Z. Liu, Y. Wang, B. Wu, C. Cui, Y. Guo, and C. Yan, "A critical review of fused deposition modeling 3D printing technology in manufacturing polylactic acid parts," *The International Journal of Advanced Manufacturing Technology*, vol. 102, pp. 2877-2889, 2019.
- [258] R. E. Conn *et al.*, "Safety assessment of polylactide (PLA) for use as a food-contact polymer," *Food and Chemical Toxicology*, vol. 33, no. 4, pp. 273-283, 1995/04/01/ 1995.
- [259] H. Tsuji, *Poly (lactic acid): synthesis, structures, properties, processing, and applications*. Wiley, 2011.
- [260] R. Mehta, V. Kumar, H. Bhunia, and S. N. Upadhyay, "Synthesis of poly(lactic acid): A review," *Journal of Macromolecular Science - Polymer Reviews*, Review vol. 45, no. 4, pp. 325-349, 2005.
- [261] T. A. Swetha *et al.*, "A comprehensive review on polylactic acid (PLA) – Synthesis, processing and application in food packaging," *International Journal of Biological Macromolecules*, vol. 234, p. 123715, 2023/04/15/ 2023.
- [262] B. Gupta, N. Revagade, and J. Hilborn, "Poly(lactic acid) fiber: An overview," *Progress in Polymer Science (Oxford)*, Review vol. 32, no. 4, pp. 455-482, 2007.
- [263] S. Ochi, "Mechanical properties of kenaf fibers and kenaf/PLA composites," *Mechanics of materials*, vol. 40, no. 4-5, pp. 446-452, 2008.
- [264] T. Gurunathan, S. Mohanty, and S. K. Nayak, "A review of the recent developments in biocomposites based on natural fibres and their application perspectives," *Composites Part A: Applied Science and Manufacturing*, vol. 77, pp. 1-25, 2015.
- [265] G. Li *et al.*, "Synthesis and Biological Application of Polylactic Acid," *Molecules*, vol. 25, no. 21, p. 5023, 2020.

- [266] M. S. Singhvi, S. S. Zinjarde, and D. V. Gokhale, "Polylactic acid: synthesis and biomedical applications," *Journal of Applied Microbiology*, vol. 127, no. 6, pp. 1612-1626, 2019.
- [267] R. Schneider, M. H. M. Facure, A. D. Alvarenga, P. A. M. Chagas, D. M. dos Santos, and D. S. Correa, "Dye Adsorption Capacity of MoS₂ Nanoflakes Immobilized on Poly(lactic acid) Fibrous Membranes," *ACS Applied Nano Materials*, vol. 4, no. 5, pp. 4881-4894, 2021/05/28 2021.
- [268] N. Mohammad and Y. Atassi, "TiO₂/PLLA Electrospun Nanofibers Membranes for Efficient Removal of Methylene Blue Using Sunlight," *Journal of Polymers and the Environment*, vol. 29, no. 2, pp. 509-519, 2021/02/01 2021.
- [269] M. Sattar, F. Hayeeye, W. Chinpa, and O. Sirichote, "Preparation and characterization of poly (lactic acid)/activated carbon composite bead via phase inversion method and its use as adsorbent for Rhodamine B in aqueous solution," *Journal of Environmental Chemical Engineering*, vol. 5, no. 4, pp. 3780-3791, 2017/08/01/ 2017.
- [270] Q. Qin *et al.*, "Degradation and adsorption behavior of biodegradable plastic PLA under conventional weathering conditions," *Science of The Total Environment*, vol. 842, p. 156775, 2022/10/10/ 2022.
- [271] W.-H. Lin, H.-Y. Wang, J. Kuo, and S.-L. Lo, "Adsorption and desorption characteristics of heavy metals onto conventional and biodegradable plastics," *Chemosphere*, vol. 333, p. 138920, 2023/08/01/ 2023.
- [272] P.-W. Chen, M.-N. Hsiao, L.-W. Xiao, and Z.-S. Liu, "Adsorption behavior of heavy metals onto microplastics derived from conventional and biodegradable commercial plastic products," *Science of The Total Environment*, vol. 951, p. 175537, 2024/11/15/ 2024.
- [273] S.-z. Hu *et al.*, "Biomimetic Polylactic Acid Electrospun Fibers Grafted with Polyethyleneimine for Highly Efficient Methyl Orange and Cr(VI) Removal," *Langmuir*, vol. 39, no. 10, pp. 3770-3783, 2023/03/14 2023.
- [274] W. Liu, T. Pan, H. Liu, M. Jiang, and T. Zhang, "Adsorption behavior of imidacloprid pesticide on polar microplastics under environmental conditions: critical role of photo-aging," *Frontiers of Environmental Science & Engineering*, vol. 17, no. 4, p. 41, 2022/10/27 2022.
- [275] Y. Jiao *et al.*, "Protein adsorption on the poly(L-lactic acid) surface modified by chitosan and its derivatives," *Chinese Science Bulletin*, vol. 54, no. 18, pp. 3167-3173, 2009/09/01 2009.
- [276] K. Lyu *et al.*, "Tracking of Protein Adsorption on Poly(l-lactic acid) Film Surfaces: The Role of Molar Mass," *Langmuir*, vol. 39, no. 38, pp. 13534-13545, 2023/09/26 2023.
- [277] D. Bui-Vinh, Y. Kwon, D.-W. Jeong, and H. Lee, "Facile fabrication of hierarchical porous electrospun poly (L-lactic acid) fiber membrane via swelling-crystallization for oil adsorption," *Journal of Industrial and Engineering Chemistry*, 2025/04/10/ 2025.
- [278] V. S. Reddy *et al.*, "A Review on Electrospun Nanofibers Based Advanced Applications: From Health Care to Energy Devices," (in eng), *Polymers (Basel)*, vol. 13, no. 21, Oct 29 2021.

-
- [279] B. Zaarour and M. F. Alhinnawi, "A comprehensive review on branched nanofibers: Preparations, strategies, and applications," *Journal of Industrial Textiles*, vol. 51, no. 1_suppl, pp. 1S-35S, 2022.
- [280] A. Nadaf *et al.*, "Recent update on electrospinning and electrospun nanofibers: current trends and their applications," *RSC Advances*, 10.1039/D2RA02864F vol. 12, no. 37, pp. 23808-23828, 2022.
- [281] B. A. Venmathi Maran, S. Jeyachandran, and M. Kimura, "A Review on the Electrospinning of Polymer Nanofibers and Its Biomedical Applications," *Journal of Composites Science*, vol. 8, no. 1, p. 32, 2024.
- [282] A. Zahir, U. Mahmood, A. Nazir, T. Hussain, and S. Abid, "2 - Biomaterials for medical and healthcare products," in *Medical Textiles from Natural Resources*, M. I. H. Mondal Ed.: Woodhead Publishing, 2022, pp. 43-86.
- [283] K. D. Patel, A. R. Padalhin, R. A. G. Franco, F. Verisqa, H. W. Kim, and L. Nguyen, "Basic concepts and fundamental insights into electrospinning," in *Biomedical Applications of Electrospinning and Electrospraying*, 2021, pp. 3-43.
- [284] J. Gostick, M. Kok, and R. Jervis, "A glimpse of porous media: Electrospun fibrous mats," in *Album of Porous Media: Structure and Dynamics*, 2023, p. 11.
- [285] M. Oroujzadeh, E. Mosaffa, and S. Mehdipour-Ataei, "Recent developments on preparation of aligned electrospun fibers: Prospects for tissue engineering and tissue replacement," *Surfaces and Interfaces*, vol. 49, p. 104386, 2024/06/01/ 2024.
- [286] L. Liu, W. Xu, Y. Ding, S. Agarwal, A. Greiner, and G. Duan, "A review of smart electrospun fibers toward textiles," *Composites Communications*, vol. 22, p. 100506, 2020/12/01/ 2020.
- [287] M. Z. A. Zulkifli, D. Nordin, N. Shaari, and S. K. Kamarudin, "Overview of Electrospinning for Tissue Engineering Applications," *Polymers*, vol. 15, no. 11, p. 2418, 2023.
- [288] A. Luraghi, F. Peri, and L. Moroni, "Electrospinning for drug delivery applications: A review," *Journal of Controlled Release*, vol. 334, pp. 463-484, 2021/06/10/ 2021.
- [289] A. Cimini, E. Imperi, A. Picano, and M. Rossi, "Electrospun nanofibers for medical face mask with protection capabilities against viruses: State of the art and perspective for industrial scale-up," (in eng), *Appl Mater Today*, vol. 32, p. 101833, Jun 2023.
- [290] M. Tebyetekerwa, Z. Xu, S. Yang, and S. Ramakrishna, "Electrospun Nanofibers-Based Face Masks," *Advanced Fiber Materials*, vol. 2, no. 3, pp. 161-166, 2020/06/01 2020.
- [291] C. Z. Mosher *et al.*, "Green electrospinning for biomaterials and biofabrication," (in eng), *Biofabrication*, vol. 13, no. 3, Jun 28 2021.
- [292] S. Sato, D. Gondo, T. Wada, S. Kanehashi, and K. Nagai, "Effects of various liquid organic solvents on solvent-induced crystallization of amorphous poly(lactic acid) film," *Journal of Applied Polymer Science*, vol. 129, no. 3, pp. 1607-1617, 2013.

- [293] H. J. Salavagione *et al.*, "Identification of high performance solvents for the sustainable processing of graphene," *Green Chemistry*, 10.1039/C7GC00112F vol. 19, no. 11, pp. 2550-2560, 2017.
- [294] A. Jash, G. Paliyath, and L.-T. Lim, "Activated release of bioactive aldehydes from their precursors embedded in electrospun poly(lactic acid) nonwovens," *RSC Advances*, 10.1039/C8RA03137A vol. 8, no. 36, pp. 19930-19938, 2018.
- [295] N. Amiri, Z. Rozbeh, T. Afrough, S. A. Sajadi Tabassi, A. Moradi, and J. Movaffagh, "Optimization of Chitosan-Gelatin Nanofibers Production: Investigating the Effect of Solution Properties and Working Parameters on Fibers Diameter," *BioNanoScience*, vol. 8, no. 3, pp. 778-789, 2018/09/01 2018.
- [296] A. Refate *et al.*, "Influence of electrospinning parameters on biopolymers nanofibers, with emphasis on cellulose & chitosan," (in eng), *Heliyon*, vol. 9, no. 6, p. e17051, Jun 2023.
- [297] S. L. Shenoy, W. D. Bates, H. L. Frisch, and G. E. Wnek, "Role of chain entanglements on fiber formation during electrospinning of polymer solutions: Good solvent, non-specific polymer-polymer interaction limit," *Polymer*, Article vol. 46, no. 10, pp. 3372-3384, 2005.
- [298] R. Abdulhussain, A. Adebisi, B. R. Conway, and K. Asare-Addo, "Electrospun nanofibers: Exploring process parameters, polymer selection, and recent applications in pharmaceuticals and drug delivery," *Journal of Drug Delivery Science and Technology*, vol. 90, p. 105156, 2023/12/01/ 2023.
- [299] J. M. Deitzel, J. Kleinmeyer, D. Harris, and N. C. Beck Tan, "The effect of processing variables on the morphology of electrospun nanofibers and textiles," *Polymer*, Article vol. 42, no. 1, pp. 261-272, 2001.
- [300] H. Shao, J. Fang, H. Wang, and T. Lin, "Effect of electrospinning parameters and polymer concentrations on mechanical-to-electrical energy conversion of randomly-oriented electrospun poly(vinylidene fluoride) nanofiber mats," *RSC Advances*, 10.1039/C4RA16360E vol. 5, no. 19, pp. 14345-14350, 2015.
- [301] A. Haider, S. Haider, and I.-K. Kang, "A comprehensive review summarizing the effect of electrospinning parameters and potential applications of nanofibers in biomedical and biotechnology," *Arabian Journal of Chemistry*, vol. 11, no. 8, pp. 1165-1188, 2018/12/01/ 2018.
- [302] W. Han, L. Minhao, C. Xin, Z. Junwei, C. Xindu, and Z. Ziming, "Study of deposition characteristics of multi-nozzle near-field electrospinning in electric field crossover interference conditions," *Aip Advances*, vol. 5, no. 4, 2015.
- [303] M. Litvinov and A. Podshivalov, "Effect of the composition and electrospinning time of gelatin solutions in acetic acid on their rheological properties and nanofiber morphology," *Journal of Polymer Research*, vol. 31, no. 4, p. 107, 2024/03/20 2024.
- [304] M. Gorji, A. A. Jeddi, and A. A. G. Agaji, *The effect of electrospinning duration on some physical and mechanical properties of Polyurethane Electrospun nano web*. 2011.

- [305] A. M. Garcia *et al.*, "Monolithic mesoporous graphitic composites as super capacitors: from Starbons to Starenes[registered sign]," *Journal of Materials Chemistry A*, 10.1039/C7TA09338A vol. 6, no. 3, pp. 1119-1127, 2018.
- [306] Q. Ke and J. Wang, "Graphene-based materials for supercapacitor electrodes – A review," *Journal of Materiomics*, vol. 2, no. 1, pp. 37-54, 2016/03/01/ 2016.
- [307] M. Prieto Lobato, "Diseño de materiales de carbono bioderivados. Aplicación como electrodos en condensadores electroquímicos," Energy Engineering, Universidad Politécnica de Madrid, 2019.
- [308] L. F. Aval, M. Ghoranneviss, and G. B. Pour, "High-performance supercapacitors based on the carbon nanotubes, graphene and graphite nanoparticles electrodes," *Heliyon*, vol. 4, no. 11, p. e00862, 2018/11/01/ 2018.
- [309] P. Butnoi, A. Pangon, R. Berger, H.-J. Butt, and V. Intasanta, "Electrospun nanocomposite fibers from lignin and iron oxide as supercapacitor material," *Journal of Materials Research and Technology*, vol. 12, pp. 2153-2167, 2021/05/01/ 2021.
- [310] G. Yang and S.-J. Park, "MnO₂ and biomass-derived 3D porous carbon composites electrodes for high performance supercapacitor applications," *Journal of Alloys and Compounds*, vol. 741, pp. 360-367, 2018/04/15/ 2018.
- [311] B. Lesbayev *et al.*, "Modification of Biomass-Derived Nanoporous Carbon with Nickel Oxide Nanoparticles for Supercapacitor Application," *Journal of Composites Science*, vol. 7, no. 1, p. 20, 2023.
- [312] P. Panith, P. Butnoi, and V. Intasanta, "The hybrid structure of nanoflower-like CoxMnyNizO₄ nanoparticles embedded biomass-lignin carbon nanofibers as free-standing and binder-free electrodes for high performance supercapacitors," *Journal of Alloys and Compounds*, vol. 918, p. 165659, 2022/10/15/ 2022.
- [313] D. Sheberla, J. C. Bachman, J. S. Elias, C. J. Sun, Y. Shao-Horn, and M. Dincă, "Conductive MOF electrodes for stable supercapacitors with high areal capacitance," *Nature Materials*, Article vol. 16, no. 2, pp. 220-224, 2017.
- [314] Y. Chen *et al.*, "MXene-Based Electrodes for Supercapacitor Energy Storage," *Energy & Fuels*, vol. 36, no. 5, pp. 2390-2406, 2022/03/03 2022.
- [315] M. A. Bissett, S. D. Worrall, I. A. Kinloch, and R. A. W. Dryfe, "Comparison of Two-Dimensional Transition Metal Dichalcogenides for Electrochemical Supercapacitors," *Electrochimica Acta*, vol. 201, pp. 30-37, 2016/05/20/ 2016.
- [316] R. G. Dickinson and L. Pauling, "The crystal structure of molybenite," *Journal of the American Chemical Society*, vol. 45, no. 6, pp. 1466-1471, 1923/06/01 1923.
- [317] J. A. Wilson and A. D. Yoffe, "The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties," *Advances in Physics*, vol. 18, no. 73, pp. 193-335, 1969/05/01 1969.
- [318] R. Frindt and A. Yoffe, "Physical properties of layer structures: optical properties and photoconductivity of thin crystals of molybdenum

- disulphide," *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, vol. 273, no. 1352, pp. 69-83, 1963.
- [319] P. Joensen, R. Frindt, and S. R. Morrison, "Single-layer mos₂," *Materials research bulletin*, vol. 21, no. 4, pp. 457-461, 1986.
- [320] M. Naffakh, A. M. Díez-Pascual, C. Marco, G. J. Ellis, and M. A. Gómez-Fatou, "Opportunities and challenges in the use of inorganic fullerene-like nanoparticles to produce advanced polymer nanocomposites," *Progress in Polymer Science*, Review vol. 38, no. 8, pp. 1163-1231, 2013.
- [321] R. Tenne, L. Margulis, M. e. Genut, and G. Hodes, "Polyhedral and cylindrical structures of tungsten disulphide," *Nature*, vol. 360, no. 6403, pp. 444-446, 1992.
- [322] Y. Feldman, E. Wasserman, D. Srolovitz, and R. Tenne, "High-rate, gas-phase growth of MoS₂ nested inorganic fullerenes and nanotubes," *Science*, vol. 267, no. 5195, pp. 222-225, 1995.
- [323] S. Joseph *et al.*, "A review of the synthesis, properties, and applications of 2D transition metal dichalcogenides and their heterostructures," *Materials Chemistry and Physics*, vol. 297, p. 127332, 2023/03/01/ 2023.
- [324] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, and A. Kis, "2D transition metal dichalcogenides," *Nature Reviews Materials*, vol. 2, no. 8, p. 17033, 2017/06/13 2017.
- [325] A. Castellanos-Gomez, "Why all the fuss about 2D semiconductors?," *Nature Photonics*, vol. 10, no. 4, pp. 202-204, 2016/04/01 2016.
- [326] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, "Electronics and optoelectronics of two-dimensional transition metal dichalcogenides," *Nature Nanotechnology*, vol. 7, no. 11, pp. 699-712, 2012/11/01 2012.
- [327] S. Bertolazzi, J. Brivio, and A. Kis, "Stretching and Breaking of Ultrathin MoS₂," *ACS Nano*, vol. 5, no. 12, pp. 9703-9709, 2011/12/27 2011.
- [328] M. Naffakh, M. Fernández, P. S. Shuttleworth, A. M. García, and D. A. Moreno, "Nanocomposite Materials with Poly(l-lactic Acid) and Transition-Metal Dichalcogenide Nanosheets 2D-TMDCs WS₂," *Polymers*, vol. 12, no. 11, p. 2699, 2020.
- [329] M. Naffakh, P. S. Shuttleworth, and G. Ellis, "Bio-based polymer nanocomposites based on nylon 11 and WS₂ inorganic nanotubes," *RSC Advances*, 10.1039/C4RA17210H vol. 5, no. 23, pp. 17879-17887, 2015.
- [330] M. Naffakh, P. Rica, C. Moya-Lopez, J. A. Castro-Osma, C. Alonso-Moreno, and D. A. Moreno, "The effect of WS₂ nanosheets on the non-isothermal cold- and melt-crystallization kinetics of poly(L-lactic acid) nanocomposites," *Polymers*, Article vol. 13, no. 13, 2021, Art no. 2214.
- [331] M. Naffakh, C. Marco, and G. Ellis, "Development of novel melt-processable biopolymer nanocomposites based on poly(l-lactic acid) and WS₂ inorganic nanotubes," *CrystEngComm*, 10.1039/C3CE42593B vol. 16, no. 23, pp. 5062-5072, 2014.
- [332] M. Naffakh, "Biopolymer nanocomposite materials based on poly(L - lactic acid) and inorganic fullerene - like ws₂ nanoparticles," *Polymers*, Article vol. 13, no. 17, 2021, Art no. 2947.

