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New compact multi option photo reactor for the removal of contaminants of emerging concern from wastewater

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ABSTRACT

The goal of this work is to design and set up a new multi option photo reactor with a high compactness to remove contaminants of emerging concern from wastewater. In this reactor, different advanced oxidation processes can be conducted simultaneously, such as electrochemical oxidation, photolysis and photocatalysis with TiO_2 nanotubes array, therefore, these simple technologies and their coupling were studied, giving rise to photo-electrocatalytic oxidation. The efficiencies of these processes were evaluated according to the removed amount of ofloxacin, a pharmaceutical compound used as model of contaminant of emerging concern. The characterization of the prepared photocatalysts/electrodes of TiO_2 nanotubes array was conducted by SEM and XRD, and it was observed that the nanotubes were formed in the anatase form (active phase for the photocatalysis process) with suitable diameter and length. The results show that the coupling of these technologies is possible, observing high process efficiencies. Therefore, the design of this new reactor opens the door to a highly efficient process to remove contaminants of emerging concern from wastewater at low cost and with easy implantation and environmental compatibility, making possible to use only sunlight as a reagent.

1. Introduction

Continuous technological advance and consumption growth in today's society increase worryingly contamination of the aqueous environment, therefore, attention, investment and research in the treatment of industrial and urban wastewater is necessarily growing [1]. Contaminants of emerging concern (CECs) are defined as chemical substances of a mainly organic nature which are resistant to photolytic, biological and chemical degradation, due to their high complexity. These are highly polluting substances for the aqueous environment because of their high toxicity, even at low concentrations, and they can be easily transmitted through air and water [2–4]. CECs include pharmaceuticals and personal care products, and endocrine disrupting compounds. These pollutants cannot be removed efficiently for conventional water treatments, thus, its presence in domestic wastewater can cause unpredictable damage to the environment and human health, such as disorders in endocrine and neurological systems, damage in reproductive capacities and hormonal control, or produce different types of cancer (breast, ovaries, prostate, testicles, etc.) [5–8]. Consequences concern even more when water is reused for irrigation, as these contaminants can be accumulated in soil and plants [3,9]. Specifically, wastewater treatment plants were not designed to remove antibiotics, such as ofloxacin, so these compounds in some cases are not completely eliminated and are still present in their effluents [10]. This fact can become dangerous for humans, animals and ecosystems.

It has been shown that prolonged exposure to antimicrobial agents favors the development of resistance in bacteria to most consumed antibiotics [11]. According to the World Health Organization, this fact is one of the greatest health dangers that we seemed to be facing in the 21st century, where 700,000 people died annually worldwide due to infection by resistant bacteria, it is estimated that by 2050 that number could increase to 10 million. In addition, because the concentrations at which antibiotics are sometimes found in environmental matrices, such as water or soil, could negatively affect the organisms that inhabit them. In this sense, there are numerous studies that show alterations in microbial communities, algae, microphytes, macrophytes, zooplankton, mosquitoes and fish [12–16].

Therefore, because of the need to improve current wastewater treatments, advanced oxidation processes, based on hydroxyl radicals generation and other oxidizing agents of persistent organic matter, can

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be considered as an efficient complementary treatment or substitute [17,18]. Among them, it is worth highlighting electrochemical oxidation and photocatalysis processes [1,7,19–24]. In addition, due to the recent interest in ultraviolet light irradiation technology as radical activation technique of oxidants for water treatment, its coupling to conventional electrochemical oxidation is being sought. Recent studies have observed that the coupling of ultraviolet radiation to electrochemical oxidation improves the process efficiency in a synergistic way [25,26]. This behaviour is due to the activation of the electrogenerated oxidizing agents in the medium, which give rise to radicals of higher oxidative capacity. In this sense, ultraviolet radiation can increase the production of hydroxyl radicals by photo-activation of the electrogenerated ozone and hydrogen peroxide, and produce radical effects by activating the different oxidizing agents present in the medium [26,27]. On the other hand, the use of nanotubes of TiO_2 in the anatase phase (active phase for photocatalysis process), entails an improvement in the photocatalysis treatment, due to nanotubes allow to increase the active surface able to generate hydroxyl radicals and other oxidizing agents of organic matter, taking into account that photocatalysis is a process that takes place mainly on the surface of the photocatalyst [28,29]. In addition, the coupling of electrochemical oxidation, photolysis and photocatalysis with TiO_2 nanotubes array, giving rise to photoelectrocatalytic oxidation, causes that ultraviolet photons reach the electrode/photocatalyst surface and form excited radicals according to Eq. 1, which can improve the treatment efficiency.