- [333] M. Naffakh and A. M. Díez-Pascual, "WS2 inorganic nanotubes reinforced poly(l-lactic acid)/hydroxyapatite hybrid composite biomaterials," *RSC Advances*, Article vol. 5, no. 80, pp. 65514-65525, 2015.
- [334] M. Naffakh and A. M. Díez-Pascual, "Nanocomposite biomaterials based on poly(ether-ether-ketone) (PEEK) and WS2 inorganic nanotubes," *Journal of Materials Chemistry B*, Article vol. 2, no. 28, pp. 4509-4520, 2014.
- [335] M. Naffakh *et al.*, "Novel poly(3-hydroxybutyrate) nanocomposites containing WS2 inorganic nanotubes with improved thermal, mechanical and tribological properties," *Materials Chemistry and Physics*, Article vol. 147, no. 1-2, pp. 273-284, 2014.
- [336] A. R. Adini, M. Redlich, and R. Tenne, "Medical applications of inorganic fullerene-like nanoparticles," *Journal of Materials Chemistry*, 10.1039/C1JM11799H vol. 21, no. 39, pp. 15121-15131, 2011.
- [337] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, "Single-layer MoS2 transistors," *Nature Nanotechnology*, vol. 6, no. 3, pp. 147-150, 2011/03/01 2011.
- [338] C. Rao, U. Maitra, and U. V. Waghmare, "Extraordinary attributes of 2-dimensional MoS2 nanosheets," *Chemical Physics Letters*, vol. 609, pp. 172-183, 2014.
- [339] G. Zhao *et al.*, "Biocarbon based template synthesis of uniform lamellar MoS2 nanoflowers with excellent energy storage performance in lithium-ion battery and supercapacitors," *Electrochimica Acta*, vol. 331, p. 135262, 2020/01/20/ 2020.
- [340] L. Ma, X. Zhou, L. Xu, X. Xu, L. Zhang, and W. Chen, "Chitosan-assisted fabrication of ultrathin MoS2/graphene heterostructures for Li-ion battery with excellent electrochemical performance," *Electrochimica Acta*, vol. 167, pp. 39-47, 2015/06/10/ 2015.
- [341] H. Simsir *et al.*, "Anode performance of hydrothermally grown carbon nanostructures and their molybdenum chalcogenides for Li-ion batteries," *MRS Communications*, vol. 8, no. 2, pp. 610-616, 2018.
- [342] D. N. Sangeetha and M. Selvakumar, "Active-defective activated carbon/MoS2 composites for supercapacitor and hydrogen evolution reactions," *Applied Surface Science*, vol. 453, pp. 132-140, 2018/09/30/ 2018.
- [343] L.-Q. Fan, G.-J. Liu, C.-Y. Zhang, J.-H. Wu, and Y.-L. Wei, "Facile one-step hydrothermal preparation of molybdenum disulfide/carbon composite for use in supercapacitor," *International Journal of Hydrogen Energy*, vol. 40, no. 32, pp. 10150-10157, 2015/08/24/ 2015.
- [344] F. Wang, J. Ma, K. Zhou, and X. Li, "MoS2/corn-cob-derived activated carbon for supercapacitor application," *Materials Chemistry and Physics*, vol. 244, p. 122215, 2020/04/01/ 2020.
- [345] Q. J. Lin, J. M. Wang, J. H. Chen, Q. Yang, L. J. Fang, and Y. D. Huang, "Collaborative Improvement Electrochemical Properties of Supercapacitor Electrodes by Loading MoS2 Nanosheets on Biomass Hierarchical Porous Carbon," *Journal of The Electrochemical Society*, vol. 169, no. 2, p. 020502, 2022/02/01 2022.
- [346] B. Hu, X. Qin, A. M. Asiri, K. A. Alamry, A. O. Al-Youbi, and X. Sun, "Synthesis of porous tubular C/MoS2 nanocomposites and their application

- as a novel electrode material for supercapacitors with excellent cycling stability," *Electrochimica Acta*, vol. 100, pp. 24-28, 2013/06/30/ 2013.
- [347] Y. Li, C. Li, H. Qi, K. Yu, and C. Liang, "Mesoporous activated carbon from corn stalk core for lithium ion batteries," *Chemical Physics*, vol. 506, pp. 10-16, 2018/04/27/ 2018.
- [348] A. Joseph, M. K. Eapen, M. E. Mampilly, and V. Sajith, "Comparison of Corrosion Resistance Properties of Electrophoretically Deposited MoS₂ and WS₂ Nanosheets Coatings on Mild Steel," *Metallurgical and Materials Transactions A*, vol. 52, no. 9, pp. 3689-3693, 2021/09/01 2021.
- [349] M. S. Corporation. "A Comparison of Tungsten Disulfide and Molybdenum Disulfide." <https://ws2coating.com/a-comparison-of-tungsten-disulfide-and-molybdenum-disulfide/> (accessed 2025).
- [350] Y. Chen and M. Sun, "Two-dimensional WS₂/MoS₂ heterostructures: properties and applications," *Nanoscale*, 10.1039/D1NR00455G vol. 13, no. 11, pp. 5594-5619, 2021.
- [351] S. C. Kerwien, "Toxicity of tungsten, molybdenum and tantalum and the environmental and occupational laws asociated with their manufacture, use and disposal," U.S. Army Armament Research, Development and Engineering Center, 1996.
- [352] A. Falin *et al.*, "Mechanical Properties of Atomically Thin Tungsten Dichalcogenides: WS₂, WSe₂, and WTe₂," *ACS Nano*, vol. 15, no. 2, pp. 2600-2610, 2021/02/23 2021.
- [353] A. S. Sethulekshmi, J. S. Jayan, A. Saritha, and K. Joseph, "Insights into the reinforcibility and multifarious role of WS₂ in polymer matrix," *Journal of Alloys and Compounds*, vol. 876, p. 160107, 2021/09/25/ 2021.
- [354] A. Sebastian, R. Pendurthi, T. H. Choudhury, J. M. Redwing, and S. Das, "Benchmarking monolayer MoS₂ and WS₂ field-effect transistors," *Nature Communications*, vol. 12, no. 1, p. 693, 2021/01/29 2021.
- [355] E. I. Emon *et al.*, "A comprehensive photovoltaic study on tungsten disulfide (WS₂) buffer layer based CdTe solar cell," *Heliyon*, vol. 9, no. 3, p. e14438, 2023/03/01/ 2023.
- [356] R. K. Prasad, K. Ghosh, P. K. Giri, D.-S. Kim, and D. K. Singh, "High-Efficiency Photodetector Based on a CVD-Grown WS₂ Monolayer," *ACS Applied Electronic Materials*, vol. 5, no. 7, pp. 3634-3640, 2023/07/25 2023.
- [357] A. Rezaei, H. Zarenezhad, S. Aber, and R. Teimuri-Mofrad, "Synergistic ORR catalysis: WS₂/CeO₂ composite in microbial fuel cells," *Process Safety and Environmental Protection*, vol. 183, pp. 1002-1012, 2024/03/01/ 2024.
- [358] P. U. Aldana, F. Dassenoy, B. Vacher, T. L. Mogne, B. Thiebaut, and A. Bouffet, "Antispalling Effect of WS₂ Nanoparticles on the Lubrication of Automotive Gearboxes," *Tribology Transactions*, vol. 59, no. 1, pp. 178-188, 2016/01/02 2016.
- [359] V. B. Niste, M. Ratoi, H. Tanaka, F. Xu, Y. Zhu, and J. Sugimura, "Self-lubricating Al-WS₂ composites for efficient and greener tribological parts," *Scientific Reports*, vol. 7, no. 1, p. 14665, 2017/11/07 2017.
- [360] T. L. Brzezinka *et al.*, "DLC and DLC-WS₂ Coatings for Machining of Aluminium Alloys," *Coatings*, vol. 9, no. 3, p. 192, 2019.

-
- [361] T. W. Scharf, "Transition Metal Dichalcogenide-Based (MoS₂, WS₂) Coatings," 2017, pp. 583-596.
 - [362] U. T. Uthappa *et al.*, "Trends and prospects of 2-D tungsten disulphide (WS₂) hybrid nanosystems for environmental and biomedical applications," *Advances in Colloid and Interface Science*, vol. 322, p. 103024, 2023/12/01/ 2023.
 - [363] D. Convertino *et al.*, "Interaction of graphene and WS₂ with neutrophils and mesenchymal stem cells: implications for peripheral nerve regeneration," *Nanoscale*, 10.1039/D3NR04927B vol. 16, no. 4, pp. 1792-1806, 2024.
 - [364] X. Cao, C. Tan, X. Zhang, W. Zhao, and H. Zhang, "Solution-Processed Two-Dimensional Metal Dichalcogenide-Based Nanomaterials for Energy Storage and Conversion," *Advanced Materials*, vol. 28, no. 29, pp. 6167-6196, 2016.
 - [365] B. Wu *et al.*, "WS₂ nanosheets vertically grown on Ti₃C₂ as superior anodes for lithium-ion batteries," *Journal of Colloid and Interface Science*, vol. 657, pp. 124-132, 2024/03/01/ 2024.
 - [366] V. V. Mohan, M. Mohan, and R. B. Rakhi, "High performance supercapacitors based on WS₂ nanoflower electrodes with commercial-level mass-loading," *Surfaces and Interfaces*, vol. 42, p. 103496, 2023/11/01/ 2023.
 - [367] A. De Adhikari, S. Singh, and I. Lahiri, "WS₂@PPy heterostructured high performance supercapacitor self-powered by PVDF piezoelectric separator," *Journal of Alloys and Compounds*, vol. 939, p. 168713, 2023/04/05/ 2023.
 - [368] X. Wang *et al.*, "Enhanced mechanical and barrier properties of polyurethane nanocomposite films with randomly distributed molybdenum disulfide nanosheets," *Composites Science and Technology*, vol. 127, pp. 142-148, 2016/04/28/ 2016.
 - [369] X. Feng *et al.*, "Molybdenum disulfide nanosheets as barrier enhancing nanofillers in thermal decomposition of polypropylene composites," *Chemical Engineering Journal*, vol. 295, pp. 278-287, 2016/07/01/ 2016.
 - [370] K. Zhou, R. Gao, Z. Gui, and Y. Hu, "The effective reinforcements of functionalized MoS₂ nanosheets in polymer hybrid composites by sol-gel technique," *Composites Part A: Applied Science and Manufacturing*, vol. 94, pp. 1-9, 2017/03/01/ 2017.
 - [371] Y. Yu *et al.*, "PbS-Decorated WS₂ Phototransistors with Fast Response," *ACS Photonics*, vol. 4, no. 4, pp. 950-956, 2017/04/19 2017.
 - [372] V. R. Raja, D. R. Rosaline, A. Suganthi, and M. Rajarajan, "Facile fabrication of PbS/MoS₂ nanocomposite photocatalyst with efficient photocatalytic activity under visible light," *Solid State Sciences*, vol. 67, pp. 99-108, 2017/05/01/ 2017.
 - [373] D. Bhattacharya, S. Bayan, R. K. Mitra, and S. K. Ray, "2D WS₂ embedded PVDF nanocomposites for photosensitive piezoelectric nanogenerators with a colossal energy conversion efficiency of ~25.6%," *Nanoscale*, 10.1039/D1NR03808G vol. 13, no. 37, pp. 15819-15829, 2021.
 - [374] S. S. Nardekar, K. Krishnamoorthy, P. Pazhamalai, S. Sahoo, and S. Jae Kim, "MoS₂ quantum sheets-PVDF nanocomposite film based self-poled piezoelectric nanogenerators and photovoltaically self-charging power cell," *Nano Energy*, vol. 93, p. 106869, 2022/03/01/ 2022.

- [375] G. Lalwani *et al.*, "Tungsten disulfide nanotubes reinforced biodegradable polymers for bone tissue engineering," *Acta Biomaterialia*, vol. 9, no. 9, pp. 8365-8373, 2013/09/01/ 2013.
- [376] A. M. Díez-Pascual, M. Naffakh, C. Marco, and G. Ellis, "Mechanical and electrical properties of carbon nanotube/poly(phenylene sulphide) composites incorporating polyetherimide and inorganic fullerene-like nanoparticles," *Composites Part A: Applied Science and Manufacturing*, Article vol. 43, no. 4, pp. 603-612, 2012.
- [377] M. Naffakh, A. M. Díez-Pascual, and C. Marco, "Polymer blend nanocomposites based on poly(l-lactic acid), polypropylene and WS₂ inorganic nanotubes," *RSC Advances*, 10.1039/C6RA05803E vol. 6, no. 46, pp. 40033-40044, 2016.
- [378] N. Francis, Y. S. Choudhary, T. Abraham, U. K. Aravind, and C. T. Aravindakumar, "TMDC-based hybrid photocatalyst for antibiotics degradation: A comprehensive review," *FlatChem*, vol. 45, p. 100653, 2024/05/01/ 2024.
- [379] C. Mutalik *et al.*, "Antibacterial Pathways in Transition Metal-Based Nanocomposites: A Mechanistic Overview," (in eng), *Int J Nanomedicine*, vol. 17, pp. 6821-6842, 2022.
- [380] V. Vishwakarma, J. Kandasamy, and S. Vigneswaran, "Surface Treatment of Polymer Membranes for Effective Biofouling Control," *Membranes*, vol. 13, no. 8, p. 736, 2023.
- [381] H. Alkhalidi *et al.*, "Sustainable polymeric adsorbents for adsorption-based water remediation and pathogen deactivation: a review," *RSC Advances*, 10.1039/D4RA05269B vol. 14, no. 45, pp. 33143-33190, 2024.
- [382] P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*. Oxford University Press, 2000.
- [383] M. Thommes, "Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)," in *Chemistry International* vol. 38, ed, 2016, p. 25.
- [384] D. B. Williams and C. B. Carter, "Diffraction in TEM," in *Transmission Electron Microscopy: A Textbook for Materials Science*, D. B. Williams and C. B. Carter Eds. Boston, MA: Springer US, 2009, pp. 197-209.
- [385] G. W. Ewing, "Ewing's Analytical Instrumentation Handbook," 1997.
- [386] G. Santoro Domingo, "Preparación y caracterización de nanocompuestos poliméricos de PP y PET con nanotubos de carbono," 2011.
- [387] S. Quiles Díaz, "Estrategias de funcionalización de grafeno para el desarrollo de nanocompuestos de matriz termoplástica," Universidad Autónoma de Madrid, 2019.
- [388] A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner, and U. Pöschl, "Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information," *Carbon*, vol. 43, no. 8, pp. 1731-1742, 2005/07/01/ 2005.
- [389] F. Tuinstra and J. L. Koenig, "Raman spectrum of graphite," *The Journal of chemical physics*, vol. 53, no. 3, pp. 1126-1130, 1970.

- [390] Y. Wang, D. C. Alsmeyer, and R. L. McCreery, "Raman spectroscopy of carbon materials: structural basis of observed spectra," *Chemistry of Materials*, vol. 2, no. 5, pp. 557-563, 1990.
- [391] T. Jawhari, A. Roid, and J. Casado, "Raman spectroscopic characterization of some commercially available carbon black materials," *Carbon*, vol. 33, no. 11, pp. 1561-1565, 1995.
- [392] A. Cuesta, P. Dhamelincourt, J. Laureyns, A. Martinez-Alonso, and J. D. Tascón, "Raman microprobe studies on carbon materials," *Carbon*, vol. 32, no. 8, pp. 1523-1532, 1994.
- [393] R. Al-Jishi and G. Dresselhaus, "Lattice-dynamical model for graphite," *Physical Review B*, vol. 26, no. 8, p. 4514, 1982.
- [394] T. W. Quadri, O. E. Fayemi, L. O. Olasunkanmi, and E. E. Ebenso, "Chapter 15 - Survey of different electrochemical and analytical techniques for corrosion measurements," in *Electrochemical and Analytical Techniques for Sustainable Corrosion Monitoring*, J. Aslam, C. Verma, and C. Mustansar Hussain Eds.: Elsevier, 2023, pp. 293-323.
- [395] A. C. Lazanas and M. I. Prodromidis, "Electrochemical Impedance Spectroscopy—A Tutorial," *ACS Measurement Science Au*, vol. 3, no. 3, pp. 162-193, 2023/06/21 2023.
- [396] E. Frackowiak and F. Béguin, "Carbon materials for the electrochemical storage of energy in capacitors," *Carbon*, vol. 39, no. 6, pp. 937-950, 2001/05/01/ 2001.
- [397] N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart, and J. L. Dempsey, "A Practical Beginner's Guide to Cyclic Voltammetry," *Journal of Chemical Education*, vol. 95, no. 2, pp. 197-206, 2018/02/13 2018.
- [398] B.-A. Mei, O. Munteshari, J. Lau, B. Dunn, and L. Pilon, "Physical Interpretations of Nyquist Plots for EDLC Electrodes and Devices," *The Journal of Physical Chemistry C*, vol. 122, no. 1, pp. 194-206, 2018/01/11 2018.
- [399] P. Kumar, R. P. Bharti, V. Kumar, and P. P. Kundu, "Chapter 4 - Polymer Electrolyte Membranes for Microbial Fuel Cells: Part A. Nafion-Based Membranes," in *Progress and Recent Trends in Microbial Fuel Cells*, P. P. Kundu and K. Dutta Eds.: Elsevier, 2018, pp. 47-72.
- [400] K. Gajewska, A. Moyseowicz, D. Minta, and G. Gryglewicz, "Effect of electrolyte and carbon material on the electrochemical performance of high-voltage aqueous symmetric supercapacitors," *Journal of Materials Science*, vol. 58, no. 4, pp. 1721-1738, 2023/01/01 2023.
- [401] A. R. Sascha *et al.*, "Measurements of hydroperoxy radicals (HO₂) at atmospheric concentrations using bromide chemical ionisation mass spectrometry," *Atmospheric Measurement Techniques*, Article vol. 12, no. 2, pp. 891-902, 2019.
- [402] R. Wang *et al.*, "Effects of hydroperoxy radical heterogeneous loss on the summertime ozone formation in the North China Plain," *Science of The Total Environment*, vol. 825, p. 153993, 2022/06/15/ 2022.
- [403] N. Spinner. "Rotating Ring Disk Electrode Fundamentals." Pine Research. <https://pineresearch.com/shop/kb/theory/hydrodynamic-electrochemistry/rotating-electrode-theory/> (accessed 2024).

- [404] A. Japan. "RRDE-3A Rotating Ring Disk Electrode Apparatus Ver.2.0." <https://www.als-japan.com/rrde-3a.html> (accessed 2025).
- [405] D. A. Skoog, "Principios de análisis instrumental," *Interamericana*, 2001.
- [406] M. Siva Sankari and S. Vivekanandhan, "Jatropha Oil Cake Based Activated Carbon for Symmetric Supercapacitor Application: A Comparative Study on Conventional and Hydrothermal Carbonization Processes," *ChemistrySelect*, Article vol. 5, no. 4, pp. 1375-1384, 2020.
- [407] B. Huang, Y. Liu, and Z. Xie, "Biomass derived 2D carbons via a hydrothermal carbonization method as efficient bifunctional ORR/HER electrocatalysts," *Journal of Materials Chemistry A*, 10.1039/C7TA08052B vol. 5, no. 45, pp. 23481-23488, 2017.
- [408] D. Upskuvienė *et al.*, "Synthesis of nitrogen-doped carbon catalyst from hydrothermally carbonized wood chips for oxygen reduction," *Catalysis Communications*, vol. 184, p. 106797, 2023/11/01/ 2023.
- [409] A. Wütscher *et al.*, "Nitrogen-Doped Metal-Free Carbon Materials Derived from Cellulose as Electrocatalysts for the Oxygen Reduction Reaction," *ChemElectroChem*, vol. 6, no. 2, pp. 514-521, 2019.
- [410] H. O. Panganoron, J. D. A. Pascasio, E. A. Esparcia, J. A. D. del Rosario, and J. D. Ocon, "Hydrothermally Carbonized Waste Biomass as Electrocatalyst Support for α -MnO₂ in Oxygen Reduction Reaction," *Catalysts*, vol. 10, no. 2, p. 177, 2020.
- [411] F. Meng, L. Li, Z. Wu, H. Zhong, J. Li, and J. Yan, "Facile preparation of N-doped carbon nanofiber aerogels from bacterial cellulose as an efficient oxygen reduction reaction electrocatalyst," *Chinese Journal of Catalysis*, vol. 35, no. 6, pp. 877-883, 2014/06/01/ 2014.
- [412] C. Zhu, J. Zhai, and S. Dong, "Bifunctional fluorescent carbon nanodots: green synthesis via soy milk and application as metal-free electrocatalysts for oxygen reduction," *Chemical Communications*, 10.1039/C2CC33844K vol. 48, no. 75, pp. 9367-9369, 2012.
- [413] Y. Hao *et al.*, "Highly porous defective carbons derived from seaweed biomass as efficient electrocatalysts for oxygen reduction in both alkaline and acidic media," *Carbon*, vol. 137, pp. 93-103, 2018/10/01/ 2018.
- [414] H. Jia, S. Wang, J. Sun, K. Yin, X. Xie, and L. Sun, "Nitrogen-doped microporous carbon derived from a biomass waste-metasequoia cone for electrochemical capacitors," *Journal of Alloys and Compounds*, vol. 794, pp. 163-170, 2019/07/25/ 2019.
- [415] S. Jung, Y. Myung, B. N. Kim, I. G. Kim, I. K. You, and T. Kim, "Activated Biomass-derived Graphene-based Carbons for Supercapacitors with High Energy and Power Density," *Scientific Reports*, Article vol. 8, no. 1, 2018, Art no. 1915.
- [416] W. Luo *et al.*, "Pyrolysis of Cellulose under Ammonia Leads to Nitrogen-Doped Nanoporous Carbon Generated through Methane Formation," *Nano Letters*, vol. 14, no. 4, pp. 2225-2229, 2014/04/09 2014.
- [417] N. Kasera, P. Kolar, and S. G. Hall, "Nitrogen-doped biochars as adsorbents for mitigation of heavy metals and organics from water: a review," *Biochar*, vol. 4, no. 1, p. 17, 2022/03/08 2022.

- [418] H. Teng and L.-Y. Hsu, "High-Porosity Carbons Prepared from Bituminous Coal with Potassium Hydroxide Activation," *Industrial & Engineering Chemistry Research*, vol. 38, no. 8, pp. 2947-2953, 1999/08/01 1999.
- [419] M. Sevilla, A. B. Fuertes, and R. Mokaya, "High density hydrogen storage in superactivated carbons from hydrothermally carbonized renewable organic materials," *Energy & Environmental Science*, 10.1039/C0EE00347F vol. 4, no. 4, pp. 1400-1410, 2011.
- [420] V. Hoffmann *et al.*, "Conductive Carbon Materials from the Hydrothermal Carbonization of Vineyard Residues for the Application in Electrochemical Double-Layer Capacitors (EDLCs) and Direct Carbon Fuel Cells (DCFCs)," *Materials*, vol. 12, p. 1703, 05/26 2019.
- [421] A. Ertas, C. Boyce, and U. Gulbulak, "Experimental Measurement of Bulk Thermal Conductivity of Activated Carbon with Adsorbed Natural Gas for ANG Energy Storage Tank Design Application," *Energies*, vol. 13, p. 682, 02/05 2020.
- [422] K. Cychosz and M. Thommes, "Progress in the Physisorption Characterization of Nanoporous Gas Storage Materials," *Engineering*, vol. 4, 06/01 2018.
- [423] M. Prieto, G. J. Ellis, V. Budarin, E. Morales, M. Naffakh, and P. S. Shuttleworth, "Understanding pore size relation in cellulose-derived, nitrogen-doped, hydrothermal carbons for improved supercapacitor performance," *Journal of Materials Chemistry A*, 10.1039/D4TA04477K 2024.
- [424] S.-E. Chun and J. F. Whitacre, "Formation of micro/mesopores during chemical activation in tailor-made nongraphitic carbons," *Microporous and Mesoporous Materials*, vol. 251, pp. 34-41, 2017/10/01/ 2017.
- [425] R. Nandi, M. K. Jha, S. K. Guchhait, D. Sutradhar, and S. Yadav, "Impact of KOH Activation on Rice Husk Derived Porous Activated Carbon for Carbon Capture at Flue Gas alike Temperatures with High CO₂/N₂ Selectivity," *ACS Omega*, vol. 8, no. 5, pp. 4802-4812, 2023/02/07 2023.
- [426] Y. Mochizuki, J. Bud, E. Byambajav, and N. Tsubouchi, "Pore properties and CO₂ adsorption performance of activated carbon prepared from various carbonaceous materials," *Carbon Resources Conversion*, p. 100237, 2024/04/02/ 2024.
- [427] P. A. Moura *et al.*, "Assessing the potential of nanoporous carbon adsorbents from polyethylene terephthalate (PET) to separate CO₂ from flue gas," *Adsorption*, vol. 24, 04/01 2018.
- [428] S. Himeno, T. Komatsu, and S. Fujita, "High-Pressure Adsorption Equilibria of Methane and Carbon Dioxide on Several Activated Carbons," *Journal of Chemical & Engineering Data*, vol. 50, no. 2, pp. 369-376, 2005/03/01 2005.
- [429] Y. Kim, D. Jeong, K. Park, J.-H. Yu, and S. Jung, "Efficient Adsorption on Benzoyl and Stearoyl Cellulose to Remove Phenanthrene and Pyrene from Aqueous Solution," *Polymers*, vol. 10, p. 1042, 09/19 2018.
- [430] D. Shao and Q. Wei, "Microwave-Assisted Rapid Preparation of Nano-ZnO/Ag Composite Functionalized Polyester Nonwoven Membrane for Improving Its UV Shielding and Antibacterial Properties," *Materials*, vol. 11, no. 8, p. 1412, 2018.

- [431] K. Haruo, "Review of Reactions and Molecular Mechanisms in Cellulose Pyrolysis," *Current Organic Chemistry*, vol. 20, no. 23, pp. 2444-2457, 2016.
- [432] J. R. Mohrig, *Techniques in Organic Chemistry*. W. H. Freeman, 2002.
- [433] D. Lin-Vien, N. B. Colthup, W. G. Fateley, and J. G. Grasselli, "CHAPTER 2 - Alkanes," in *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, D. Lin-Vien, N. B. Colthup, W. G. Fateley, and J. G. Grasselli Eds. San Diego: Academic Press, 1991, pp. 9-28.
- [434] I. Ibrahim, S. Yunus, and A. Hashim, "Relative Performance of Isopropylamine, Pyrrole and Pyridine as Corrosion Inhibitors for Carbon Steels in Saline Water at Mildly Elevated Temperatures," *International Journal of Scientific and Engineering Research*, vol. 4, 03/01 2013.
- [435] P. Furlan, S. Scott, and M. H. Peaslee, "FTIR-ATR study of pH effects on egg albumin secondary structure," *Spectroscopy Letters*, vol. 40, pp. 475-482, 05/01 2007.
- [436] Z. Elassal *et al.*, "Synthesis and FT-IR study of the acido-basic properties of the V2O5 catalysts supported on zirconia," *Arabian Journal of Chemistry*, vol. 4, no. 3, pp. 313-319, 2011/07/01/ 2011.
- [437] P. Ruz, S. Banerjee, M. Pandey, V. Sudarsan, P. U. Sastry, and R. J. Kshirsagar, "Structural evolution of turbostratic carbon: Implications in H2 storage," *Solid State Sciences*, vol. 62, pp. 105-111, 2016/12/01/ 2016.
- [438] D. B. Schuepfer *et al.*, "Assessing the structural properties of graphitic and non-graphitic carbons by Raman spectroscopy," *Carbon*, vol. 161, pp. 359-372, 2020/05/01/ 2020.
- [439] A. Gupta, S. R. Dhakate, P. Pal, A. Dey, P. K. Iyer, and D. K. Singh, "Effect of graphitization temperature on structure and electrical conductivity of poly-acrylonitrile based carbon fibers," *Diamond and Related Materials*, vol. 78, pp. 31-38, 2017/09/01/ 2017.
- [440] C.-F. Liu, Y.-C. Liu, T.-Y. Yi, and C.-C. Hu, "Carbon materials for high-voltage supercapacitors," *Carbon*, vol. 145, pp. 529-548, 2019/04/01/ 2019.
- [441] Y. Katsuyama, Y. Nakayasu, H. Kobayashi, Y. Goto, I. Honma, and M. Watanabe, "Rational Route for Increasing Intercalation Capacity of Hard Carbons as Sodium-Ion Battery Anodes," *ChemSusChem*, vol. 13, no. 21, pp. 5762-5768, 2020.
- [442] Y. Katsuyama, Y. Nakayasu, K. Oizumi, Y. Fujihara, H. Kobayashi, and I. Honma, "Quinone-Based Redox Supercapacitor Using Highly Conductive Hard Carbon Derived from Oak Wood," *Advanced Sustainable Systems*, vol. 3, no. 11, p. 1900083, 2019.
- [443] M. Sevilla and A. B. Fuertes, "The production of carbon materials by hydrothermal carbonization of cellulose," *Carbon*, vol. 47, no. 9, pp. 2281-2289, 2009/08/01/ 2009.
- [444] M. A. Lillo-Ródenas, D. Cazorla-Amorós, and A. Linares-Solano, "Understanding chemical reactions between carbons and NaOH and KOH: An insight into the chemical activation mechanism," *Carbon*, vol. 41, no. 2, pp. 267-275, 2003/02/01/ 2003.
- [445] R. Arrigo, M. Hävecker, R. Schlögl, and D. S. Su, "Dynamic surface rearrangement and thermal stability of nitrogen functional groups on

- carbon nanotubes," *Chemical Communications*, 10.1039/B812769G no. 40, pp. 4891-4893, 2008.
- [446] R. J. J. Jansen and H. van Bekkum, "XPS of nitrogen-containing functional groups on activated carbon," *Carbon*, vol. 33, no. 8, pp. 1021-1027, 1995/01/01/ 1995.
- [447] E. Raymundo-Piñero *et al.*, "High surface area carbon nanotubes prepared by chemical activation," *Carbon*, vol. 40, no. 9, pp. 1614-1617, 2002/08/01/ 2002.
- [448] M. A. Wójtowicz, J. R. Pels, and J. A. Moulijn, "The fate of nitrogen functionalities in coal during pyrolysis and combustion," *Fuel*, vol. 74, no. 4, pp. 507-516, 1995/04/01/ 1995.
- [449] K. Tian *et al.*, "Single-site pyrrolic-nitrogen-doped sp²-hybridized carbon materials and their pseudocapitance," *Nature Communications*, vol. 11, no. 1, p. 3884, 2020/08/04 2020.
- [450] L. Yan, J. Yu, J. Houston, N. Flores, and H. Luo, "Biomass derived porous nitrogen doped carbon for electrochemical devices," *Green Energy & Environment*, vol. 2, no. 2, pp. 84-99, 2017/04/01/ 2017.
- [451] S. Huang, Q. Liang, J. Geng, H. Luo, and Q. Wei, "Sulfurized biochar prepared by simplified technic with superior adsorption property towards aqueous Hg(II) and adsorption mechanisms," *Materials Chemistry and Physics*, vol. 238, p. 121919, 2019/12/01/ 2019.
- [452] L. Leng *et al.*, "An overview of sulfur-functional groups in biochar from pyrolysis of biomass," *Journal of Environmental Chemical Engineering*, vol. 10, no. 2, p. 107185, 2022/04/01/ 2022.
- [453] V. Tauson, A. Sapozhnikov, S. Shinkareva, and E. Lustenberg, "The nature of the stability of an incommensurate 3D structural modulation in Baikal lazurite: Experimental data at 550°C," *Geochemistry International*, vol. 47, pp. 815-830, 08/01 2009.
- [454] J. Liu *et al.*, "N,S Co-Doped Carbon Nanofibers Derived from Bacterial Cellulose/Poly(Methylene blue) Hybrids: Efficient Electrocatalyst for Oxygen Reduction Reaction," *Catalysts*, vol. 8, no. 7, p. 269, 2018.
- [455] M. Jerigová, M. Odziomek, and N. López-Salas, "'We Are Here!' Oxygen Functional Groups in Carbons for Electrochemical Applications," *ACS Omega*, vol. 7, no. 14, pp. 11544-11554, 2022/04/12 2022.
- [456] D. Shen, J. Ye, R. Xiao, and H. Zhang, "TG-MS analysis for thermal decomposition of cellulose under different atmospheres," *Carbohydrate Polymers*, vol. 98, no. 1, pp. 514-521, 2013/10/15/ 2013.
- [457] M. Mases, D. Jacobsson, D. Wahlqvist, M. Ek, and H. Wiinikka, "The oxidation of carbon nanostructures imaged by electron microscopy: Comparison between in-situ TEM and TGA experiments," *Applied Surface Science*, vol. 672, p. 160755, 2024/11/01/ 2024.
- [458] V. S. Šelih, M. Strlič, J. Kolar, and B. Pihlar, "The role of transition metals in oxidative degradation of cellulose," *Polymer Degradation and Stability*, vol. 92, no. 8, pp. 1476-1481, 2007/08/01/ 2007.
- [459] J. M. Montes, F. G. Cuevas, J. Cintas, and F. Ternero, "Porosity effect on the thermal conductivity of sintered powder materials," *Applied Physics A*, vol. 131, no. 2, p. 149, 2025/01/30 2025.

- [460] S. De, S. Niranjana, B. S. Satyanarayana, and K. Mohan Rao, "Raman spectroscopy and conductivity variation of nanocluster carbon thin films grown using a room temperature based cathodic arc process," *Scientia Iranica*, vol. 18, no. 3, pp. 797-803, 2011/06/01/ 2011.
- [461] G. Xia *et al.*, "Effect of oxygen-containing functional groups of carbon materials on the performance of Li-O₂ batteries," *Electrochemistry Communications*, vol. 60, pp. 26-29, 2015/11/01/ 2015.
- [462] B. Sen Thapa, S.-E. Oh, S. G. Peera, and L. Singh, "Chapter 1 - Fundamentals of bioelectroactive fuel cells," in *Bioremediation, Nutrients, and Other Valuable Product Recovery*, L. Singh, D. M. Mahapatra, and S. Thakur Eds.: Elsevier, 2021, pp. 1-23.
- [463] C. V. V. Muralee Gopi, S. Alzahmi, V. Narayanaswamy, R. Vinodh, B. Issa, and I. M. Obaidat, "Supercapacitors: A promising solution for sustainable energy storage and diverse applications," *Journal of Energy Storage*, vol. 114, p. 115729, 2025/04/01/ 2025.
- [464] H. Li, F. Shi, Q. An, S. Zhai, K. Wang, and Y. Tong, "Three-dimensional hierarchical porous carbon derived from lignin for supercapacitors: Insight into the hydrothermal carbonization and activation," *International Journal of Biological Macromolecules*, vol. 166, pp. 923-933, 2021/01/01/ 2021.
- [465] L. Wei, M. Sevilla, A. B. Fuertes, R. Mokaya, and G. Yushin, "Hydrothermal Carbonization of Abundant Renewable Natural Organic Chemicals for High-Performance Supercapacitor Electrodes," *Advanced Energy Materials*, vol. 1, no. 3, pp. 356-361, 2011/05/01 2011.
- [466] H. Ma, Z. Chen, X. Wang, Z. Liu, and X. Liu, "A simple route for hierarchically porous carbon derived from corn straw for supercapacitor application," *Journal of Renewable and Sustainable Energy*, vol. 11, no. 2, p. 024102, 2019/03/01 2019.
- [467] C. Li *et al.*, "Fabricating an Aqueous Symmetric Supercapacitor with a Stable High Working Voltage of 2 V by Using an Alkaline-Acidic Electrolyte," (in eng), *Adv Sci (Weinh)*, vol. 6, no. 1, p. 1801665, Jan 9 2019.
- [468] C. C. Lai, F. H. Hsu, S. Y. Hsu, M. J. Deng, K. T. Lu, and J. M. Chen, "1.8 V Aqueous Symmetric Carbon-Based Supercapacitors with Agarose-Bound Activated Carbons in an Acidic Electrolyte," (in eng), *Nanomaterials (Basel)*, vol. 11, no. 7, Jun 30 2021.
- [469] Y. Xu, Z. Lin, X. Huang, Y. Liu, Y. Huang, and X. Duan, "Flexible Solid-State Supercapacitors Based on Three-Dimensional Graphene Hydrogel Films," *ACS Nano*, vol. 7, no. 5, pp. 4042-4049, 2013/05/28 2013.
- [470] P. Leuaa, D. Priyadarshani, D. Choudhury, R. Maurya, and M. Neergat, "Resolving charge-transfer and mass-transfer processes of VO(2+)/VO(2) (+) redox species across the electrode/electrolyte interface using electrochemical impedance spectroscopy for vanadium redox flow battery," (in eng), *RSC Adv*, vol. 10, no. 51, pp. 30887-30895, Aug 17 2020.
- [471] R. K. Emmett, M. Grady, and M. E. Roberts, "Increasing Charge Transfer at the Liquid-Solid Interface Using Electrodes Modified with Redox Mediators," *Advanced Energy and Sustainability Research*, vol. 3, no. 1, p. 2100132, 2022.

- [472] H. H. Hegazy *et al.*, "2D-based electrode materials for supercapacitors – status, challenges, and prospects," *RSC Advances*, 10.1039/D4RA05473C vol. 14, no. 45, pp. 32958-32977, 2024.
- [473] J. Ji, S. Park, and J. H. Choi, "Morphology Engineering of Hybrid Supercapacitor Electrodes from Hierarchical Stem-like Carbon Networks with Flower-like MoS₂ Structures," *ACS Omega*, vol. 8, no. 19, pp. 16833-16841, 2023/05/16 2023.
- [474] S. Tanwar, A. Arya, A. Gaur, and A. L. Sharma, "Transition metal dichalcogenide (TMDs) electrodes for supercapacitors: a comprehensive review," *Journal of Physics: Condensed Matter*, vol. 33, no. 30, p. 303002, 2021/06/14 2021.
- [475] I. C. Martínez, "Preparación de materiales gráficos: aplicación como ánodos en baterías de ión-litio," ed, 2011.
- [476] F. Cao *et al.*, "The influence of deposited potential on the ORR activity of Pt catalysts on glassy carbon electrode," *RSC Advances*, 10.1039/C7RA02444D vol. 7, no. 41, pp. 25429-25436, 2017.
- [477] H. Yang, N. An, Z. Kang, P. W. Menezes, and Z. Chen, "Understanding Advanced Transition Metal-Based Two Electron Oxygen Reduction Electrocatalysts from the Perspective of Phase Engineering," *Advanced Materials*, vol. 36, no. 25, p. 2400140, 2024.
- [478] J. Guo *et al.*, "Emerging Carbon-Based Catalysts for the Oxygen Reduction Reaction: Insights into Mechanisms and Applications," *Inorganics*, vol. 12, no. 12, p. 303, 2024.
- [479] T. J. Bandosz, "Revealing the impact of small pores on oxygen reduction on carbon electrocatalysts: A journey through recent findings," *Carbon*, vol. 188, pp. 289-304, 2022/03/01/ 2022.
- [480] G. A. Ferrero, A. B. Fuertes, M. Sevilla, and M.-M. Titirici, "Efficient metal-free N-doped mesoporous carbon catalysts for ORR by a template-free approach," *Carbon*, vol. 106, pp. 179-187, 2016/09/01/ 2016.
- [481] L. Wang, W. Jia, X. Liu, J. Li, and M. M. Titirici, "Sulphur-doped ordered mesoporous carbon with enhanced electrocatalytic activity for the oxygen reduction reaction," *Journal of Energy Chemistry*, vol. 25, no. 4, pp. 566-570, 2016/07/01/ 2016.
- [482] Y. Liu *et al.*, "Soybean straw biomass-derived Fe–N co-doped porous carbon as an efficient electrocatalyst for oxygen reduction in both alkaline and acidic media," *RSC Advances*, 10.1039/C9RA07539A vol. 10, no. 12, pp. 6763-6771, 2020.
- [483] C. Guo *et al.*, "A Highly Nanoporous Nitrogen-Doped Carbon Microfiber Derived from Bioresource as a New Kind of ORR Electrocatalyst," *Nanoscale Research Letters*, vol. 14, no. 1, p. 22, 2019/01/15 2019.
- [484] M. Zhang *et al.*, "Lignosulfonate biomass derived N and S co-doped porous carbon for efficient oxygen reduction reaction," *Sustainable Energy & Fuels*, 10.1039/C8SE00231B vol. 2, no. 8, pp. 1820-1827, 2018.
- [485] C. Sathiskumar, S. Ramakrishnan, M. Vinothkannan, A. Rhan Kim, S. Karthikeyan, and D. J. Yoo, "Nitrogen-Doped Porous Carbon Derived from Biomass Used as Trifunctional Electrocatalyst toward Oxygen Reduction,

- Oxygen Evolution and Hydrogen Evolution Reactions," *Nanomaterials*, vol. 10, no. 1, p. 76, 2020.
- [486] S. Ullah *et al.*, "Activated carbon derived from biomass for wastewater treatment: Synthesis, application and future challenges," *Journal of Analytical and Applied Pyrolysis*, vol. 179, p. 106480, 2024/05/01/ 2024.
- [487] I. Slavik, T. S. Bechle, and W. Uhl, "Practical implications of adding powdered activated carbon in advanced wastewater treatment for process and plant design," *Water Practice and Technology*, vol. 19, no. 11, pp. 4303-4310, 2024.
- [488] Z. K. Nazarkina *et al.*, "Activated Carbon-Enriched Electrospun-Produced Scaffolds for Drug Delivery/Release in Biological Systems," (in eng), *Int J Mol Sci*, vol. 24, no. 7, Apr 4 2023.
- [489] M. Fronczak, K. Pyrzyńska, A. Bhattarai, P. Pietrowski, and M. Bystrzejewski, "Improved adsorption performance of activated carbon covalently functionalised with sulphur-containing ligands in the removal of cadmium from aqueous solutions," *International Journal of Environmental Science and Technology*, vol. 16, no. 12, pp. 7921-7932, 2019/12/01 2019.
- [490] Q. Zhang *et al.*, "Graphene oxide-modified electrospun polyvinyl alcohol nanofibrous scaffolds with potential as skin wound dressings," *RSC Advances*, 10.1039/C7RA03997B vol. 7, no. 46, pp. 28826-28836, 2017.
- [491] N. Zhang, Y. Qi, S. Tian, Y. Wang, P. Cui, and W. Jiang, "Bottom-up and up-down strategy to obtain the highly porous polystyrene foam for oily water remediation," *Separation and Purification Technology*, vol. 262, p. 118233, 2021/05/01/ 2021.
- [492] M. T. Amin, A. A. Alazba, and M. Shafiq, "Nanofibrous membrane of polyacrylonitrile with efficient adsorption capacity for cadmium ions from aqueous solution: Isotherm and kinetic studies," *Current Applied Physics*, vol. 40, pp. 101-109, 2022/08/01/ 2022.
- [493] T. D. Cuong, L. Q. Dien, and P. H. Hoang, "Preparation of bio-based porous material with high oil adsorption capacity from bio-polyurethane and sugarcane bagasse," *RSC Advances*, 10.1039/D4RA00469H vol. 14, no. 10, pp. 6938-6947, 2024.
- [494] C. Liang *et al.*, "Material Flows of Polyurethane in the United States," *Environmental Science & Technology*, vol. 55, no. 20, pp. 14215-14224, 2021/10/19 2021.
- [495] T. A. Adegbola, O. Agboola, and O. S. I. Fayomi, "Review of polyacrylonitrile blends and application in manufacturing technology: recycling and environmental impact," *Results in Engineering*, vol. 7, p. 100144, 2020/09/01/ 2020.
- [496] A. Z. Naser, I. Deiab, F. Defersha, and S. Yang, "Expanding Poly(lactic acid) (PLA) and Polyhydroxyalkanoates (PHAs) Applications: A Review on Modifications and Effects," *Polymers*, vol. 13, no. 23, p. 4271, 2021.
- [497] M. Julinová, L. Vaňharová, and M. Jurča, "Water-soluble polymeric xenobiotics – Polyvinyl alcohol and polyvinylpyrrolidone – And potential solutions to environmental issues: A brief review," *Journal of Environmental Management*, vol. 228, pp. 213-222, 2018/12/15/ 2018.