$$MO_x(\cdot OH) \longrightarrow^{h\nu} MO_x(\cdot OH)* \quad (1)$$

Taking into account that electrochemical oxidation and photocatalysis entail these reactions [19,30]:

$$H_2O \rightarrow \bullet OH + H^+ + e^- \quad (2)$$

$$OH^- \rightarrow \bullet OH + e^- \quad (3)$$

$$2\ \bullet OH \rightarrow H_2O_2 \quad (4)$$

$$\bullet OH + O_2 \rightarrow O_3 + H^+ \quad (5)$$

Many authors have studied the treatment of wastewater to remove CECs by electrochemical oxidation and photocatalysis with TiO_2 nanotubes array, obtaining good results [7,19,31–35]. However, few authors have studied the coupling of these technologies, and, in all cases, they indicate that new studies are necessary in order to improve the results obtained, such as Feng et al. [36] show in their review work.

With this background, the goal of this work is to study the coupling of electrochemical oxidation, photolysis and photocatalysis looking for an increase on the process efficiency for the removal of CECs from wastewater. To do this, a new multi option photo reactor (MOPR) with a high compactness has been designed in order to apply these technologies simultaneously for the removal of ofloxacin from synthetic wastewater, as an antibiotic model of CEC (widely used in today's society and, consequently, present in municipal wastewater). Thus, photoelectrocatalytic oxidation is studied, and the efficiency of the process is compared to that of simple technologies. In this context, it is important to highlight that this work is a preliminary study carried out in order to evaluate the efficiency of the reactor and study the different possibilities that it offers to apply different advanced oxidation processes. Therefore, it is important to carry it out with a target contaminant in synthetic wastewater at higher concentration that it can be found in municipal wastewater, in order to correctly evaluate the influence of the different operating conditions on the system. However, future studies will be necessary to study the system to treat real wastewater on a larger scale.

2. Materials and methods

2.1. Chemicals

Ti plates (5 × 5 cm; 1 mm thickness; 99.2% purity) were supplied by Alfa Aesar (Ward Hill, Massachusetts, United States of America). Ofloxacin (OFX), nickel plate, ammonium fluoride, sodium chloride, ethylene glycol and acetone were supplied by Sigma-Aldrich (Steinheim, Germany) with > 99.0% purity. Sulfuric acid and sodium hydroxide were used to adjust the pH of the cleaning solution, with analytical grade and supplied by Panreac Química S.A. (Barcelona, Spain).

2.2. Photocatalyst preparation

An anodizing process is conducted on the titanium plates to synthetize the photocatalysts. Before the anodization, the titanium plate requires a previous cleaning treatment with clean water and drying it with paper; and after that, acetone and water ultrasonic baths for 15 min. The titanium plate is used as anode and a nickel plate as cathode. The electrodes are immersed in an electrolyte solution (250 mL of NH_4F 0.1 M in a solvent formed by 20% v/v of water in ethylene glycol) and an electrical potential of 2 V min^{-1} is applied during the first 30 min, and continued at 60 V for another 90 min. After anodizing, the titanium plate is cleaned with water and dried with a nitrogen stream. The nanotubes obtained in the titanium plate surface must be treated by heat treatment to transform the amorphous phase into crystalline-phase TiO_2 nanotubes. This heat treatment is applied to the plate reaching 450 ºC in a muffle J.P Selecta S.A. (ramp up from room temperature to 350 °C at 2 °C min^{-1}, stabilization for 30 min, new ramp at 2 °C min^{-1} to 450 °C, stabilization for 150 min, descent to room temperature). In this way, the TiO_2 nanotubes increase their catalytic capacity after crystallizing in their anatase form [31,37].

These treated titanium plates will be also used as anode in the electrochemical processes.

2.3. Analytical procedures

TiO_2 nanotubes were analyzed by X-ray powder diffraction (XRD) with a D5000 diffractometer (Siemens/Bruker, Karlsruhe, Germany) using Cu Kα1,2 radiation operating under 30 mA and 40 kV, and by scanning electron microscopy (SEM) with a JEOL JSM-820 analyzer.