- [498] I. Gaytán, M. Burelo, and H. Loza-Tavera, "Current status on the biodegradability of acrylic polymers: microorganisms, enzymes and metabolic pathways involved," (in eng), *Appl Microbiol Biotechnol*, vol. 105, no. 3, pp. 991-1006, Feb 2021.
- [499] S. Kubowicz and A. M. Booth, "Biodegradability of Plastics: Challenges and Misconceptions," *Environmental Science & Technology*, vol. 51, no. 21, pp. 12058-12060, 2017/11/07 2017.
- [500] K. Skleničková, A. Sabina, H. Martin, K. Vladimír, and H. and Beneš, "Biodegradability and ecotoxicity of polyurethane foams: A review," *Critical Reviews in Environmental Science and Technology*, vol. 52, no. 2, pp. 157-202, 2022/01/17 2022.
- [501] Z. Qi, H. Yu, Y. Chen, and M. Zhu, "Highly porous fibers prepared by electrospinning a ternary system of nonsolvent/solvent/poly(l-lactic acid)," *Materials Letters*, vol. 63, no. 3, pp. 415-418, 2009/02/15/ 2009.
- [502] F. Yang, R. Murugan, S. Wang, and S. Ramakrishna, "Electrospinning of nano/micro scale poly(l-lactic acid) aligned fibers and their potential in neural tissue engineering," *Biomaterials*, vol. 26, no. 15, pp. 2603-2610, 2005/05/01/ 2005.
- [503] J. Zeng *et al.*, "Biodegradable electrospun fibers for drug delivery," *Journal of Controlled Release*, vol. 92, no. 3, pp. 227-231, 2003/10/30/ 2003.
- [504] F. Yang, R. Murugan, S. Ramakrishna, X. Wang, Y. X. Ma, and S. Wang, "Fabrication of nano-structured porous PLLA scaffold intended for nerve tissue engineering," *Biomaterials*, vol. 25, no. 10, pp. 1891-1900, 2004/05/01/ 2004.
- [505] M. Naffakh, "Nanocomposite Materials Based on TMDCs WS₂ Modified Poly(l-Lactic Acid)/Poly(Vinylidene Fluoride) Polymer Blends," *Polymers*, vol. 13, no. 13, p. 2179, 2021.
- [506] M. Naffakh and P. S. Shuttleworth, "Investigation of the Crystallization Kinetics and Melting Behaviour of Polymer Blend Nanocomposites Based on Poly(L-Lactic Acid), Nylon 11 and TMDCs WS₂," *Polymers*, vol. 14, no. 13, p. 2692, 2022.
- [507] Y. Dong *et al.*, "Synthesis of mesoporous carbon fibers with a high adsorption capacity for bulky dye molecules," *Journal of Materials Chemistry A*, 10.1039/C3TA10787F vol. 1, no. 25, pp. 7391-7398, 2013.
- [508] S. Imaizumi, H. Matsumoto, M. Ashizawa, M. Minagawa, and A. Tanioka, "Nanosize effects of sulfonated carbon nanofiber fabrics for high capacity ion-exchanger," *RSC Advances*, 10.1039/C2RA20103H vol. 2, no. 7, pp. 3109-3114, 2012.
- [509] Z. Liu, K. Zhao, D. Li, G. Xing, and Y. Tang, "Pore size regulation of BN fibers and its effect on tetracycline adsorption," *Journal of the American Ceramic Society*, vol. 106, no. 12, pp. 7803-7811, 2023.
- [510] X. Cao, W. Chen, P. Zhao, Y. Yang, and D.-G. Yu, "Electrospun Porous Nanofibers: Pore-Forming Mechanisms and Applications for Photocatalytic Degradation of Organic Pollutants in Wastewater," *Polymers*, vol. 14, no. 19, p. 3990, 2022.
- [511] J. E. Karbowniczek, D. P. Ura, and U. Stachewicz, "Nanoparticles distribution and agglomeration analysis in electrospun fiber based

- composites for desired mechanical performance of poly(3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) scaffolds with hydroxyapatite (HA) and titanium dioxide (TiO₂) towards medical applications," *Composites Part B: Engineering*, vol. 241, p. 110011, 2022/07/15/ 2022.
- [512] Y. Jin, D. Yang, D. Kang, and X. Jiang, "Fabrication of Necklace-like Structures via Electrospinning," *Langmuir*, vol. 26, no. 2, pp. 1186-1190, 2010/01/19 2010.
- [513] S. H. Wu and P. Pendleton, "Adsorption of Anionic Surfactant by Activated Carbon: Effect of Surface Chemistry, Ionic Strength, and Hydrophobicity," *Journal of Colloid and Interface Science*, vol. 243, no. 2, pp. 306-315, 2001/11/15/ 2001.
- [514] H. Kaur, A. Bansawal, G. Hippargi, and G. R. Pophali, "Effect of hydrophobicity of pharmaceuticals and personal care products for adsorption on activated carbon: Adsorption isotherms, kinetics and mechanism," (in eng), *Environ Sci Pollut Res Int*, vol. 25, no. 21, pp. 20473-20485, Jul 2018.
- [515] P. K. Chow *et al.*, "Wetting of Mono and Few-Layered WS₂ and MoS₂ Films Supported on Si/SiO₂ Substrates," *ACS Nano*, vol. 9, no. 3, pp. 3023-3031, 2015/03/24 2015.
- [516] D. Kolbuk, M. Ciechomska, O. Jeznach, and P. Sajkiewicz, "Effect of crystallinity and related surface properties on gene expression of primary fibroblasts," (in eng), *RSC Adv*, vol. 12, no. 7, pp. 4016-4028, Jan 28 2022.
- [517] E. W. Fischer, H. J. Sterzel, and G. Wegner, "Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions," *Kolloid-Zeitschrift und Zeitschrift für Polymere*, vol. 251, no. 11, pp. 980-990, 1973/11/01 1973.
- [518] Z. Su, Q. Li, Y. Liu, W. Guo, and C. Wu, "The nucleation effect of modified carbon black on crystallization of poly(lactic acid)," *Polymer Engineering & Science*, vol. 50, no. 8, pp. 1658-1666, 2010.
- [519] N. Angin, M. Ertas, S. Caylak, and M. S. Fidan, "Thermal and electrical behaviors of activated carbon-filled PLA/PP hybrid biocomposites," *Sustainable Materials and Technologies*, vol. 37, p. e00655, 2023/09/01/ 2023.
- [520] H.-S. Xu, X. J. Dai, P. R. Lamb, and Z.-M. Li, "Poly(L-lactide) crystallization induced by multiwall carbon nanotubes at very low loading," *Journal of Polymer Science Part B: Polymer Physics*, vol. 47, no. 23, pp. 2341-2352, 2009.
- [521] D. Wu, L. Wu, W. Zhou, M. Zhang, and T. Yang, "Crystallization and biodegradation of polylactide/carbon nanotube composites," *Polymer Engineering & Science*, vol. 50, no. 9, pp. 1721-1733, 2010.
- [522] A. Dobrev and I. Gutzow, "Activity of substrates in the catalyzed nucleation of glass-forming melts. I. Theory," *Journal of Non-Crystalline Solids*, vol. 162, no. 1, pp. 1-12, 1993/09/01/ 1993.
- [523] A. Dobrev and I. Gutzow, "Activity of substrates in the catalyzed nucleation of glass-forming melts. II. Experimental evidence," *Journal of Non-Crystalline Solids*, vol. 162, no. 1, pp. 13-25, 1993/09/01/ 1993.

-
- [524] H. E. Kissinger, "Variation of peak temperature with heating rate in differential thermal analysis," *Journal of Research of the National Bureau of Standards*, vol. 57, pp. 217-221, 1956.
 - [525] M. Naffakh, C. Marco, and G. Ellis, "Non-Isothermal Cold-Crystallization Behavior and Kinetics of Poly(l-Lactic Acid)/WS2 Inorganic Nanotube Nanocomposites," *Polymers*, vol. 7, no. 11, pp. 2175-2189, 2015.
 - [526] M. Naffakh, C. Marco, and G. Ellis, "Inorganic WS2 nanotubes that improve the crystallization behavior of poly(3-hydroxybutyrate)," *CrystEngComm*, 10.1039/C3CE41987H vol. 16, no. 6, pp. 1126-1135, 2014.
 - [527] L. Zhao, X. Liu, Y. Cai, and W. Chen, "Crystallization and properties of nucleated poly(l-lactic acid): Effect of cyclopentanecarboxylic acid derivative as a new nucleating agent," *Journal of Thermoplastic Composite Materials*, vol. 36, no. 1, pp. 218-233, 2023.
 - [528] S. Mohammadzadehmoghadam, Y. Dong, and I. Jeffery Davies, "Recent progress in electrospun nanofibers: Reinforcement effect and mechanical performance," *Journal of Polymer Science Part B: Polymer Physics*, vol. 53, no. 17, pp. 1171-1212, 2015.
 - [529] F. Jiang, L. Chen, N. Song, L. Shi, and P. Ding, "Influence of activated carbon fibres with different specific surface areas on the thermal conductive and electrical insulating properties of polyamide-imide composites," *High Voltage*, vol. 2, no. 3, pp. 161-166, 2017.
 - [530] M. Mollaei, F. Karbasi, A. Sharifi Haddad, and H. Baniasadi, "Fabrication of biocomposite materials with polycaprolactone and activated carbon extracted from agricultural waste," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 702, p. 135175, 2024/12/05/ 2024.
 - [531] P. C. C. Faria, J. J. M. Órfão, and M. F. R. Pereira, "Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries," *Water Research*, vol. 38, no. 8, pp. 2043-2052, 2004/04/01/ 2004.
 - [532] M. Alkhabbas, A. M. Al-Ma'abreh, G. Edris, T. Saleh, and H. Alhmood, "Adsorption of Anionic and Cationic Dyes on Activated Carbon Prepared from Oak Cupules: Kinetics and Thermodynamics Studies," *International Journal of Environmental Research and Public Health*, vol. 20, no. 4, p. 3280, 2023.
 - [533] A. Ouedrhiri *et al.*, "Adsorption of anionic and cationic dyes in aqueous solution by a sustainable and low-cost activated carbon based on argan solid waste treated with H₃PO₄," *Environmental Science and Pollution Research*, vol. 31, no. 53, pp. 62010-62021, 2024/11/01 2024.
 - [534] N. U. M. Nizam, M. M. Hanafiah, E. Mahmoudi, A. A. Halim, and A. W. Mohammad, "The removal of anionic and cationic dyes from an aqueous solution using biomass-based activated carbon," *Scientific Reports*, vol. 11, no. 1, p. 8623, 2021/04/21 2021.
 - [535] Y. S. Ho and G. McKay, "Pseudo-second order model for sorption processes," *Process Biochemistry*, vol. 34, no. 5, pp. 451-465, 1999/07/01/ 1999.
 - [536] T. Wang, M. Jiang, X. Yu, N. Niu, and L. Chen, "Application of lignin adsorbent in wastewater Treatment: A review," *Separation and Purification Technology*, vol. 302, p. 122116, 2022/12/01/ 2022.

- [537] S. Netpradit, P. Thiravetyan, and S. Towprayoon, "Adsorption of three azo reactive dyes by metal hydroxide sludge: effect of temperature, pH, and electrolytes," *Journal of Colloid and Interface Science*, vol. 270, no. 2, pp. 255-261, 2004/02/15/ 2004.
- [538] Y. S. Al-Degs, M. I. El-Barghouthi, A. H. El-Sheikh, and G. M. Walker, "Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon," *Dyes and Pigments*, vol. 77, no. 1, pp. 16-23, 2008/01/01/ 2008.
- [539] H. J. Abdoul *et al.*, "Efficient adsorption of bulky reactive dyes from water using sustainably-derived mesoporous carbons," *Environmental Research*, vol. 221, p. 115254, 2023/03/15/ 2023.
- [540] W. Shi, Z. Wang, F. Li, Y. Xu, and X. Chen, "Multilayer adsorption of lead (Pb) and fulvic acid by *Chlorella pyrenoidosa*: Mechanism and impact of environmental factors," (in eng), *Chemosphere*, vol. 329, p. 138596, Jul 2023.
- [541] B. M. Thamer, F. A. Al-aizari, and H. S. Abdo, "Enhanced Adsorption of Textile Dyes by a Novel Sulfonated Activated Carbon Derived from Pomegranate Peel Waste: Isotherm, Kinetic and Thermodynamic Study," *Molecules*, vol. 28, no. 23, p. 7712, 2023.
- [542] D. S. d. C. Coltre *et al.*, "Study of dye desorption mechanism of bone char utilizing different regenerating agents," *SN Applied Sciences*, vol. 2, no. 12, p. 2150, 2020/12/04 2020.
- [543] A. B. Al-Odayni, F. S. Alsubaie, and W. S. Saeed, "Nitrogen-Rich Polyaniline-Based Activated Carbon for Water Treatment: Adsorption Kinetics of Anionic Dye Methyl Orange," (in eng), *Polymers (Basel)*, vol. 15, no. 4, Feb 6 2023.
- [544] H. Li, V. L. Budarin, J. H. Clark, M. North, and X. Wu, "Rapid and efficient adsorption of methylene blue dye from aqueous solution by hierarchically porous, activated starbons®: Mechanism and porosity dependence," *Journal of Hazardous Materials*, vol. 436, p. 129174, 2022/08/15/ 2022.
- [545] X. Zhang *et al.*, "Preparation of sucrose-derived activated carbon in one pot with desirable hierarchically porous structure for efficient dyes removal," *Applied Surface Science Advances*, vol. 19, p. 100556, 2024/02/01/ 2024.
- [546] Z. Li *et al.*, "Adsorption of congo red and methylene blue dyes on an ashitaba waste and a walnut shell-based activated carbon from aqueous solutions: Experiments, characterization and physical interpretations," *Chemical Engineering Journal*, Article vol. 388, 2020, Art no. 124263.
- [547] Z. Hua, Y. Pan, and Q. Hong, "Adsorption of Congo red dye in water by orange peel biochar modified with CTAB," *RSC Advances*, Article vol. 13, no. 18, pp. 12502-12508, 2023.
- [548] A. A. Khan *et al.*, "Algal biochar: A natural solution for the removal of Congo red dye from textile wastewater," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 166, p. 105312, 2025/01/01/ 2025.
- [549] S. Wei, Z. Tan, Z. Liu, H. Zuo, Y. Xia, and Y. Zhang, "Removal of methyl orange dye by high surface area biomass activated carbon prepared from bamboo fibers," *Industrial Crops and Products*, vol. 218, p. 118991, 2024/10/15/ 2024.

- [550] S.-S. Wang, Y.-M. Yan, C.-H. Hsu, and H.-P. Lin, "Waste bamboo-derived biochar and multiporous carbon as adsorbents for methyl orange removal," *Journal of the Chinese Chemical Society*, vol. 70, no. 8, pp. 1628-1635, 2023.
- [551] B. Zhang, W. Yunhai, and L. and Cha, "Removal of methyl orange dye using activated biochar derived from pomelo peel wastes: performance, isotherm, and kinetic studies," *Journal of Dispersion Science and Technology*, vol. 41, no. 1, pp. 125-136, 2020/01/02 2020.
- [552] N. Kaya and Z. Y. Uzun, "Investigation of effectiveness of pine cone biochar activated with KOH for methyl orange adsorption and CO₂ capture," *Biomass Conversion and Biorefinery*, vol. 11, no. 3, pp. 1067-1083, 2021/06/01 2021.
- [553] R. L. Tseng, F. C. Wu, and R. S. Juang, "Liquid-phase adsorption of dyes and phenols using pinewood-based activated carbons," *Carbon*, Article vol. 41, no. 3, pp. 487-495, 2003.
- [554] A. A. Spagnoli, D. A. Giannakoudakis, and S. Bashkova, "Adsorption of methylene blue on cashew nut shell based carbons activated with zinc chloride: The role of surface and structural parameters," *Journal of Molecular Liquids*, Article vol. 229, pp. 465-471, 2017.
- [555] O. S. Bello, K. A. Adegoke, O. O. Sarumi, and O. S. Lameed, "Functionalized locust bean pod (*Parkia biglobosa*) activated carbon for Rhodamine B dye removal," *Heliyon*, vol. 5, no. 8, p. e02323, 2019/08/01/ 2019.
- [556] H. M. H. Gad and A. A. El-Sayed, "Activated carbon from agricultural by-products for the removal of Rhodamine-B from aqueous solution," *Journal of Hazardous Materials*, vol. 168, no. 2, pp. 1070-1081, 2009/09/15/ 2009.
- [557] A. K. Behera, K. P. Shadangi, and P. K. Sarangi, "Efficient removal of Rhodamine B dye using biochar as an adsorbent: Study the performance, kinetics, thermodynamics, adsorption isotherms and its reusability," *Chemosphere*, vol. 354, p. 141702, 2024/04/01/ 2024.
- [558] Y. Hou, G. Huang, J. Li, Q. Yang, S. Huang, and J. Cai, "Hydrothermal conversion of bamboo shoot shell to biochar: Preliminary studies of adsorption equilibrium and kinetics for rhodamine B removal," *Journal of Analytical and Applied Pyrolysis*, vol. 143, p. 104694, 2019/10/01/ 2019.
- [559] S. Cao, T. Liu, S. Hussain, W. Zeng, X. Peng, and F. Pan, "Hydrothermal synthesis of variety low dimensional WS₂ nanostructures," *Materials Letters*, vol. 129, pp. 205-208, 2014/08/15/ 2014.
- [560] N. McCann, M. Maeder, and H. Hasse, "Prediction of the overall enthalpy of CO₂ absorption in aqueous amine systems from experimentally determined reaction enthalpies," *Energy Procedia*, vol. 4, pp. 1542-1549, 2011/01/01/ 2011.
- [561] M. Naffakh and C. Marco, "Isothermal crystallization kinetics and melting behavior of poly(l-lactic acid)/WS₂ inorganic nanotube nanocomposites," *Journal of Materials Science*, vol. 50, no. 18, pp. 6066-6074, 2015/09/01 2015.

Annexes

Annex 1: Enthalpy calculations

CO₂ sorption isotherms were obtained in the P/P₀ range of 10⁻⁴-0.03. This data represents partial pressure against the amount of CO₂ adsorbed (in mmol/g).

For each temperature, the logarithm of the partial pressure was calculated for different values of adsorbed CO₂. A graph was then constructed representing the inverse of temperature against the logarithm of the absolute pressure, in order to calculate the enthalpy according to the Clausius-Clapeyron equation [560]:

$$\ln(P) = \frac{-\Delta H}{R \cdot T} \rightarrow \ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H}{R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{Equation A1}$$

The slope is $\frac{-\Delta H}{R}$ and enthalpy can be calculated by multiplying by the negative value of R (-8.314 · 10⁻³ kJ/mol · K). Table A1 shows the calculation of enthalpy from C 1-4 data:

Table A1: Enthalpy determination for C 1-4 at 0.4 mmol/g.

Q (mmol/g)	T=273 K Ln (P)	T=298 K Ln (P)	T=323 K Ln (P)	Slope (K ⁻¹)	R ²	Enthalpy (kJ/mol)
0.4	0.542	1.552	2.371	-3225.67	0.9999	26.818

However, to ensure an accurate data representation, it was decided to analyse a minimum of 10 different points (with Q values from 0.1 to 2 mmol/g, if possible) so a representative analysis of the sorption process can be carried out. Nevertheless, in order to conduct this analysis, it would imply the manual search of 10 (points) · 3 (temperatures) · 8 (samples) = 240 different values. To avoid this task, a third-degree polynomial fitting was calculated for each sample (P as a function of Q), enabling direct calculation of the corresponding pressure to Q values for each sample.

All of the fittings were truncated at the maximum adsorption load of each sample at 323 K to avoid data extrapolation. Figure A1 represents the actual isotherms and the third-degree fitting for each isotherm of the C 1-4 sample.

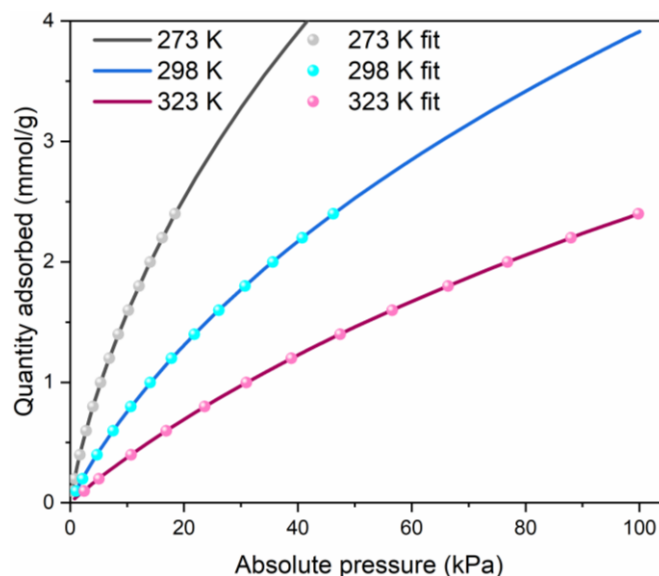


Figure A1: Comparison between actual isotherms and polynomial fit for C 1-4.

It can be observed from Figure A1 that the polynomial curve exhibits a perfect fit with the obtained data. Consequently, P was determined at increasing Q values ranging from 0.1 mmol/g up to the maximum adsorption value at 323 K (2.4 mmol/g for C 1-4, as previously indicated in the figure). $\ln P$ was determined for each pressure and plotted against $1/T$, so the enthalpy at different Q values can be calculated.

Finally, the enthalpy for different Q values for the C 1-4 sample are presented in Table A2. These are the same values displayed in Figure 4.14.

Table A2: Different enthalpies for C 1-4.

Q (mmol /g)	Enthalpy (kJ/mol)	Q (mmol /g)	Enthalpy (kJ/mol)
0.1	27.66	1.4	25.25
0.2	27.36	1.6	25.10
0.4	26.82	1.8	24.98
0.6	26.37	2.0	24.89
0.8	26.00	2.2	24.83
1.0	25.69	2.4	24.79
1.2	25.45		

Annex 2: SEM and TEM micrographs of the remaining carbons

The SEM micrographs of the remaining samples are displayed in Figure A2:

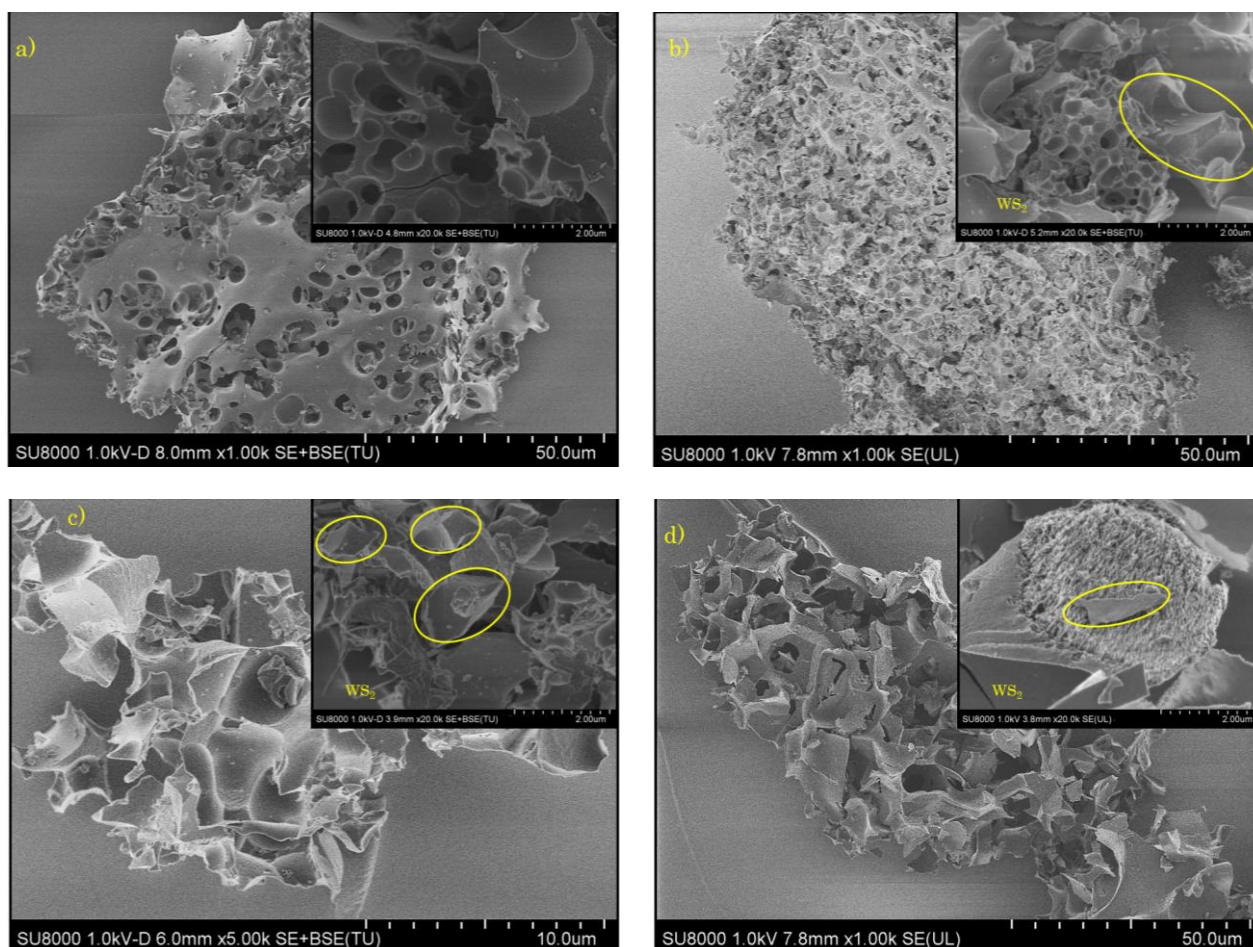


Figure A2: SEM images of a) CA 1-1.5; b) C 1-1.5 W; c) CA 1-1.5 W and d) CA 1-4 W.

Furthermore, after SEM characterisation, TEM analyses were carried out to obtain a better view of the internal structure of the carbon. A total of 41 micrographs were taken at different rotation angles for C 1-4 W sample. These images were compiled into a video file that illustrates the rotation of the internal structure of the sample. The video is presented in the following QR code:



QR A1: TEM analysis of C 1-4 W rotation.

Annex 3: Electrical conductivity calculations

Electrical resistivity (ρ) of the samples was calculated using Equation A2:

$$\rho = \frac{R \cdot W \cdot T}{L} \quad \text{Equation A2}$$

With W, T and L being the dimensions of the container (measured in m), as shown in Figure 3.2, and R, the electrical resistance of the measured material, measured in ohms (Ω). Four measurements were conducted for each sample in the experimental determination of the electrical resistance. Table A3 presents the voltage vs. current values obtained for the C 1-4 sample:

Table A3: Voltage and current measurements for C 1-4.

Voltage (V)	0.01	0.015	0.02	0.025
Current (A)	$6.45 \cdot 10^{-4}$	$9.67 \cdot 10^{-4}$	0.0013	0.0016

With these values, a new graph can be built by plotting voltage vs. current, with its slope being the resistance (R), according to Ohm's law. Figure A3 represents the resistance for all the C 1-4 set of samples:

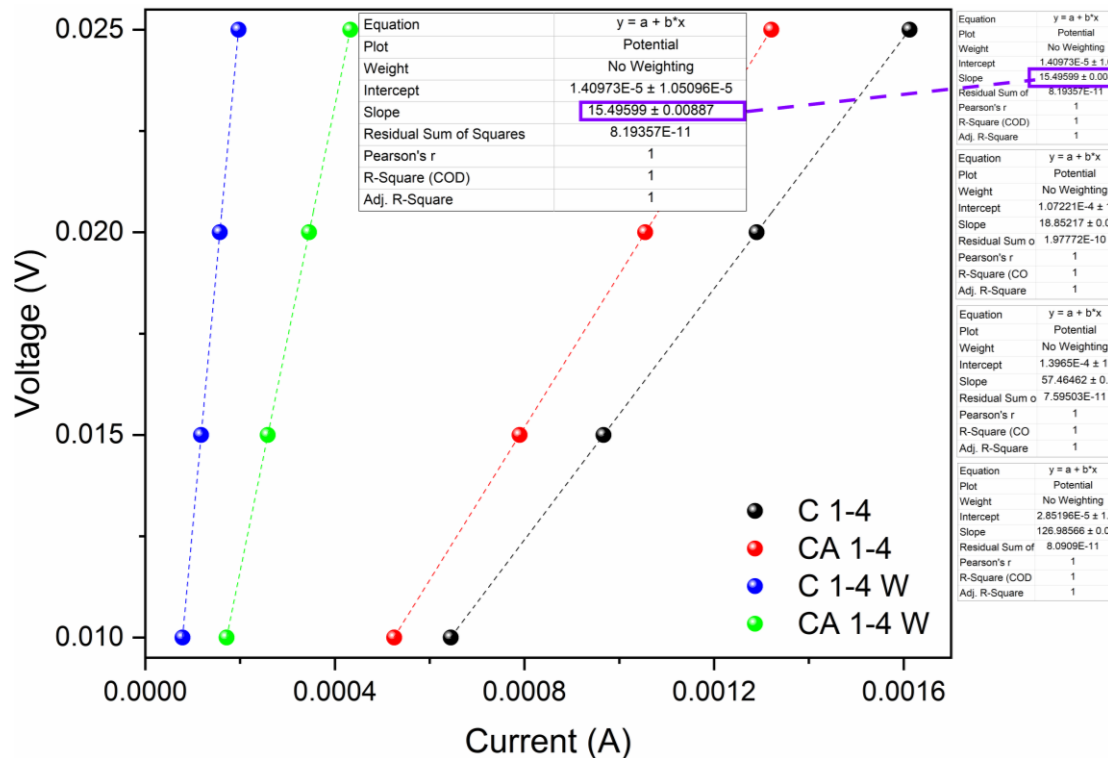


Figure A3: Resistance of C 1-4 derived samples.

The results of this graph shows that the resistance of C 1-4 is 15.496 Ω . Substituting this value into the previous equation, the resistivity can be determined:

$$\rho = \frac{R \cdot W \cdot T}{L} = \frac{15.496 \Omega \cdot 17.76 \cdot 10^{-3} m \cdot 1.71 \cdot 10^{-3} m}{2.68 \cdot 10^{-3} m} = 0.176 \Omega \cdot m$$

Considering the electrical conductivity is the inverse of the resistivity, then:

$$\sigma = \frac{1}{\rho} = \frac{1}{0.176 \Omega \cdot m} = \mathbf{5.7 S/m}$$

Annex 4: Cyclic voltammetry results of the prepared ACs

This annex presents a comparison of the voltammograms of different final ACs with and without albumin and WS₂ nanosheets. To enable easier visualisation, the conductivity of the cells has been calculated (current divided by scan rate). For the comparison, voltammograms of the C 1-4 set of samples will be shown at scan rates of 2 and 40 mV/s.

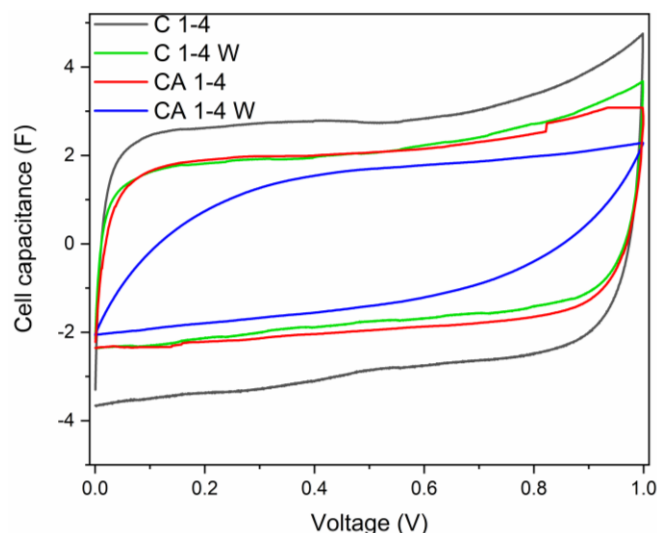


Figure A4: Voltammograms of the C 1-4 set of samples at a scan speed of 2 mV/s.

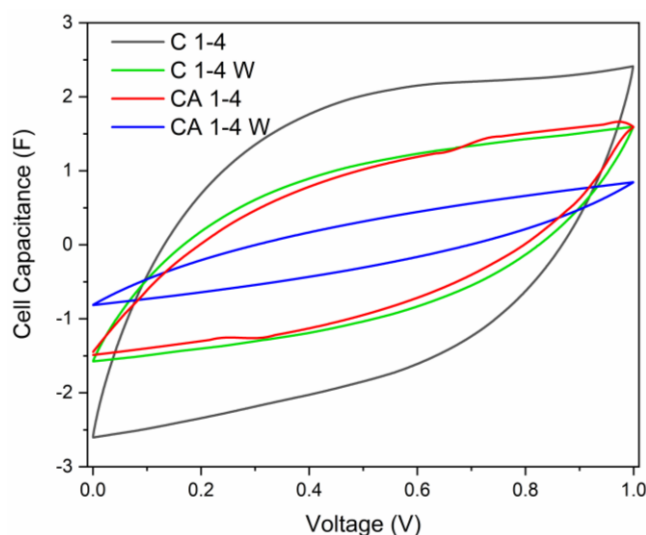


Figure A5: Voltammograms of the C 1-4 set of samples at a scan speed of 40 mV/s.

It can be observed from these figures that none of the samples, independently of the presence or absence of albumin or /and WS₂, exhibit any redox peaks (see Figure 3.3 for an example of a voltammogram with redox peaks).

Annex 5: Determination of specific capacitance through cyclic voltammetry experiments

Specific capacitance can be calculated from CV experiment by using Equation A3:

$$C_{sp} = \frac{2 \cdot \int_{V_{Max}}^{V_{Min}} I dV}{\Delta V \cdot m \cdot v} \quad \text{Equation A3}$$

Where C_{sp} is the specific capacitance of the material at a determined scan rate, measured in F/g, $\int_{V_{Max}}^{V_{Min}} I dV$ refers to the integration of the discharge curve of the voltammogram (since the discharge step is the one that determines the capacitance of the material), ΔV is the working voltage window provided by the electrolyte (in the case of H_2SO_4 aqueous electrolyte, the maximum voltage is 1V and the minimum is 0 V, therefore, $\Delta V = 1\text{V}$); m is the amount of active material (activated carbon, i.e., 60% of the total electrode, as explained in Section 4.3.3) of the lightest electrode (the one that will work at its full potential) and v stands for the different scan rates, ranging from 1 mV/s to 100 mV/s.

For this example, the capacitance of the sample C 1-4 measured at 40 mV/s will be calculated. The first step is the determination of the integral of the discharge curve. With this purpose, the discharge curve of the fifth voltammetry cycle (assuming at this point the supercapacitor reaches a stable behaviour) is plotted and the integral is calculated using OriginPro®, as Figure A6 shows:

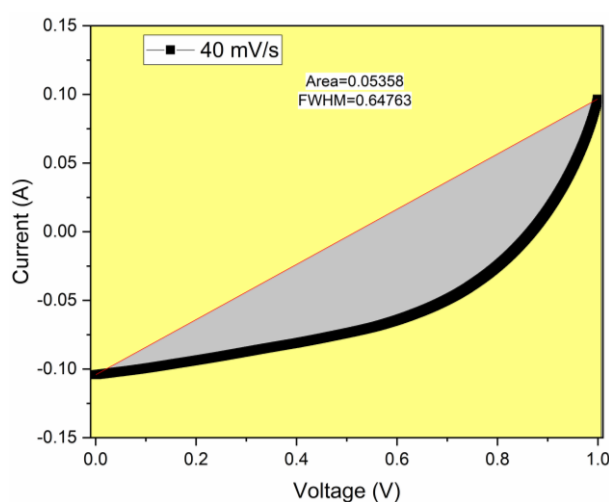


Figure A6: Integration of the discharge curve of C 1-4 at 40 mV/s.

The area resulting from the integration is $0.05358 \text{ A} \cdot \text{V}$. Knowing that $\Delta V = 1 \text{ V}$ and $v = 0.04 \text{ V/s}$, the last step to calculate the capacitance of the sample at this rate is the determination of the active material mass.

Electrodes were prepared trying to obtain a constant electrode mass of 50 mg for each electrode. In the case of C 1-4, the mass of the first electrode was 49.5 mg and the second, 50.6 mg. As explained before, we will use the mass of the lightest electrode for capacitance calculation. Before using this value, it must be remembered that electrodes are composed of 60% activated carbon, 30% binder and 10% of carbon black. For this reason, the mass of active material is 60% of the mass of the total electrode. Knowing this value, C_{sp} can be determined:

$$C_{sp} = \frac{2 \cdot 0.05358 \text{ A} \cdot \text{V}}{1 \text{ V} \cdot 0.6 \cdot (49.5 \cdot 10^{-3}) \text{ g} \cdot 0.04 \text{ V/s}} = 90.2 \frac{\text{A}}{\text{g} \cdot \text{V/s}} = 90.2 \text{ F/g}$$

yielding a capacitance of approximately 90 F/g, the same as depicted in Figure 4.30. Following this procedure, the capacitance of all samples at different scan rates can be determined. Figure A7 presents the capacitance values of C 1-4 for the selected scan rates:

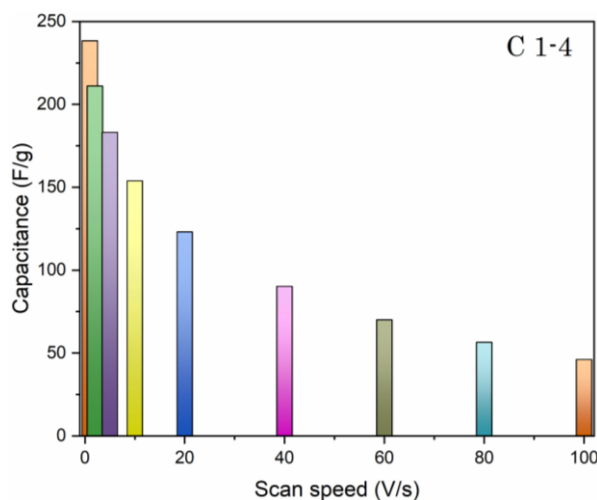


Figure A7: Capacitances of C 1-4 at different scan rates.

Annex 6: Determination of electrochemical parameters through galvanostatic cycling

In order to calculate the electrochemical parameters of a supercapacitor, it is necessary to understand first the different parts of a chronopotentiogram (voltage vs. time plot):

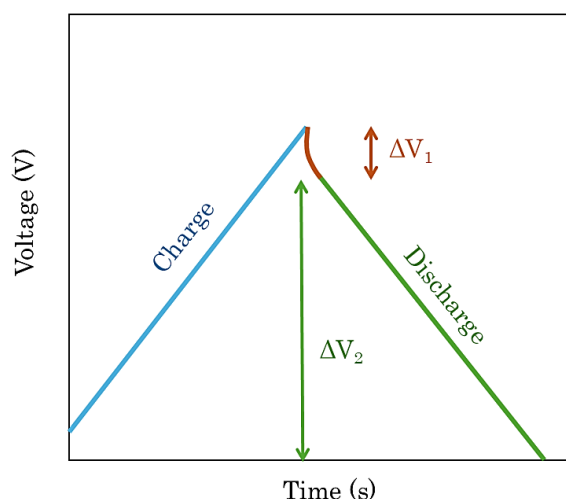


Figure A8: Parts of a voltage vs. time graph representing charge and discharge cycles.

As Figure A8 shows, three different parts can be observed in this graph. The first one, represented in blue, is a constant voltage increase with increasing time, representative of the charging process. After reaching the maximum voltage (1V in the case of H₂SO₄), a non-linear voltage loss appears (orange curve), which is named ΔV_1 , representing losses due to internal resistance (ohmic drop), followed by a linear process of voltage decrease with time, which is known as the discharge process, with its associated voltage difference, ΔV_2 , due to the capacitive process.

After understanding the different processes taking place in charge/discharge cycles, the specific capacitance of each electrode can be calculated with Equation A4:

$$C_{sp} = \frac{2 \cdot I \cdot t_d}{\Delta V_2 \cdot m} \quad \text{Equation A4}$$

Where all the parameters have been explained in the previous Annex, with the exception of t_d , being the discharge time, measured in s, and ΔV_2 being the voltage difference of the capacitive process in the discharge stage.