The maximal absorption wavelength of the OFX solution was determined from the scan graph measured in a UV–VIS spectrophotometer (UVIKON 941 plus), and it was obtained at a value of 332 nm. OFX concentration was measured using a HPLC Jasco MD-2010/2015 with a 5 μm C18 analytical column (4.6 mm × 250 mm), using a mobile phase of acetonitrile/water (50/50 v/v %) at the flow rate of 1 mL min^{-1}. The column temperature was 25 ℃ and samples of 5 μL were injected. The wavelength was set at 332 nm, value determined by UV–VIS spectrophotometry. Before analysis, the samples were filtered by 0.45 μm cellulose filter.

2.4. Experimental procedures

The MOPR designed by this research group and manufactured by APRIA Systems S.L. It is a simple parallel flow reactor, where the cathode and the anode are facing each other in a parallel position, allowing the use of different types of electrodes, easily interchangeable. It has a minimum distance between anode and cathode of 5 mm (this improves the flow conditions and the mass transfer), which are connected to an external power source.

Likewise, it is allowed to use a mesh cathode, so that, if desired, UV radiation can be on the anode surface that faces the cathode, which will allow its passage from its rear (thus, UV radiation can improve the generation and/or activation of oxidizing agents, which are mainly found on the anodic surface [26,38]).

Reactor worked out discontinuously, with continuous recirculation of the wastewater (a centrifugal pump with flow rate 21.4 $dm^3\ h^{-1}$ is used), that is initially stored in a glass tank (volume = 1 dm^3). In all cases, the initial concentration of OFX was of 20 mg dm^{-3} (synthetic wastewater), a value chosen to clearly observe the influence of the different processes applied, which can be considered a typical concentration found in industrial discharges [39]. A heat exchanger coupled with a controlled thermostatic bath (Digiterm 100, JP Selecta, Barcelona, Spain) is used to maintain the temperature at the desired set point (25 ºC).

In non-electrochemical processes (photolysis and photocatalysis), the power supply will remain disconnected.

Likewise, the use of this reactor allows anodizing in situ, with subsequent external heat treatment, in order to obtain the desired photocatalysts of TiO_2 nanotubes array.

The system includes a lamp with LED technology made up of 9 UV LEDs located on a plate: λ = 365–370 nm, 1200 mW. The total radiated power can be regulated. It contains a forced air convection ventilation system and a Pt-100 temperature sensor to control the temperature of the LEDs. The electric console includes PLC for monitoring, temperature control and power consumed by the lamp (with indication of intensity, voltage, power and temperature). In the electrochemical oxidation process, this system will remain disconnected.

Electrochemical processes are conducted under galvanostatic conditions. 0.035 mol L^{-1} NaCl is used as supporting electrolyte [40,41]. The applied current density is 15 mA cm^{-2} [23,28]. The cell voltage did not vary during each experiment, indicating that electrodes layers did not undergo appreciable deterioration or passivation. Prior to use in galvanostatic assays, the electrode was polarized for 10 min in a 0.035 mol L^{-1} Na_2SO_4 (pH = 2) solution at 15 mA cm^{-2} to remove any kind of impurity from its surface.

In addition, the coupling of ultrasound radiation is possible. To do this, the storage tank of the wastewater can be placed in an ultrasound bath, or an ultrasound probe can be inserted in the tank. In this way it will be possible, on the one hand, to improve the transfer of the organic mass, to be degraded on the anode (controlling process), where most of the oxidizing agents generated are found, and on the other hand, to increase the generation and/or activation of oxidizing agents [42–45].

Fig. 1 shows a scheme of the MOPR and the experimental set-up. Details are explained in the figure.

3. Results and discussion

3.1. Catalyst characterization

Characterization of TiO_2 nanotubes array formed by anodizing process was carried out in order to correlate their physicochemical properties with the behavior of the different studied technologies.

Fig. 2 shows the surface micrograph by SEM-EDS analysis of the TiO_2 nanotubes in an upper view (part a) and in a profile view (part b), where the nanotubes length can be observed. In general, nanotubes are perpendicular to the electrode surface with a uniform distribution. Therefore, the active surface is increased significantly, looking for a high efficiency in the photocatalysis processes [31]. Nanotubes measure approx. 1 μm long and the outer diameter is approx. 100 nm. Therefore, the size of the nanotubes is optimal to carry out the photocatalysis and photoelectrocatalysis of contaminants of emerging concern [29].

The XRD pattern of the anodized plate is presented in the Fig. 3. The main characteristics diffraction peaks of Titanium at 2θ values of 35.07, 38.41, 40.15, 53.01 and 62.97 and TiO_2-anatase at 2θ values of 25.28, 37.80, 48.05, 53.89 and 55.06 are clearly observed. The diffraction peaks of the TiO_2-rutile are not present. It is important to note that the intensities of the two identified phases do not correspond with the intensities of the powder materials, according to the International Centre for Diffraction Data Powder Diffraction Files (ICDD PDF), due to the preferential orientation. In the case of titanium, this is due to the lamination treatment performed to manufacture the plate and, in the case of the anatase, it is because of the morphology of the nanotubes, that are perpendicular to the plate [28,37].