Now, with the experimental data of C 1-4 at a current of 40 mA, displayed in Figure A9, all parameters can be determined:

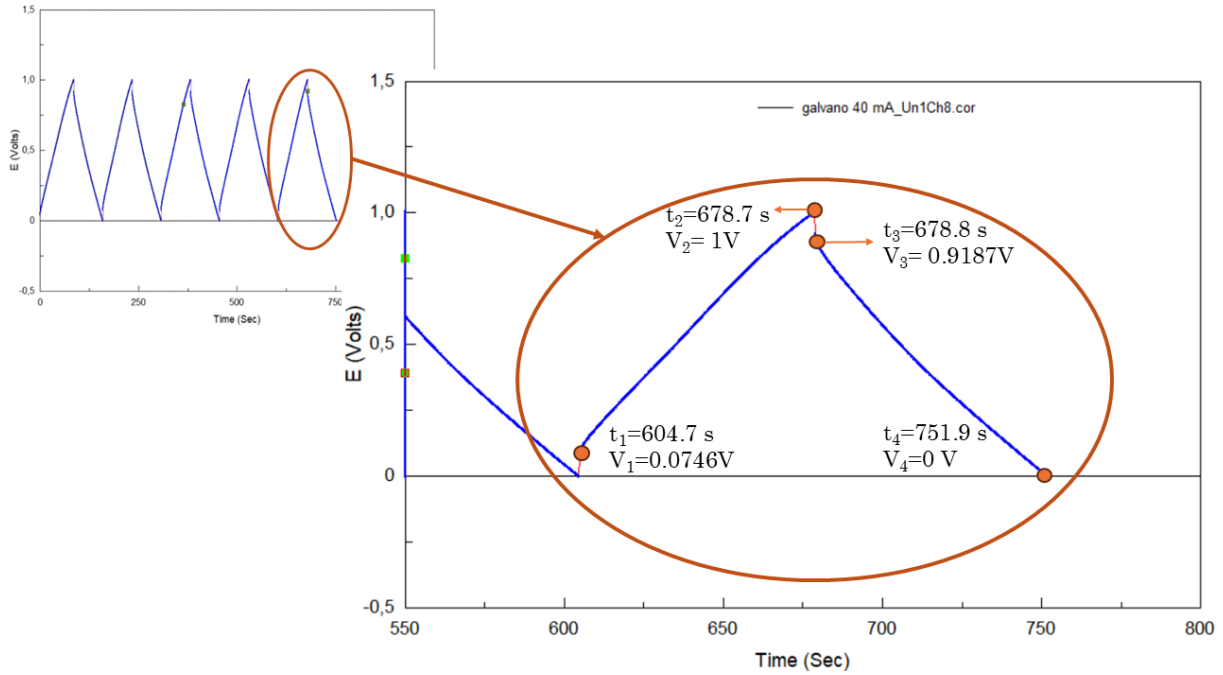


Figure A9: Experimental galvanostatic curve of C 1-4 at 40 mA.

From this graph, points 1 and 2 belong to the charging process, while points 3 and 4 correspond to the discharge part. For this reason, the voltage gap between points 2 and 3 is the corresponding to the internal resistance causing voltage loss. According to this, charging and discharging time can be calculated as it follows:

$$t_c = t_2 - t_1 = 678.7 - 604.7 = 74 \text{ s}$$

$$t_d = t_4 - t_3 = 751.9 - 678.8 = 73.1 \text{ s}$$

And, consequently, supercapacitor efficiency can be determined as the relationship between discharge and charge time:

$$Efficiency (\%) = \frac{t_d}{t_c} \cdot 100 = \frac{73.1}{74} \cdot 100 = 99 \%$$

Moreover, the parameters ΔV_1 and ΔV_2 , which will be further used, can also be determined:

$$\Delta V_1 = V_3 - V_2 = 1 - 0.9187 = 0.0813 \text{ V}$$

$$\Delta V_2 = V_3 - V_4 = 0.9187 - 0 = 0.9187 \text{ V}$$

Meaning that approximately 8.13% of the total voltage is lost due to internal resistance when working at a current of 40 mA. After the determination of these parameters, specific capacitance can be calculated:

$$C_{sp} = \frac{2 \cdot I \cdot t_d}{\Delta V_2 \cdot m} = \frac{2 \cdot 0.04 \text{ A} \cdot 73.1 \text{ s}}{0.9187 \text{ V} \cdot 0.6 \cdot (49.5 \cdot 10^{-3}) \text{ g}} = 214.3 \text{ F/g}$$

With this procedure, capacitances can be determined for all samples for a wide range of currents, as presented in Figure 4.32. Furthermore, the energy and power densities of the whole electrochemical cell (not of the single electrodes) can be calculated with Equation A5 and Equation A6:

$$E = \frac{1}{2} \cdot C_{sp_{cell}} \cdot V^2 \quad \text{Equation A5}$$

Where V is the maximum voltage that the electrolyte can reach (i.e. 1 V) and $C_{sp_{cell}}$ is the specific capacitance of the cell, which is $\frac{1}{4}$ of the specific capacitance of a single electrode, as shown in Section 4.4.2.1. Consequently:

$$E = \frac{1}{2} \cdot C_{sp_{cell}} \cdot V^2 = \frac{1}{2} \cdot \left(\frac{214.3}{4} \right) \text{ F/g} \cdot 1 \text{ V}^2 = 26.79 \frac{\text{J}}{\text{g}} = 7.44 \frac{\text{W} \cdot \text{h}}{\text{kg}}$$

Then, power density of the electrochemical cell can be determined as:

$$P = \frac{V^2}{4 \cdot ESR \cdot m} \quad \text{Equation A6}$$

In this case, the used mass is the sum of the active mass of the two electrodes. The rest of the parameters are known, except ESR , which is the equivalent series resistance (ohmic drop), measured in ohms (Ω). ESR represents the voltage loss due to internal resistance and can be calculated by Equation A7:

$$ESR = \frac{\Delta V_1}{2 \cdot I} \quad \text{Equation A7}$$

$$ESR = \frac{\Delta V_1}{2 \cdot I} = \frac{0.0813 \text{ V}}{2 \cdot 0.04 \text{ A}} = 1.016 \Omega$$

$$P = \frac{V^2}{4 \cdot ESR \cdot m} = \frac{1 \text{ V}^2}{4 \cdot 1.016 \Omega \cdot (0.6 \cdot (49.5 + 50.6) \cdot 10^{-6}) \text{ kg}} = 4093.5 \text{ W/kg}$$

With this calculation, a Ragone plot can be built representing the variation of energy and power densities through a range of currents as presented in Figure 4.33. Table A4 presents the calculation of all electrochemical parameters of the symmetric supercapacitor built with C 1-4 electrodes through the measuring range of 1-120 mA:

Table A4: Electrochemical parameters of C 1-4.

Current	Efficiency	C_{sp} electrode	Retention	Cell energy density	ESR	Cell power density
(A)	(%)	(F/g)	(%)	(W · h/kg)	(Ω)	(W/kg)
0.001	70%	275.35	100%	9.56	1.455	2859
0.002	85%	267.28	97%	9.28	1.837	2264
0.003	90%	261.45	95%	9.08	1.312	3172
0.004	92%	257.22	93%	8.93	1.300	3200
0.005	94%	253.94	92%	8.82	1.287	3232
0.01	97%	242.19	88%	8.41	1.272	3270
0.015	98%	234.52	85%	8.14	1.138	3656
0.02	98%	228.76	83%	7.94	1.120	3715
0.025	98%	223.82	81%	7.77	1.101	3777
0.03	98%	221.70	81%	7.70	1.039	4005
0.035	98%	217.76	79%	7.56	1.004	4144
0.04	99%	214.33	78%	7.44	1.016	4093
0.045	98%	211.21	77%	7.33	1.020	4078
0.05	98%	207.90	76%	7.22	1.028	4047
0.06	99%	202.97	74%	7.05	0.971	4284
0.07	99%	198.16	72%	6.88	0.958	4343
0.08	99%	192.72	70%	6.69	0.974	4272
0.09	98%	188.32	68%	6.54	0.970	4291
0.1	96%	186.29	68%	6.47	0.933	4457
0.11	96%	182.72	66%	6.34	0.879	4735
0.12	98%	177.74	65%	6.17	0.937	4441

Annex 7: Determination of ring's collection efficiency

In order to determine the electrocatalytic parameters, it is necessary to calculate first the collection efficiency of the ring. This parameter typically ranges from 30 to 40%, and it can be calculated using Equation A8, a formula based on the geometry of the equipment:

$$N = 1 - F\left(\frac{\alpha}{\beta}\right) + \beta^{\frac{2}{3}} \cdot (1 - F(\alpha)) - (1 + \alpha + \beta)^{\frac{2}{3}} \cdot \left(1 - F\left(\frac{\alpha}{\beta}\right) \cdot (1 + \alpha + \beta)\right)$$

Equation A8

Being N the maximum collection efficiency of the ring, and:

$$F(x) = \frac{3^{\frac{1}{2}}}{4\pi} \cdot \ln \frac{\left(1 + x^{\frac{1}{3}}\right)^3}{1 + x} + \frac{3}{2\pi} \cdot \arctan \left(\frac{2 \cdot x^{\frac{1}{3}} - 1}{3^{\frac{1}{2}}} \right) + \frac{1}{4}$$

Equation A9

$$\alpha = \left(\frac{r_2}{r_1}\right)^3 - 1$$

Equation A10

$$\beta = \left(\frac{r_3}{r_1}\right)^3 - \left(\frac{r_2}{r_1}\right)^3$$

Equation A11

Where r_1 , r_2 and r_3 are the internal radiuses of the ring and disk. Figure A10 shows the values of these radiuses, as well as the N value supplied by the manufacturer.

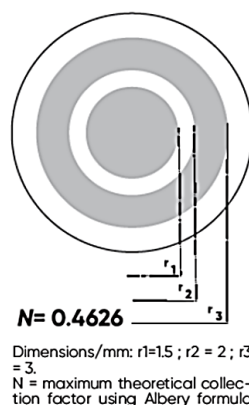


Figure A10: Geometrical RRDE electrode values.

Therefore, the geometrical parameters can be calculated, as shown in Table A5:

Table A5: Geometrical parameters for the determination of collection efficiency.

Parameter	Value	Parameter	Value	Parameter	Value
r_2/r_1	1.33	β	5.63	$F(\alpha)$	0.733
r_3/r_1	2	α/β	0.243	$F(\alpha/\beta)$	0.489
α	1.37	$(\alpha/\beta) \cdot (1+\alpha+\beta)$	1.95	$F[(\alpha/\beta) \cdot (1+\alpha+\beta)]$	0.777

Therefore:

$$N = 1 - 0.489 + 5.63^{\frac{2}{3}} \cdot (1 - 0.733) - (1 + 1.37 + 5.63)^{\frac{2}{3}} \cdot (1 - 0.777) = 0.4616$$

Meaning the collection efficiency of the ring is approximately 46%. Nevertheless, an experimental determination of N can be carried out as well. For this determination, a 100 mL solution of $K_4Fe(CN)_6 \cdot 3H_2O$ ($5 \cdot 10^{-3}M$) in 0.5 M KCl was prepared and a glassy carbon electrode was used. This solution was used as electrolyte and a RRDE experiment was carried out with the same experimental parameters as explained in Section 3.2.14.1. In this experiment, the ring and disk current were recorded with voltage under different rotation speeds (600, 1600 and 2600 rpm), until constant current was reached, as shown in Figure A11.

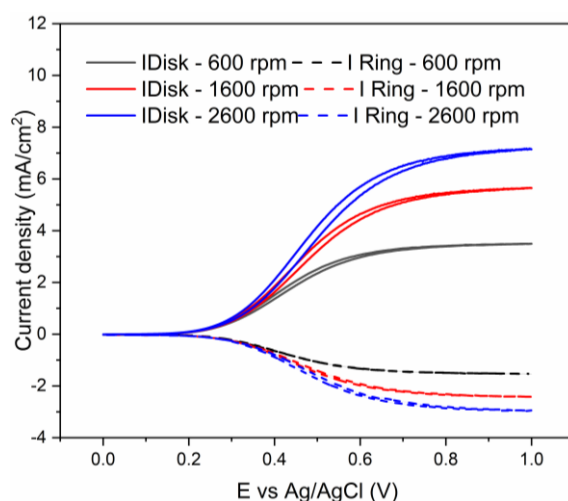


Figure A11: Ring and disk currents at different rotation speeds.

With these data, the experimental collection efficiency can be calculated by determining the absolute value of the division of disk current by the ring current, as shown in Table A6:

Table A6: Collection efficiency at different rotation speeds.

Rotation speed (rpm)	Collection efficiency (%)
600	43.67
1600	42.78
2600	41.35

With an average collection efficiency of 42.6%, slightly lower than the calculated maximum theoretical value.

Annex 8: Calculation example of RRDE parameters

After the cyclic voltammetry/chronoamperometry experiment, the currents of both ring and disk are obtained, as plotted in the following example:

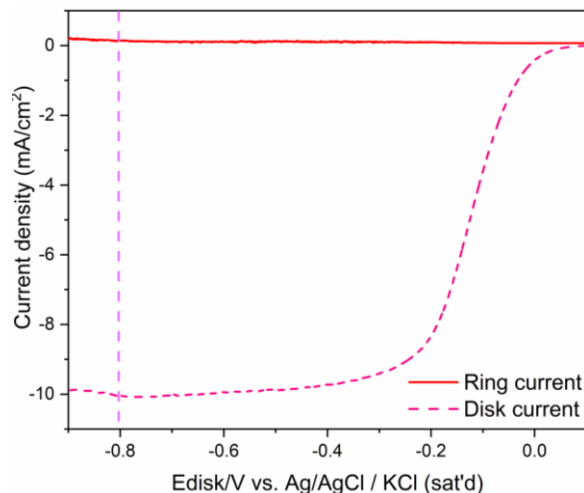


Figure A12: Ring and disk currents of the Pt/C electrode.

The ring and disk current values that will be used are the ones obtained at -0.9 V (see purple line), as constant current values are obtained at this potential. Furthermore, the determination of electrocatalytic parameters can be carried out using Equation A12 and Equation A13:

$$n = \frac{4 \cdot I_{Disk}}{I_{Disk} + (I_{Ring})/N} \quad \text{Equation A12}$$

$$\% HO_2^- = \frac{2 \cdot (I_{Ring})/N}{I_{Disk} + (I_{Ring})/N} \cdot 100 \quad \text{Equation A13}$$

With n being the number of transferred electrons and N , the empirical collection efficiency (0.426). For the presented example, the values of ring and disk current (absolute value) are 0.144 and 10.03 mA/cm², respectively. Therefore:

$$n = \frac{4 \cdot 10.03}{10.03 + (0.144)/0.426} = 3.87 \text{ electrons}$$

$$\% HO_2^- = \frac{2 \cdot (0.144)/0.426}{10.03 + (0.144)/0.426} \cdot 100 = 6.5\%$$

Revealing that a glassy carbon electrode coated with a Pt-C catalyst can transfer an average of 3.87 electrons in the ORR reaction producing OH⁻ (4 electron pathway), while only a 6.5% of oxygen is converted to HO₂⁻ (2 electron pathway). The results of the rest of the samples are presented in Section 4.4.3.1.

Annex 9: SEM micrographs of the prepared fibres

Figure A13 shows the effect of polymer concentration and distance to collector on the prepared electrospun PLLA fibres. PLLA fibres spun with polymer concentrations ranging from 4 to 12% w/v, at distances from needle to collector of 12 and 16 cm (all with an electrospinning time of 30 min) are presented:

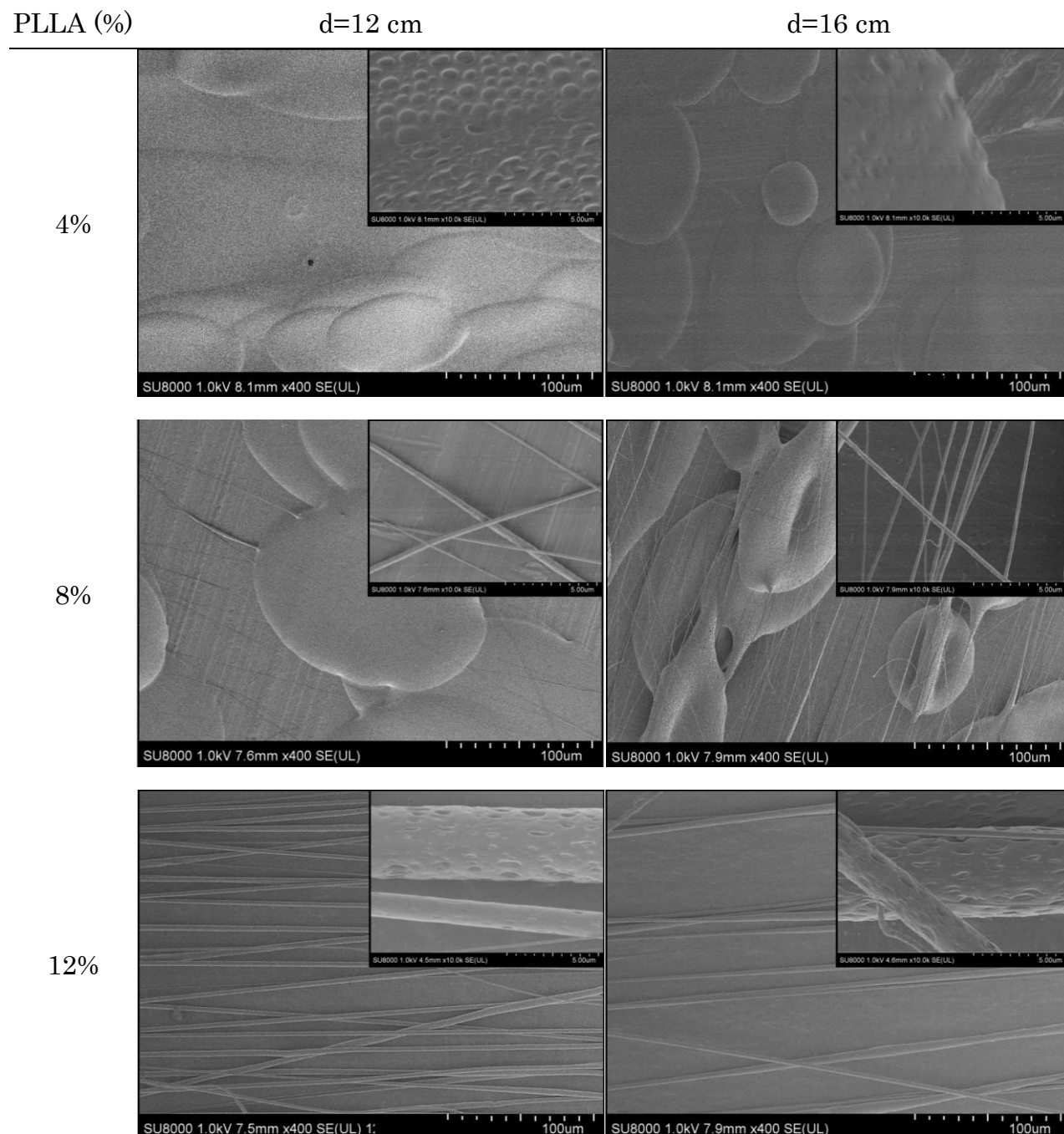


Figure A13: SEM micrographs of PLLA 4%, 8% and 12% w/v and at at needle-to-collector distances of 12 and 16 cm are shown.

Additionally, Figure A14 assesses the effect of electrospinning time, as well as WS₂ nanosheet presence. For this purpose, fibres prepared using a fixed PLLA concentration (10% w/v) under different electrospinning times (with a distance of 12 cm), and with and without WS₂ addition are presented:

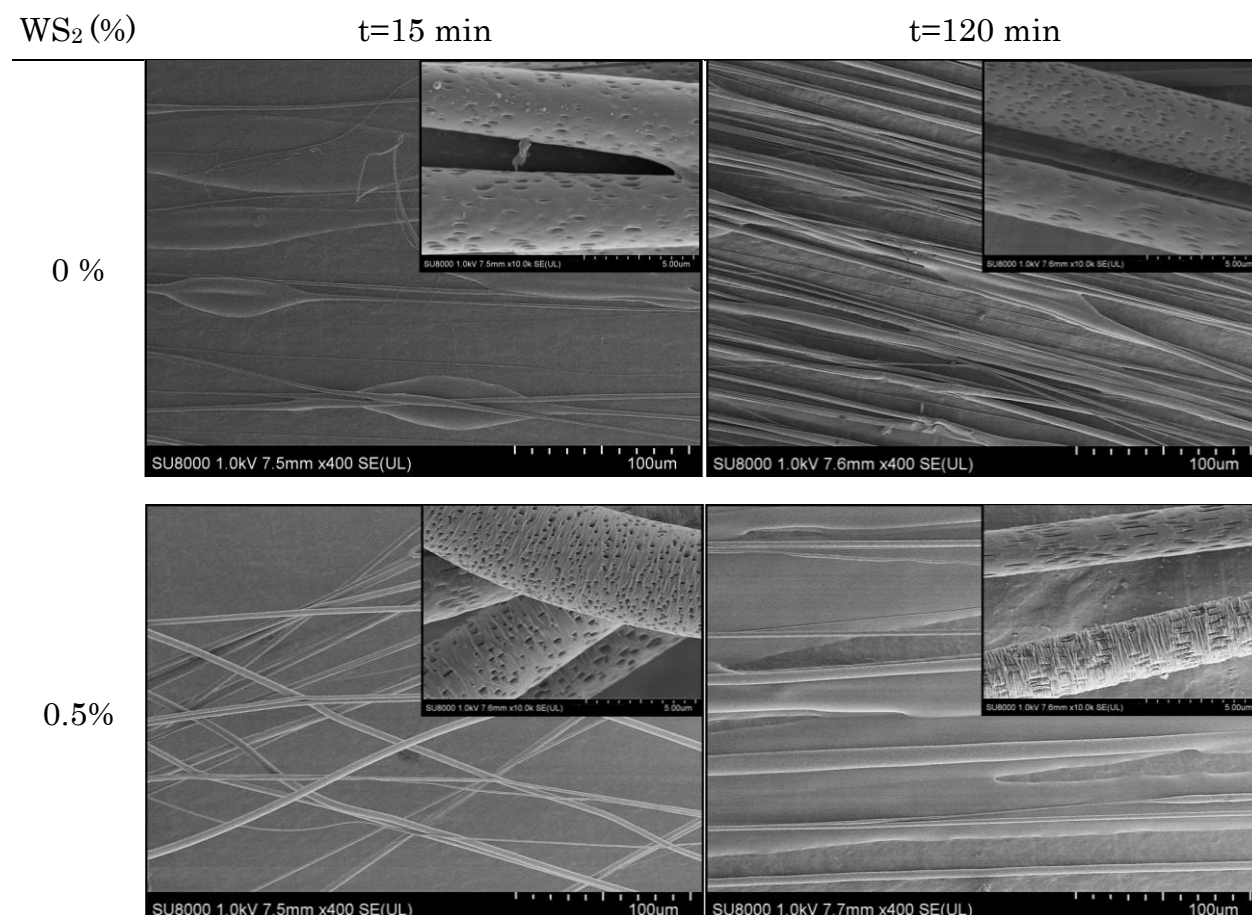


Figure A14: SEM micrographs of PLLA and PLLA-W fibres produced at electrospinning times of 15 and 120 minutes.

All the conclusions regarding these figures have been presented in Section 5.3.2.2

Annex 10: Calculation of AC & WS₂ concentrations via TGA

From the thermograms of the fibres displayed in Figure 5.11, and also knowing the thermal stability of the carbons presented in Figure 4.26, the final carbon concentration inside the fibres can be calculated, and also WS₂ concentration can be verified. In order to determine WS₂ concentration within the produced fibres, a TGA of pure WS₂ was first performed. The results of this experiment are displayed in Figure A15:

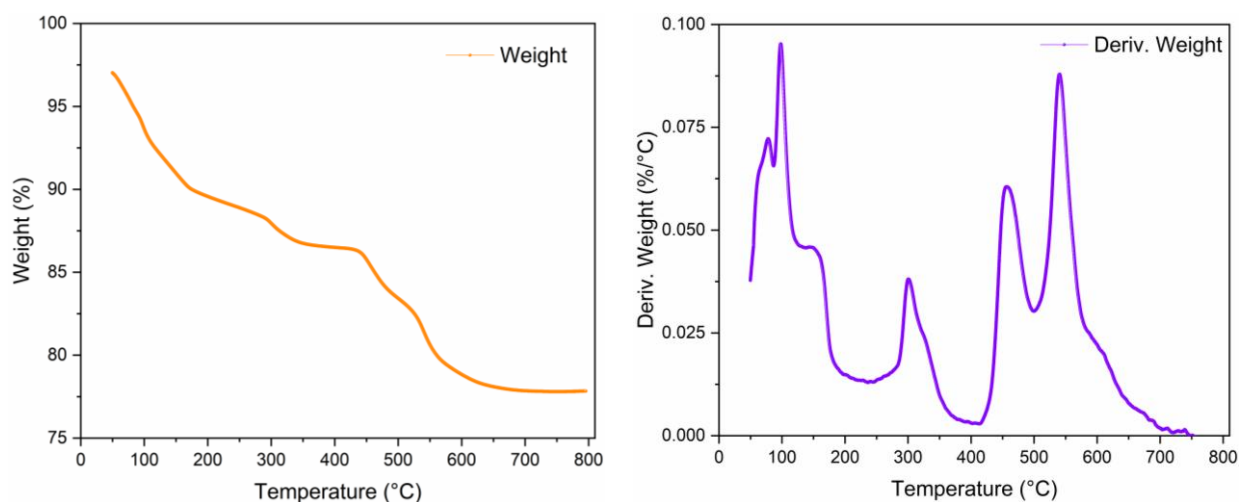


Figure A15: TGA and DTG of WS₂ nanosheets under N₂ atmosphere.

With this data, the stability of each material is presented in Table A7:

Table A7: Thermal stability of PLLA fibres and its individual components.

Sample	PLLA	PLLA-AC	PLLA-W	PLLA-AC-W	C 1-4	WS ₂
Residue (%) at 800°C	2.2	9.9	2.6	10.3	86	78

The concentration of AC (x) in a PLLA-AC fibre can be calculated using the following equation:

$$PLLA\ AC_{residue} = x \cdot AC_{residue} + (1 - x) \cdot PLLA_{residue}$$

Using the data from Table A7:

$$9.9 = x \cdot 86 + (1 - x) \cdot 2.2 \rightarrow x = 9.2\%$$

Therefore, the AC concentration within the fibre is 9.2 % w/w. Using this same equation with the data from PLLA-W, the WS₂ concentration (y) in the PLLA-W fibre can be calculated as:

$$PLLA\ W_{residue} = y \cdot WS2_{residue} + (1 - y) \cdot PLLA_{residue}$$

$$2.6 = y \cdot 78 + (1 - y) \cdot 2.2 \rightarrow y = 0.5\%$$

Having a nanosheet concentration of 0.5% w/w, exactly as indicated in the experimental procedure.

Using the data from PLLA-W-AC, the concentrations of AC and WS₂ are the same as the ones presented before, indicating a constant additive concentration throughout the whole sample set.

Annex 11: Determination of the nucleating activity using the Dobрева model

A straightforward method for assessing the nucleating capability of a material is the Dobрева-Gutzow method, which correlates the nucleating activity (ϕ) with the crystallisation temperature using Equation A14:

$$\phi = \frac{B'}{B} \quad \text{Equation A14}$$

Here, B is a parameter related to homogeneous nucleation, while B' stands for this same parameter during heterogeneous nucleation. If the substrate is extremely active the value of B' (and, therefore ϕ) will approach 0, while for inert particles ϕ approaches 1 ($B \approx B'$). For this case study, B is related to the nucleation activity of pure PLLA, while B' represents the nucleation activity of the particle-doped fibres. Both parameters can be experimentally determined using Equation A15:

$$\ln(\phi) = A - \frac{B(\text{ or } B')}{\Delta T_c^2} \quad \text{Equation A15}$$

With ϕ being the cooling rate ($^{\circ}\text{C}/\text{min}$), A being a constant, and ΔT_c standing for the degree of supercooling, calculated as:

$$\Delta T_c = T_m^0 - T_c \quad \text{Equation A16}$$

Where T_c is the crystallisation temperature ($^{\circ}\text{C}$), and T_m^0 the equilibrium melting point of PLLA, found to be 195°C [561]. Therefore, a plot of $\ln(\phi)$ versus $\frac{1}{\Delta T_c^2}$ using the T_c from Table 5.4 allows the calculation of B' (or B), as shown in Figure A16.

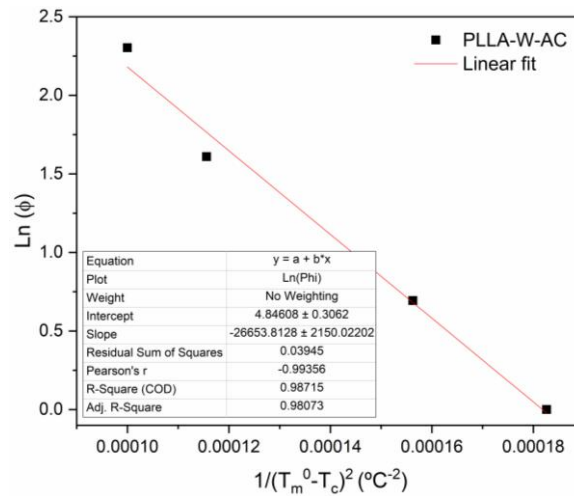


Figure A16: Dobрева-Gutzow linear fit of the PLLA-W-AC crystallisation process carried out at different cooling rates.

From which, the negative value of the slope (26653) reveals the value of B'. If this same procedure is applied using the data of PLLA, the slope (125920) allows the calculation of B.

Finally, considering the values of both B and B', the nucleation activity of PLLA-W-AC can be calculated as it follows:

$$\varphi = \frac{26653}{125920} = 0.211$$

This significantly low value indicates that the nucleating activity of the inserted particles is substantially high.

Annex 12: Calculation of the crystallisation activation energy using Kissinger model

To evaluate the crystal growth ability of the prepared materials, it is first necessary to calculate the crystallisation activation energy. For this purpose, the Kissinger model offers a straightforward method using Equation A17:

$$\ln\left(\frac{\phi}{T_c^2}\right) = A - \frac{\Delta E}{RT_c} \quad \text{Equation A17}$$

With A being a constant, ΔE the crystallisation activation energy (J/mol), R is the universal gas constant (J/mol·K) and T_c is the crystallisation temperature, measured in K.

Using the data available in Table 5.4, a plot of $\ln\left(\frac{\phi}{T_c^2}\right)$ versus $1/T_c$ can be constructed (see Figure A17):

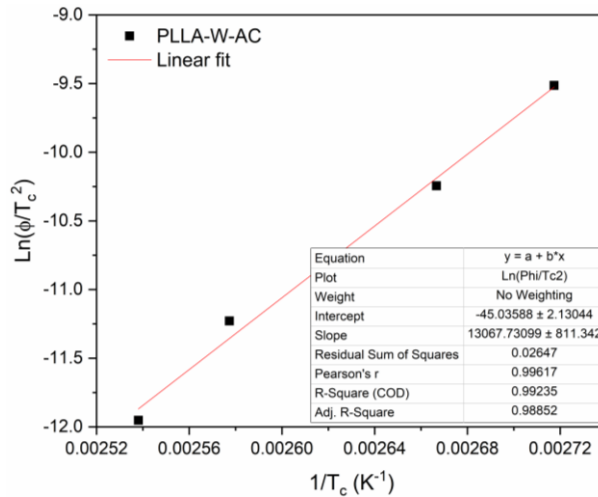


Figure A17: Kissinger plot for PLLA-W-AC crystallisation.

From this plot, the activation energy can be obtained from the negative value of the slope (-13067) of the linear fit, according to the following equation:

$$13068 = \frac{\Delta E}{R} \rightarrow \Delta E = -8.314 \cdot 13068 = -108.7 \text{ kJ/mol}$$

Yielding the values presented in Section 5.4.1.3.

Annex 13: Calibration curves of dyes

For each dye, solutions of 0.1, 0.5, 1, 5, 10, 15 and 20 ppm were prepared and measured in different wavelength ranges in order to find characteristic peaks of each molecule and create a calibration curve. In the case of Congo Red, two differentiating peaks were observed at 342 and 500 nm, as shown in the UV-Vis spectra in Figure A18:

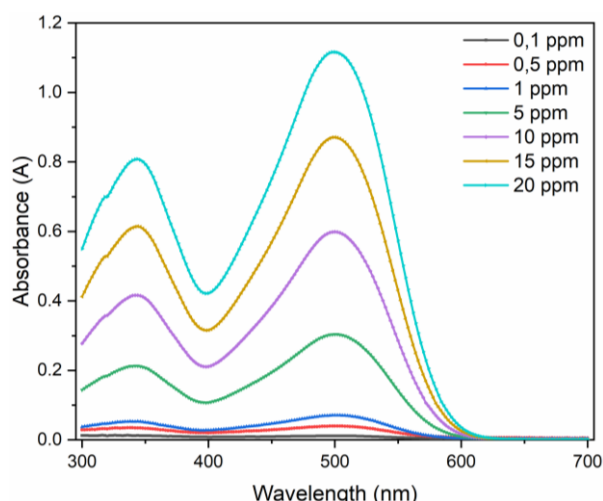


Figure A18: UV-Vis spectra of Congo Red at different aqueous solution concentrations.

As explained in Section 3.2.15, the concentration of a solution can be calculated according to Beer-Lambert law. However, this law is only applicable for absorbance values lower than 1. For this reason, the fitting equation for Congo Red was determined using the 342 nm peak, obtaining the absorbance values for the different solution concentrations at the maxima this peak, and after plotting these values versus dye concentrations a linear fit was obtained, defined by this equation:

$$C = 24.4989 * A$$

Where C is the dye concentration, measured in ppm and A is the absorbance. This same procedure was followed for the rest of the dyes. First, for Methyl Orange, it was found that there were two prominent peaks at 274 and 466 nm (see Figure A19). The first one presents absorbances lower than 1, which makes it applicable for every concentration, but exhibits negligible absorbance values when the dye concentration is 1 ppm or lower. On the other hand, the peak at 466 nm exceeds 1 absorbance unit at concentrations over 15 ppm, but presents more intense peaks at lower concentrations. For this reason, two linear fittings were calculated, one

for concentrations of 5 ppm or higher (274 nm), and another one for concentrations of 5 ppm or lower (466 nm). Both fittings are presented in Figure A20.

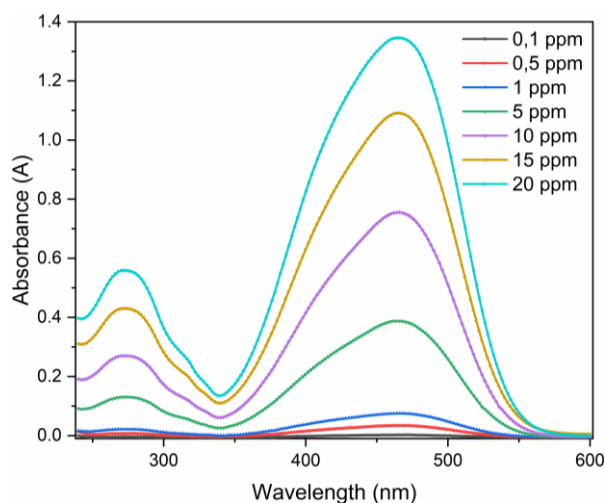


Figure A19: UV-Vis spectra of Methyl Orange at different aqueous solution concentrations.

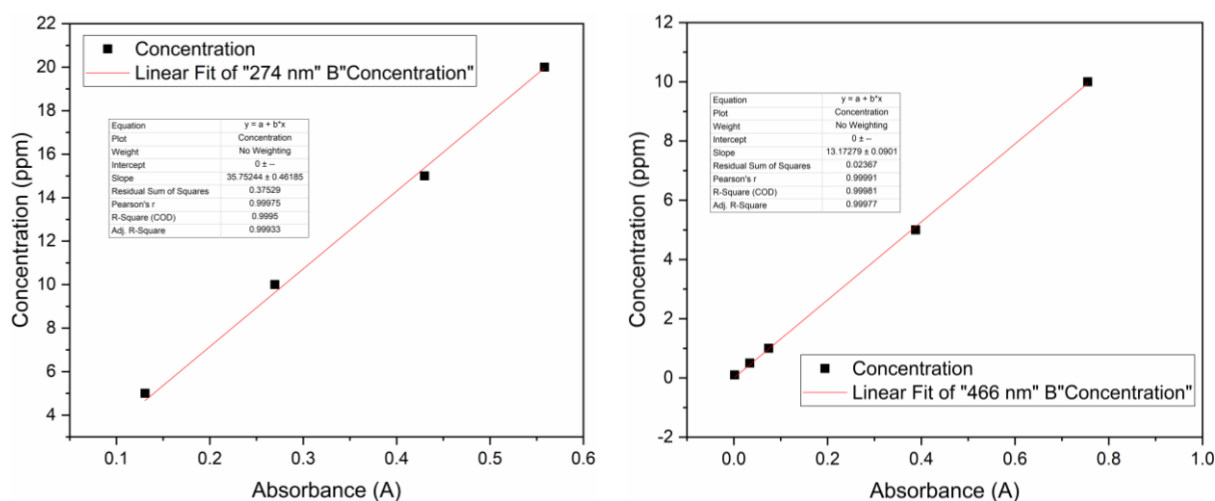


Figure A20: Linear fitting for the different Methyl Orange concentrations.

In the case of cationic dyes, the same procedure was applied, as two different linear fittings had to be built according to the obtained spectra:

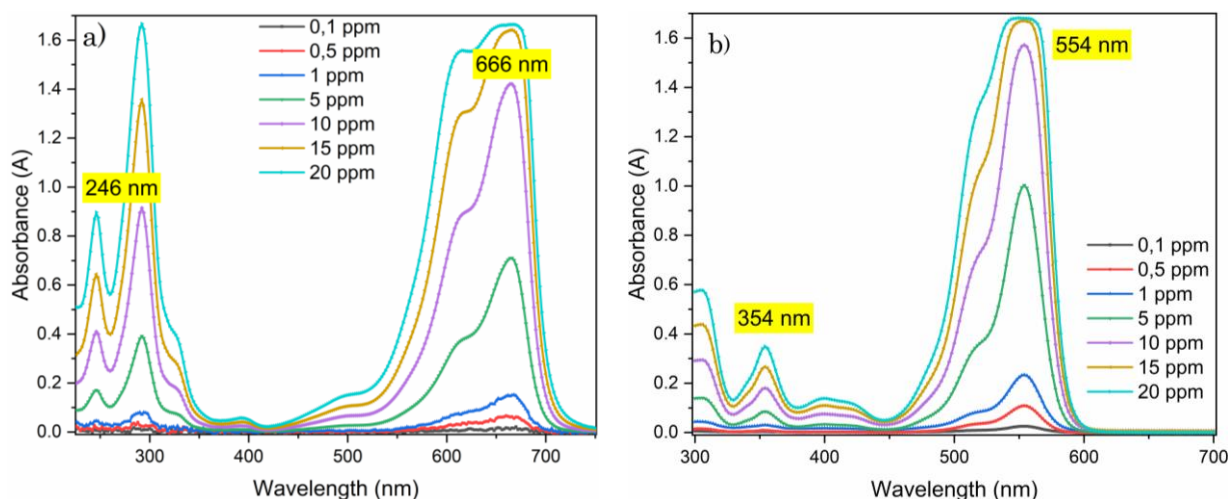


Figure A21: UV-Vis spectra of a) Methylene Blue and b) Rhodamine B at different aqueous solution concentrations.

Finally, linear fittings of the prepared dyes are summarised in the following table:

Table A8: Linear fitting equations for all the studied dyes.

Dye	Concentration range	
	$C \leq 5 \text{ ppm}$	$C \geq 5 \text{ ppm}$
Congo Red	$C = 24.50 \cdot A$ (at 344 nm)	
Methyl Orange	$C = 13.17 \cdot A$ (at 466 nm)	$C = 35.75 \cdot A$ (at 274 nm)
Methylene Blue	$C = 7.03 \cdot A$ (at 666 nm)	$C = 20.73 \cdot A$ (at 246 nm)
Rhodamine B	$C = 5.04 \cdot A$ (at 554 nm)	$C = 56.83 \cdot A$ (at 354 nm)

Annex 14: Determination of adsorption kinetics

Various kinetic models were analysed for each dye in order to determine the adsorption kinetics. The studied models are the following:

Pseudo 1st order:

This kinetic model assumes that the adsorption process is reversible and mainly controlled by a physical mechanism (physisorption). It is characterised by Equation A18:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 \cdot t \quad \text{Equation A18}$$

Where Q_e is the adsorption capacity at equilibrium (mg/g), Q_t is the adsorption capacity at a measured time t (min) and k_1 is the kinetic constant (min^{-1}).

Given a dataset of Q_t versus time, as the one presented in Table A9:

Table A9: Kinetic data for Methyl Orange adsorption.

Time (min)	Dye concentration (ppm)	Removal (%)	Q_t (mg/g)
1	18.88	5.62%	19.12
2	15.74	21.32%	72.51
3	12.48	37.59%	127.87
4	10.66	46.68%	158.76
5	9.14	54.28%	184.63
10	6.33	68.33%	232.41
15	3.77	81.14%	275.97
30	2.22	88.92%	302.44
60	1.62	91.90%	312.57
120	0.95	95.23%	323.92
240	0.74	96.31%	327.59
360	0.74	96.31%	327.59
480	0.48	97.62%	332.04
1440	0.00	100.00%	340.14

Where the value of Q_e is 340.14 mg/g.

Furthermore, the value of $\ln(Q_e - Q_t)$ can be calculated for different times and plotted against time, yielding Figure A22:

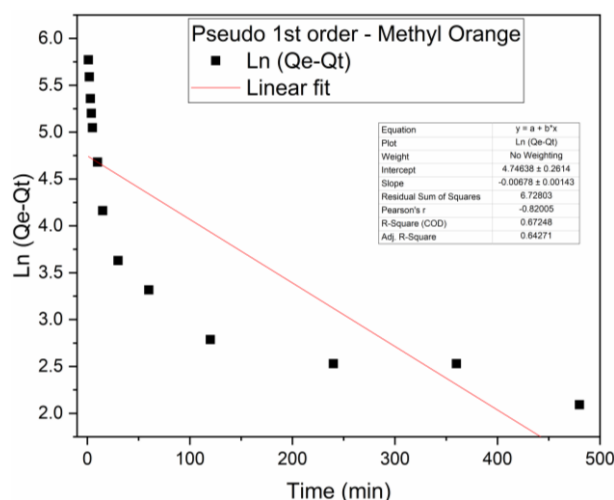


Figure A22: Pseudo 1st order kinetic fit for Methyl Orange adsorption.

The negative value of the slope (0.00678 min^{-1}) represents the kinetic constant, k_1 , and the intercept (4.746) can be used to determine the theoretical Q_e using the following formula:

$$\ln Q_e = 4.746 \rightarrow Q_e = 115.12 \text{ mg/g}$$

This value substantially differs from the experimentally calculated Q_e , and the correlation coefficient $R^2=0.6725$ indicates a poor fit. Therefore, this process cannot be accurately described by the pseudo 1st order kinetic model.