3.2. Wastewater treatment

Fig. 4 shows the OFX degradation profiles of the experiments conducted applying the different studied technologies. In all cases, synthetic wastewater is prepared with an initial concentration of 20 mg dm^{-3} of OFX, and 0.035 mol L^{-1} NaCl is used as supporting electrolyte in the electrochemical processes. Concentration of the pollutant is normalized for a better comparison. Each experiment was carried out three times and the error bars are shown in the figure.

In all cases, can be observed a removal of the pollutant from the wastewater, between 5% for photolysis and 32% for photocatalysis, for a test time of 120 min. Photolysis entails a low degradation rate by molecule breakdown, but mineralization cannot be conducted [46,47]. Therefore, reaction intermediates are formed and these compounds can present a high toxicity in the medium, even higher than that of the initial contaminant, while electrochemical oxidation, photocatalysis and photoelectrocatalytic oxidation allows the removal of the compound forming CO_2 as final product, as many authors have observed [31,48,49]. In this context, it is important to highlight that the formation of reaction intermediates was not observed during these experiments by HPLC analysis. Thus, this fact indicates that only OFX is present in the reaction medium and, as the concentration of this species decreases with treatment, it can be said that the final toxicity is lower than the initial one.

It is important to take into account that the efficiencies of the photocatalysis and electrochemical oxidation processes can be improved looking for the optimal operating conditions (UV power, applied current density, pollutant concentration, etc.), as many authors have studied [7, 31,32,50].

On the other hand, in the photoelectrocatalytic oxidation process, where the different single technologies are coupled, a high generation of oxidizing agents and/or the promotion of the activation of oxidants produced electrochemically to the formation of radicals can take pace [25,32]. The production of hydroxyl radicals in electrochemical processes can be enhanced via Eq. 5 and Eq. 6 [51], caused by the conversion to other oxidizing species (H_2O_2 and O_3) under UV radiation. In this case, the effect of these radicals can be extended to the bulk phase, significantly improving the removal efficiency [27].

$$H_2O_2 \rightarrow 2\ \bullet \quad (5)$$

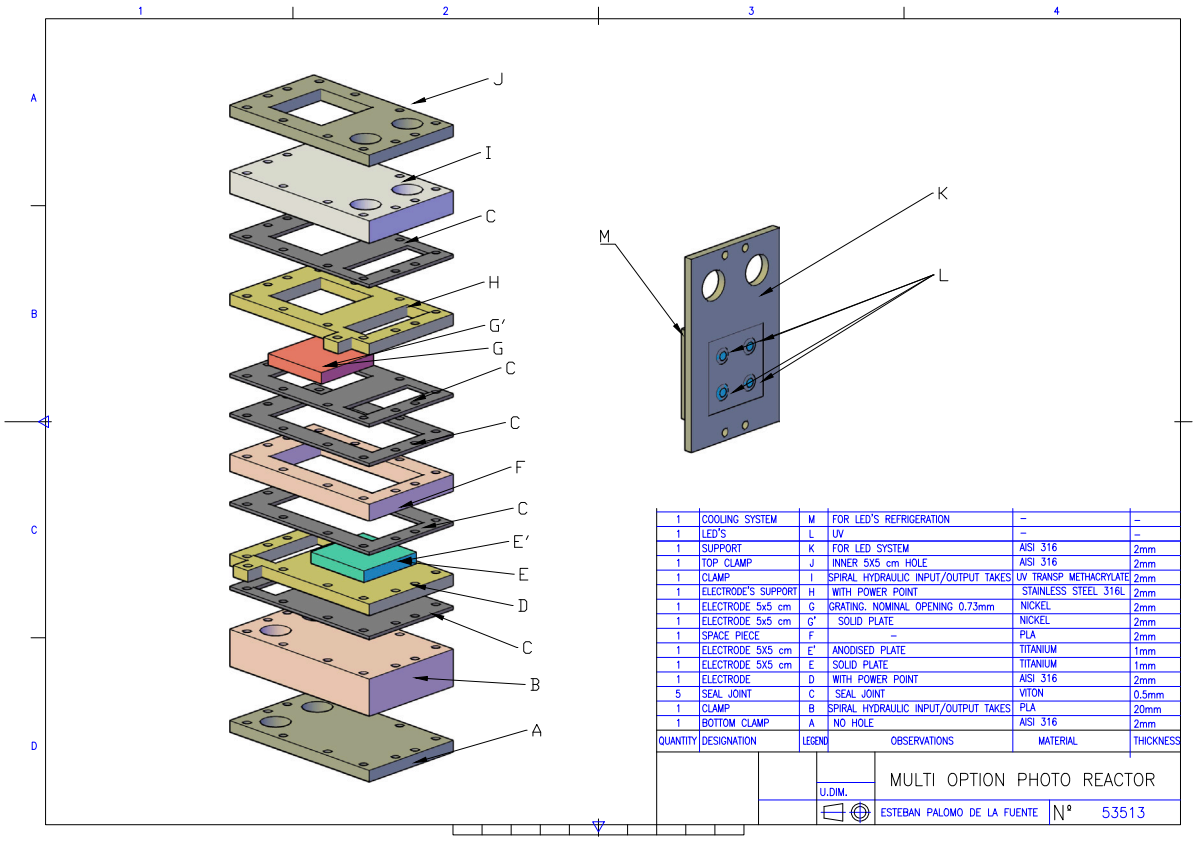
$$H_2O_2 + 2\ O_3 \rightarrow 2\ \bullet OH + 3\ O_2 \quad (6)$$

However, an antagonistic effect can be observed in the experiment carried out by photoelectrocatalytic oxidation. This fact can be due to a massive formation of oxidizing agents that would combine with each other to form species with greater chemical stability and lower oxidation capacity, preventing their direct or indirect action for the oxidation of OFX (Eq. 7 and Eq. 8) [26].

$$2\ \bullet OH \rightarrow H_2O_2 \quad (7)$$

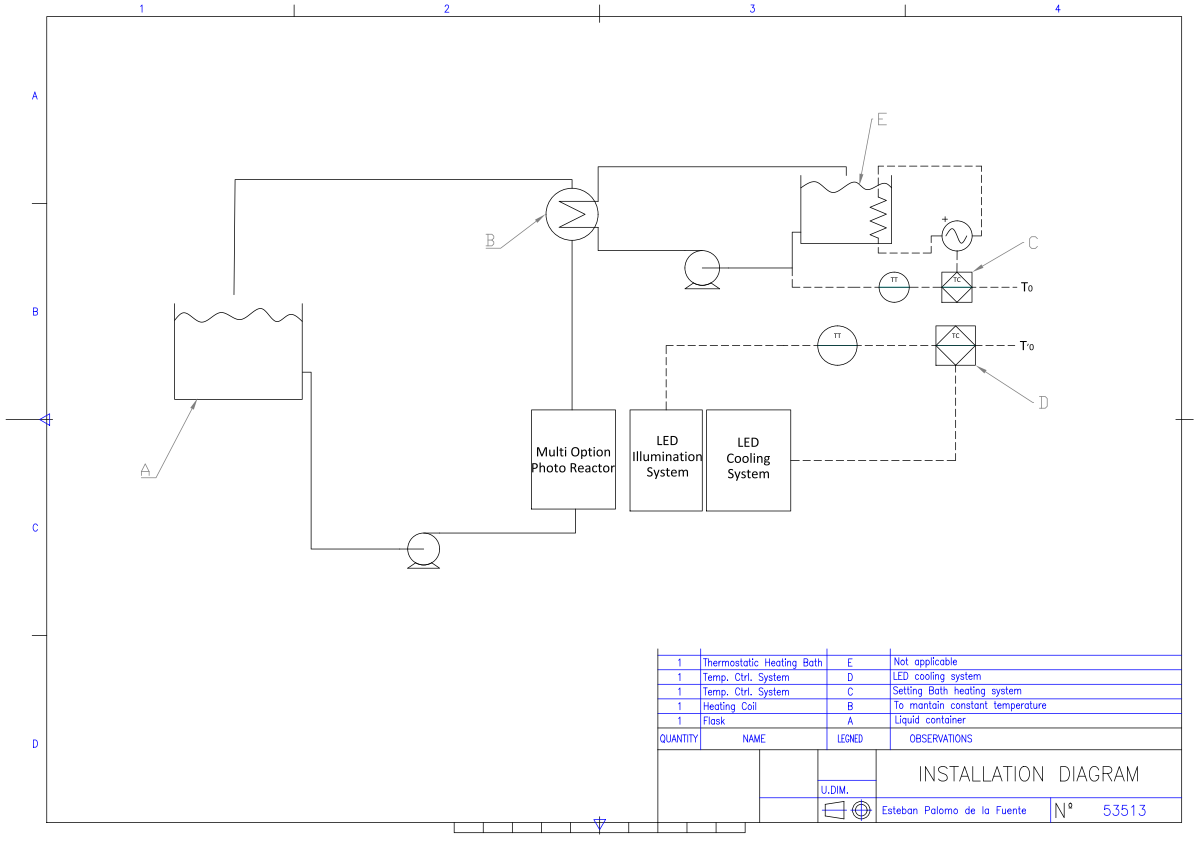
$$H_2O_2 \rightarrow H_2O + 1/2\ O_2 \quad (8)$$