Pseudo 2nd order:

The pseudo 2nd order kinetic model describes adsorption based on a chemical interaction between adsorbent and adsorbate (chemisorption, irreversible process). It is represented by Equation A19:

$$\frac{t}{Q_t} = \frac{1}{Q_e} \cdot t + \frac{1}{k_2 \cdot Q_e^2} \quad \text{Equation A19}$$

With k_2 being the pseudo 2nd order kinetic constant, measured in $\text{g}/(\text{mg} \cdot \text{min})$ and the rest of the parameters being the same as in the previous analysis. Using the data from Table A9, a plot of t/Q_t versus time yields the graph shown in Figure A23, which demonstrates an excellent fit, confirming that Methyl Orange adsorption is best described by a chemisorption mechanism.

The theoretical value Q_e of can be calculated from the slope of the graph (0.00293) using the following formula:

$$0.00293 = \frac{1}{Q_e} \rightarrow Q_e = 341.3 \text{ mg/g}$$

This theoretical value deviates by only 0.3% from the experimental value, highlighting the accuracy of the fit, as evidenced by the high R^2 value (0.9999). The kinetic constant, k_2 , can be determined from the intercept according to the following equation:

$$0.02154 = \frac{1}{k_2 \cdot Q_e^2} \rightarrow 0.02154 = \frac{1}{k_2 \cdot 341.3^2} \rightarrow k_2 = 3.99 \cdot 10^{-4} \frac{g}{mg \cdot min}$$

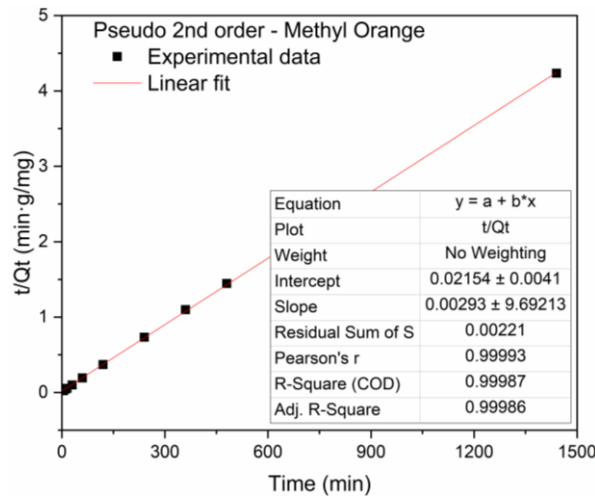


Figure A23: Pseudo 2nd order kinetic fit for Methyl Orange adsorption.

Intra-particle diffusion model:

Given that these adsorption experiments involve highly porous materials, the intra-particle diffusion kinetic model was also evaluated. This model assumes that adsorbate transport through the pores is the limiting step and is described by Equation A20:

$$Q_t = k_I \cdot t^{0.5} + C \quad \text{Equation A20}$$

Where k_I is the diffusion constant ($mg \cdot g^{-1} \cdot min^{-1/2}$) and C is an independent term that, when different to 0, reveals the existence of additional mechanisms apart from pore diffusion processes.

Using the data from the previous table, a plot of Q_t versus the square root of time yields the graph shown in Figure A24, yielding a k_I of $6.75 \text{ mg} \cdot g^{-1} \cdot min^{-1/2}$ and a R^2 value of 0.4509, which indicates that this kinetic model does not accurately represent MO adsorption onto the developed materials. Furthermore, the high value of the intercept (173.83 mg/g) confirms the existence of an alternative process—chemisorption, as previously identified.

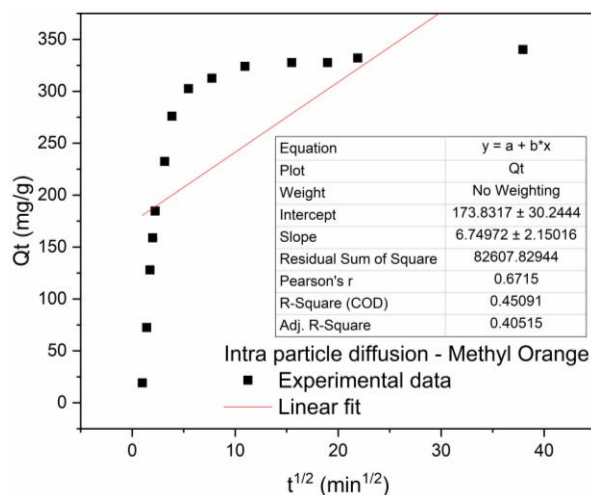


Figure A24: Intra particle diffusion kinetic fit for Methyl Orange adsorption.

Elovich model:

Finally, the Elovich model was also assessed to further investigate the mechanism of MO adsorption. This model is commonly used to describe adsorption onto heterogeneous surfaces, and follows Equation A21:

$$Q_t = \frac{1}{\beta} \cdot \ln(t) + \frac{1}{\beta} \cdot \ln(\alpha \cdot \beta) \quad \text{Equation A21}$$

With α and β being constants related to the adsorption rate and surface coverage, respectively. Thus, plotting Q_t against $\ln(t)$, Figure A25 is obtained:

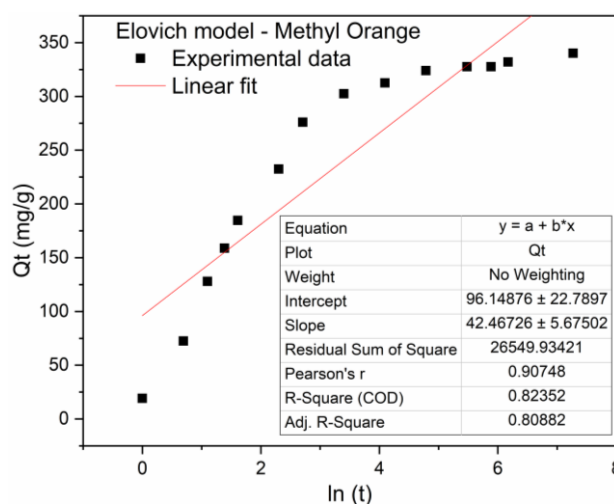


Figure A25: Elovich kinetic fit for Methyl Orange adsorption.

Using this data, the value of β can be calculated as the inverse of the slope, resulting in a value of 0.235. With this value, and knowing the intercept (96.148), α can be determined using the following formula:

$$96.148 = \frac{1}{\beta} \cdot \ln(\alpha \cdot \beta) \rightarrow 96.148 = \frac{1}{0.235} \cdot \ln(\alpha \cdot 0.235) \rightarrow \alpha = 409.4$$

However, the goodness of fit ($R^2=0.8235$) indicates that the Elovich model does not fully explain the adsorptive behaviour of this system. While it provides a moderate fit, the pseudo 2nd order kinetic model presents a much stronger correlation with the experimental data.

Annex 15: Determination of adsorption isotherms

Several adsorption models were analysed to understand the underlying mechanism governing dye adsorption. These models were the following:

Langmuir model:

This isotherm model assumes a monolayer adsorption onto a homogeneous surface, with a limited number of identical adsorption sites. The Langmuir model follows Equation A22:

$$Q_e = \frac{Q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad \text{Equation A22}$$

Which can be linearised to Equation A23:

$$\frac{Q_e}{C_e} = -Q_e \cdot K_L + Q_m \cdot K_L \quad \text{Equation A23}$$

Where Q_m is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg) and C_e is the equilibrium concentration (mg/L).

To perform the fitting, the adsorption capacities at each starting concentration (for each dye) were determined, and presented in Table A10:

Table A10: Isotherm data at different starting concentrations for each dye.

Dye	C ₀ (mg/L)	C _e (mg/L)	Q _e (mg/g)	Dye	C ₀ (mg/L)	C _e (mg/L)	Q _e (mg/g)
Congo Red	50	3.77	82	Methylene Blue	50	0.09	250
	100	19.51	152		100	8.70	456
	150	55.03	225		150	43.60	532
	200	80.53	347		200	39.62	802
Methyl Orange	50	7.81	211	Rhodamine B	50	11.80	191
	100	44.18	279		100	51.60	242
	150	92.03	290		150	81.57	342
	200	140.63	297		200	109.24	454

From this table, as in the previous Annex, the data of Methyl Orange adsorption will be used as example for the calculation of each isotherm model. For the Langmuir model, a plot of Q_e vs Q_e/C_e yields the graph shown in Figure A26:

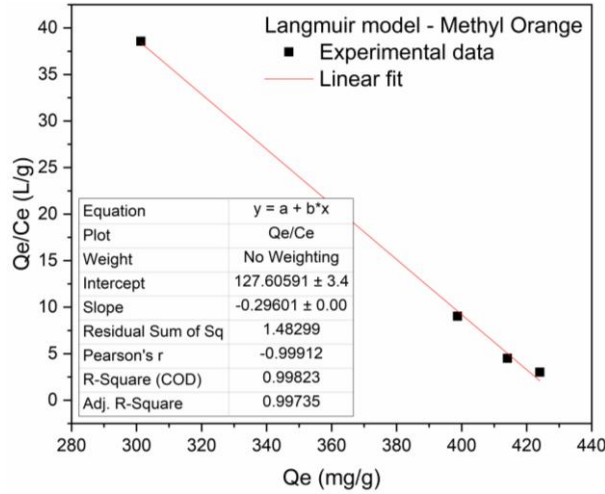


Figure A26: Langmuir isotherm fit for Methyl Orange adsorption.

This graph shows an excellent fit with a R^2 value of 0.9982 and a Langmuir constant of 0.296 L/mg. From the intercept (127.6), the maximum adsorption capacity can be calculated using the following formula:

$$127.6 = Q_m \cdot K_L = Q_m \cdot 0.296 \rightarrow Q_m = 431.1 \text{ mg/g}$$

Yielding a close value to the experimentally determined maximum adsorption capacity (424 mg/g).

Freundlich model:

The Freundlich model was also applied to the adsorption data of all dyes. In contrast to the Langmuir model, Freundlich assumes a multilayer adsorption mechanism taking place on a heterogeneous surface. The Freundlich model is described by Equation A24:

$$\log Q_e = \frac{1}{n_F} \cdot \log C_e + \log K_F \quad \text{Equation A24}$$

Where K_F is the Freundlich constant, measured in mg/g, and $1/n_F$ is the dimensionless reaction order, which is usually lower than 1.

Using the data displayed in Table A10, a plot of $\log Q_e$ vs $\log C_e$ was constructed, as shown in Figure A27.

The slope value of the linear fit yields $1/n_F = 0.121$, indicating a favourable adsorption process. Moreover, the intercept value (2.379) corresponds to:

$$2.379 = \log K_F \rightarrow K_F = 10^{2.379} = 239.3 \text{ mg/L}$$

Overall, this model provides a reasonably good fit, with a goodness of fit (R^2) of 0.9506, but slightly lower than that of the Langmuir model.

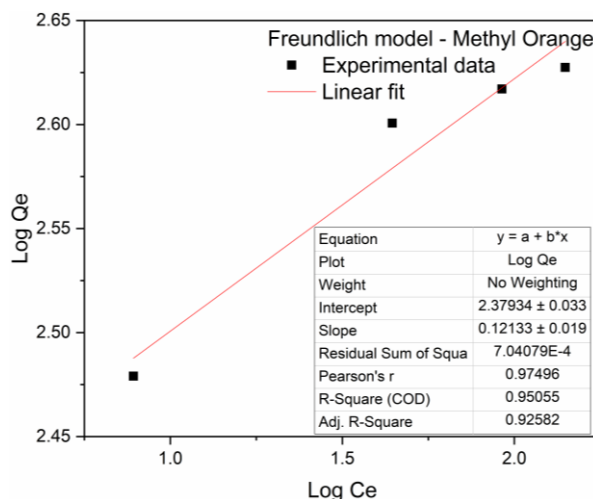


Figure A27: Freundlich isotherm fit for Methyl Orange adsorption.

Temkin model:

The Temkin model provides a more detailed perspective, considering adsorbate-adsorbent interactions and assumes a decreasing heat of adsorption as the adsorbent's surface coverage increases. This model is described by Equation A25:

$$Q_e = B \cdot \ln C_e + B \cdot \ln K_T \quad \text{Equation A25}$$

With K_T being the Temkin equilibrium constant (L/g) and B being a dimensionless constant that can be calculated according to Equation A26:

$$B = \frac{R \cdot T}{b} \quad \text{Equation A26}$$

Where R is the ideal gas constant (8.314 J/mol·K), T is temperature measured in K and b is the Temkin constant related to adsorption energy, measured in J/mol.

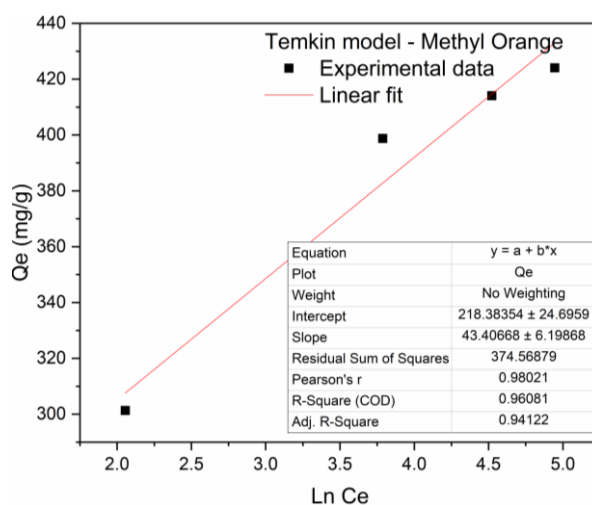


Figure A28: Temkin isotherm fit for Methyl Orange adsorption.

From the linear plot of Q_e vs. $\ln C_e$ shown in Figure A28, the slope (43.407) corresponds to B . Using this value, b can be calculated as:

$$B = \frac{R \cdot T}{b} \rightarrow b = \frac{R \cdot T}{B} = \frac{8.314 \cdot 298}{43.407} = 57.078 \text{ J/mol}$$

From the intercept (218.38), the Temkin equilibrium constant can be calculated:

$$218.38 = B \cdot \ln K_T \rightarrow K_T = e^{218.38/B} = e^{218.38/43.407} = 153.1 \text{ L/g}$$

This model also presents a strong correlation ($R^2=0.9608$), but still lower than that of the Langmuir model.

Dubinin-Radushkevich model:

Finally, the Dubinin-Radushkevich model was evaluated. This model assumes a physisorption process occurring in a porous and heterogeneous surface, and is defined by Equation A27:

$$\ln Q_e = \ln Q_m - \beta \cdot \varepsilon^2 \quad \text{Equation A27}$$

With β being the activity coefficient related to the adsorption energy and ε being an equation parameter that is summarised by Equation A28:

$$\varepsilon = R \cdot T \cdot \ln \left(1 + \frac{1}{C_e} \right) \quad \text{Equation A28}$$

Furthermore, a plot of $\ln(Q_e)$ vs ε results in the graph shown in Figure A29:

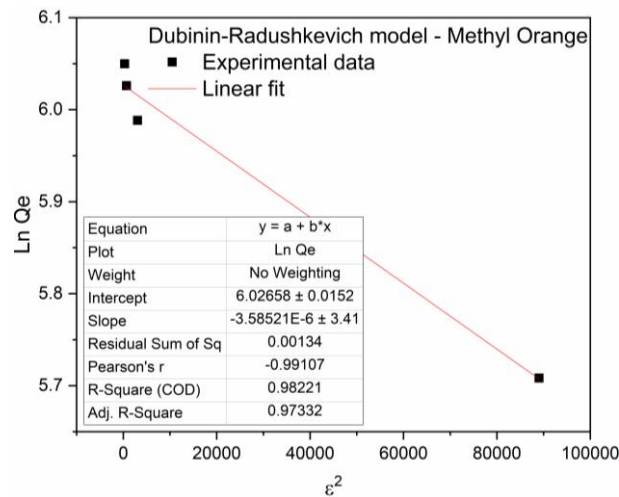


Figure A29: Dubinin-Radushkevich isotherm fit for Methyl Orange adsorption.

Where the negative value of the slope ($3.585 \cdot 10^{-6} \text{ mol}^2/\text{J}^2$) corresponds to β , from which the adsorption energy (E) can be calculated as follows:

$$E = \frac{1}{\sqrt{2 \cdot \beta}} = \frac{1}{\sqrt{2 \cdot 3.58 \cdot 10^{-6}}} = 373.61 \text{ J/mol}$$

Moreover, the intercept value (6.027) allows the determination of Q_m :

$$6.027 = \ln Q_m \rightarrow Q_m = 414.3 \text{ mg/g}$$

Although the D-R model offers a high R^2 value (0.982) and a Q_m value close to the Q_e observed at the highest initial concentration, the Langmuir model still offers a better overall fit. Additionally, the calculated adsorption energy is indicative of a physisorption process, which is in contrast with the results obtained from the kinetic analysis. These differences make the Dubinin-Radushkevich less effective in describing the mechanism governing Methyl Orange adsorption compared to the Langmuir model.

Publications

This chapter will cover the main scientific contributions derived from this thesis, mainly peer-reviewed journal articles and conference papers and presentations.

Articles published in indexed journals

1. Manuel Prieto, Gary J. Ellis, Vitaliy L. Budarin, Enrique Morales, Mohammed Naffakh and Peter S. Shuttleworth, **“Understanding pore size relation in cellulose-derived, nitrogen-doped, hydrothermal carbons for improved supercapacitor performance”**, *J. Mater. Chem. A*, Volume 12, Issue 43, 29698-29707, 2024. <https://doi.org/10.1039/D4TA04477K>
2. Prieto, Manuel, Hangbo Yue, Nicolas Brun, Gary J. Ellis, Mohammed Naffakh, and Peter S. Shuttleworth, **"Hydrothermal Carbonization of Biomass for Electrochemical Energy Storage: Parameters, Mechanisms, Electrochemical Performance, and the Incorporation of Transition Metal Dichalcogenide Nanoparticles"**, *Polymers* 16, no. 18: 2633, 2024. <https://doi.org/10.3390/polym16182633>
3. Hayman J. Abdoul, Minghao Yi, Manuel Prieto, Hangbo Yue, Gary J. Ellis, James H. Clark, Vitaliy L. Budarin, Peter S. Shuttleworth, **“Efficient adsorption of bulky reactive dyes from water using sustainably-derived mesoporous carbons”**, *Environmental Research*, Volume 221, 2023. <https://doi.org/10.1016/j.envres.2023.115254>.

Presentations at national and international congresses

Oral communications

1. M. Prieto Lobato, P. Pereira, G. Ellis, M. Naffakh, P. Shuttleworth, **“Biodegradable, sustainably modified Poly-L-lactic acid fibers for excellent dye adsorption”** *Polychar 2024*, Madrid, 29th May 2024
2. M. Prieto Lobato, P. Shuttleworth, M. Naffakh, **“Nanocompuestos biopoliméricos avanzados basados en nanoláminas 2D-TMDCs”**, *Industriales Research Meeting 2024*, Madrid, 11th May 2024.
3. M. Prieto Lobato, G. Ellis, E. Morales, P. Shuttleworth, **“Synthesis of biomass-derived, inorganic-doped carbons for improved electrochemical performance in supercapacitors”**, *Workshop on Porous and Hybrid Materials: PorHyMat 2023*, Montpellier (France), 9th June 2023.
4. M. Prieto Lobato, M. Yi, H. Salavagione, A. Flores, M. Gómez-Fatou, V. Budarin, G. Ellis, E. Morales, P. Shuttleworth, **“Natural polymer derived mesoporous structures regulated via temperature control and nanocomposite addition”**, *Polychar 2023*, Auckland (New Zealand), 22-27th January 2023.
5. M. Prieto Lobato, G. Ellis, E. Morales, P. Shuttleworth, **“Sustainable bio-based carbonaceous materials for application as electrodes in supercapacitors”**, *Power Our Future 2022*, Vitoria, 6th June 2022.
6. M. Prieto Lobato, G. Ellis, E. Morales, P. Shuttleworth, V. Budarin, **“Supercapacitor electrode materials from sustainable-derived nanocomposite-enhanced mesoporous carbons”**, *AMAPOLA Workshop: “Role of polymers in batteries and capacitors: Towards sustainable, safer, and more efficient devices”*, Madrid, 28th September 2021.

Poster communications

1. M. Prieto Lobato, G. Ellis, E. Morales, M. Naffakh, P. Shuttleworth, “**From waste to wonder: Biomass-derived, multifunctional materials for energy storage and contaminant removal**”, *III PhDay Campus Serrano*, Madrid, 12th June 2025.
2. M. Prieto Lobato, G. Ellis, E. Morales, P. Shuttleworth, “**Synthesis of bio-based carbonaceous materials for their application as electrodes in electrochemical capacitors**”, *Congreso Bienal 2022 de la Real Sociedad Española de Química*, Granada, 29th June 2022. **Best poster award in the Materials and Energy category.**
3. M. Prieto Lobato, P. Shuttleworth, M. Naffakh, “**Biopolymeric advanced nanocomposites based on 2D-TMDC nanosheets**”, *Industriales Research Meeting 2022*, Madrid, 27th May 2022.
4. M. Prieto Lobato, G. Ellis, E. Morales, P. Shuttleworth, “**Biomass derived mesoporous carbons for their application as electrodes in supercapacitors**”, *CIRMAT: “Nuevos desarrollos para una economía circular”*, Madrid, 24th February 2022.