Thus, this negative effect can counteract the possibility of increasing the efficiency of the process by coupling different advanced oxidation processes. In this sense, it would be advisable to evaluate the influence of the operating conditions of the process, such as the current density or the power of the UV radiation, in order to achieve the desired synergistic effect. It is important to highlight that the effect of the applied technology depends on the pollutant evaluated, and better results can be found for photoelectrocatalytic oxidation process if this technology is studied for the degradation of other CECs, as Cotillas et al. [52] and Martín de Vidales et al. [27,53] noted in their researches about wastewater treatment by different electrochemical processes. On the other



QUANTITY	DESIGNATION	LEGEND	OBSERVATIONS	MATERIAL	THICKNESS
1	COOLING SYSTEM	M	FOR LED'S REFRIGERATION	–	–
1	LED'S	L	UV	–	–
1	SUPPORT	K	FOR LED SYSTEM	AISI 316	2mm
1	TOP CLAMP	J	INNER 5X5 cm HOLE	AISI 316	2mm
1	CLAMP	I	SPIRAL HYDRAULIC INPUT/OUTPUT TAKES	UV TRANSP METHACRYLATE	2mm
1	ELECTRODE'S SUPPORT	H	WITH POWER POINT	STAINLESS STEEL 316L	2mm
1	ELECTRODE 5x5 cm	G	GRATING. NOMINAL OPENING 0.73mm	NICKEL	2mm
1	ELECTRODE 5x5 cm	G'	SOLID PLATE	NICKEL	2mm
1	SPACE PIECE	F	–	PLA	2mm
1	ELECTRODE 5X5 cm	E'	ANODISED PLATE	TITANIUM	1mm
1	ELECTRODE 5X5 cm	E	SOLID PLATE	TITANIUM	1mm
1	ELECTRODE	D	WITH POWER POINT	AISI 316	2mm
5	SEAL JOINT	C	SEAL JOINT	VITON	0.5mm
1	CLAMP	B	SPIRAL HYDRAULIC INPUT/OUTPUT TAKES	PLA	20mm
1	BOTTOM CLAMP	A	NO HOLE	AISI 316	2mm

MULTI OPTION PHOTO REACTOR
U.DIM.
ESTEBAN PALOMO DE LA FUENTE N° 53513



QUANTITY	NAME	LEGNED	OBSERVATIONS
1	Thermostatic Heating Bath	E	Not applicable
1	Temp. Ctrl. System	D	LED cooling system
1	Temp. Ctrl. System	C	Setting Bath heating system
1	Heating Coil	B	To mantain constant temperature
1	Flask	A	Liquid container

INSTALLATION DIAGRAM
U.DIM.
Esteban Palomo de la Fuente N° 53513

Fig. 1. (a) MOPR scheme. b) Experimental set-up.

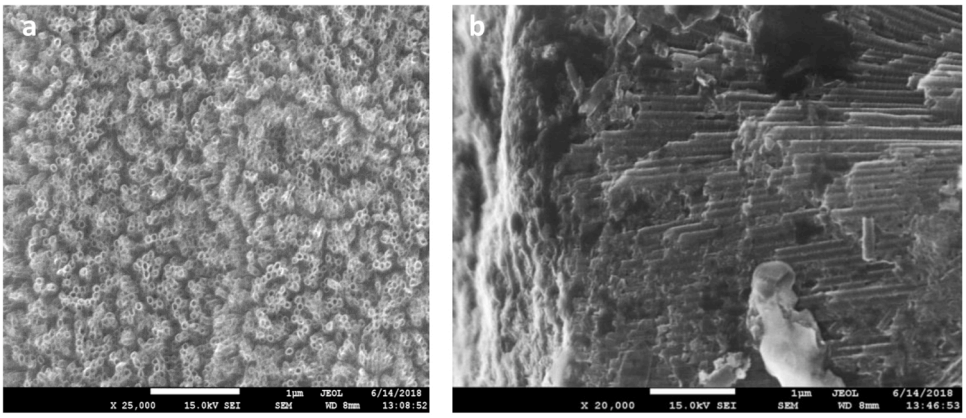


Fig. 2. SEM micrograph of TiO_2 nanotubes formed by anodizing process. a) Upper view. b) Profile view - nanotubes length.

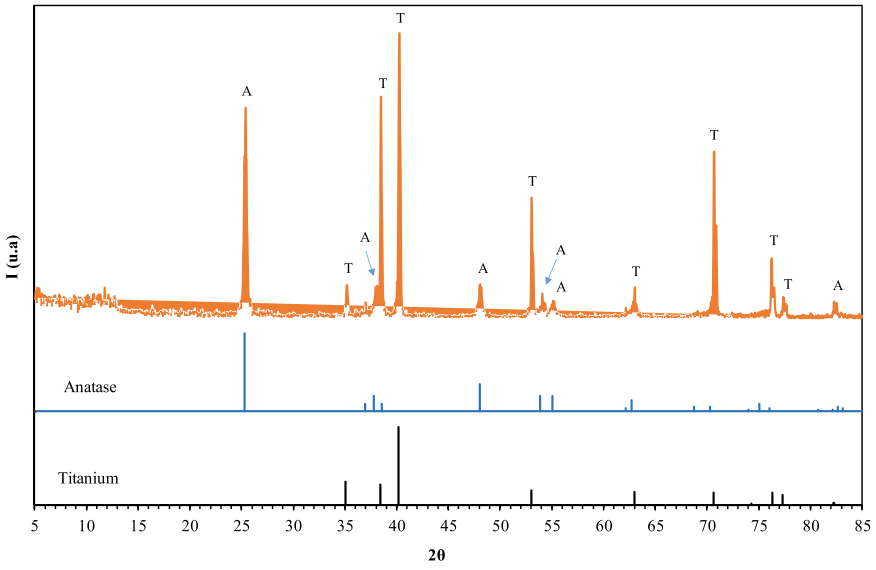


Fig. 3. X-ray diffractograms of the anodized plate (upper). A and T represent anatase and titanium, respectively. The pattern of anatase (medium) and Ti (below) from PDF database are included.

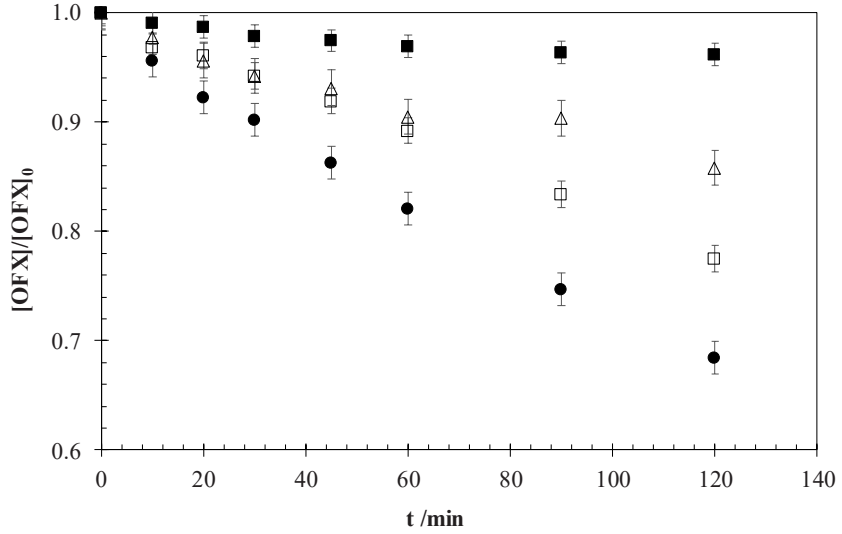


Fig. 4. Profiles of OFX concentration (normalized) obtained for the wastewater treatment by photolysis (■), photocatalysis (•), electrochemical oxidation (Δ) and photoelectrocatalytic oxidation (□). $[OFX]_0 = 20$ mg dm^{-3}. Electrochemical processes: 0.035 mol L^{-1} NaCl. UV LEDs: λ = 365–370 nm.

hand, the negative effect observed in the photoelectrocatalytic oxidation process may be influenced by the fact that high potential values could destroy the structure and conductivity of the titanium dioxide nanotubes, as described by Roy et al.[54].

Therefore, as shown in Fig. 4, the most suitable process was photocatalysis, where the generation and/or activation of oxidizing agents took place in the most efficient way. This fact is in accordance with the highly ordered TiO_2 nanotubular array catalyst obtained, with a high proportion of anatase form and a good morphology, as demonstrated in the previous section.

For further comparison, a kinetic analysis was performed. The oxidation of organic compounds by irradiation techniques can be well fitted to a pseudo-first order kinetic model, where the kinetic constant depends on the irradiated energy. For electrochemical oxidation processes, the first-order model also performs well and, in this case, the kinetic constant is related to the mass transfer coefficient and to the kinetic constants of the mediated oxidation processes that might coexist [55–57]. This phenomenon can be explained taking into account the existence of indirect oxidation by electrogenerated oxidants (persulfates, ozone, hydrogen peroxide and, of course, hydroxyl radicals), giving rise to pseudo-first order kinetics, that depends on both the concentration of organic matter (CEC in this case) and that of the oxidizing species, the latter being included in the apparent kinetic constant (Eq. 9) [22,56].

$$r = K\,[CEC] = k'\,[\text{Oxidizing agent}]\,[CEC] \quad (9)$$

Fig. 5 shows the pseudo-first order kinetic constants calculated in terms of pollutant removal for the technologies studied in this work. This figure also compares these kinetic constants with the values expected according to the addition of the different single contributions.

In this figure similar observations to those obtained in Fig. 4 can be described, where photocatalysis is selected as the most efficient technology, with the highest kinetic constant. In addition, this figure reveals that although photoelectrocatalytic oxidation process presents an antagonistic effect with respect to the sum of photocatalysis and electrochemical oxidation, the kinetic constant is higher than that of the sum of photolysis and electrochemical oxidation.

Thus, this preliminary study opens the door to the use of a MOPR with a high compactness to the removal of CECs from wastewater with higher efficiency, although future studies are necessary to optimize the operating conditions working with real wastewater on a higher scale. In addition, it is possible to use only sunlight as a reagent, because energy can contribute in this way for electrochemical and photocatalysis processes, taking into account that the supporting electrolyte is not necessary when real wastewater is treated by electrochemical technologies, because it has enough conductivity. Therefore, this is a promising technology because of its low cost, easy implantation, high efficiency and environmental compatibility.

4. Conclusions

From this work, the following conclusions can be drawn:

- A new compact multi option photo reactor has been designed in order to couple different advanced oxidation processes: electrochemical oxidation, photolysis and photocatalysis with TiO_2 nanotubes array. Therefore, these simple technologies and their coupling can be studied, giving rise to photoelectrocatalytic oxidation.
- The efficiencies of these technologies have been evaluated for the removal of contaminants of emerging concern from wastewater, specifically, ofloxacin degradation has been tested.
- Characterization of the prepared photocatalysts/electrodes of TiO_2 nanotubes array is carried out by SEM and XRD, and results show that the nanotubes are formed with suitable diameter and length in the anatase form (active phase for the photocatalysis process).

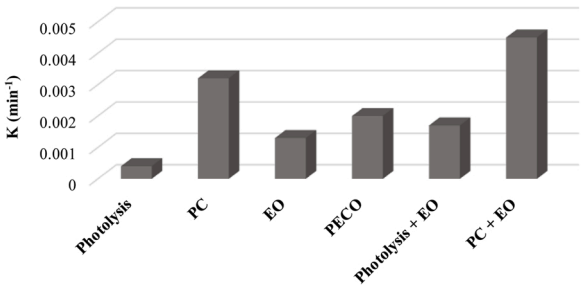


Fig. 5. Kinetic constants calculated in terms of pollutant removal for the different processes (four first columns on the left) and comparison with the values calculated by the addition of the single contributions (last two columns on the right). PC: photocatalysis, EO: electrochemical oxidation, PECO: photoelectrocatalytic oxidation.

- The experiments carried out show that the most efficient technology is photocatalysis, which entails a 32% removal of OFX. An antagonistic effect for photoelectrocatalytic oxidation can be observed with respect to the sum of photocatalysis and electrochemical oxidation, which may be due to a massive formation of oxidants that combine with each other to form more stable species.
- The design of this compact MOPR opens the door to the coupling of different advanced oxidation processes looking for synergistic effects with a high efficiency for the removal of CECs from wastewater with low cost, easy implantation and environmental compatibility, being possible to use only sunlight as a reagent.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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