Electrochemical systems equipped with 2D and 3D microwave-made anodes for the highly efficient degradation of antibiotics in urine

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Abstract

This work focuses on the importance of choosing a suitable electrochemical cell to remove antibiotics from urines. For this purpose, we investigate the use of two electrochemical cells for electrolysis and photo-electrolysis of urine polluted with a mixture of Penicillin G, Meropenem, and Chloramphenicol. The two reactors studied were a conventional flow pass electrochemical cell (E-cell) and a microfluidic flow-through reactor (MF-Reactor). Both reactors are equipped with a mixed metal oxide anode (MMO-RuO_2IrO_2) produced by hybrid heating using microwaves. The MMO coating was deposited on a Ti plate for the E-cell (2-D electrode) and on a Ti foam for the MF-Reactor (3-D electrode). Results demonstrate that the MF-Reactor stands out to reduce two important factors in electrochemical oxidation, the ohmic resistance associated with the microfluidic concept and the mass transfer limitations associated with the flow-through configuration. Moreover, it allows operating at a lower effective current density because of its larger active anodic surface area. Photo-electrolysis results in faster removal of all antibiotics studied in the MF-Reactor and E-cell, compared to the single electrolysis, thereby highlighting the significance of UV light-mediated electrochemical oxidation processes. This work highlights that despite the large number of papers focused on the selection of suitable electrodes for the electrochemical treatment of different types of wastes, the choice of the electrochemical cell can be even more important than the selection of those electrode materials, and it demonstrates that even using the same coating as the anode, highly different outcomes can be reached.

Keywords: Three-dimensional anode; Penicillin G; Meropenem; Chloramphenicol; flow-through; electrochemical cell

1. Introduction

Nowadays, contamination by micropollutants of reservoirs of water generates enormous concern since it may cause serious environmental problems for the aquatic ecosystem and human health [1]. The technologies applied in conventional wastewater treatment facilities are inappropriate to completely remove these compounds from urban or industrial wastewater. Hence, they are starting to be accumulated in the environment [2], so it has become a relevant research area in recent years. According to the WHO (World Health Organization), the presence of drugs that kill specific microorganisms (i.e., antibiotics, antiparasitic and antifungal) is one of the main concerns because they can promote the development of resistant bacteria [3,4]. Consequently, it is imperative to minimize their occurrence and, in turn, their later accumulation in the environment.

For that purpose, the efficient treatment of hospital wastewater has emerged as a priority since they contain drugs in high concentrations (in order mg L^{-1}) and represent an important source for the entrance of antibiotics into the environment [5,6]. Among hospital effluents, urine is considered one of the wastes with higher chemical and biological risk due to the variety of medicines and pathogens that it contains [7]. The treatment of hospital urine is a challenge, as it is an extremely complex matrix with a high concentration of different pharmaceuticals and their metabolites. In this topic, Advanced Oxidative Processes (AOP) have shown promising removal outcomes [8–13].

Electrochemical oxidation is one of the most significant AOP since it can eliminate organic pollutants through the electro-generation of different radicals via direct and indirect anodic oxidation [14,15]. Several researchers are studying the influence of anodic material and the design of the cell/electrochemical reactor to optimize the process [16]. Among the anodes, MMO (mixed metal oxides) are plenty promising, as they have a low cost of synthesis and excellent electrocatalytic properties [17,18]. As reported in the literature [19,20], when MMO is used, two

processes will occur concurrently, the direct oxidation that occurs on the surface of this material (through adsorbed hydroxyl radicals) and oxidation mediated by electrogenerated oxidants (contained in the electrolyte), being fundamental to increase the efficiency of electrolysis [21].

Commonly, the electrochemical processes are performed using a two-dimensional (2D) anode, which has some disadvantages, such as the limitation of mass transfer, the low area-volume ratio, the increase in temperature during the process, and low current efficiency [22]. In order to overcome these drawbacks, some research proposes the use of three-dimensional (3D) electrodes. The direct oxidation of organic pollutants using 3D anodes is superior due to the larger contact surface and more active sites than 2D electrodes [23]. Evidently, to implement these 3D electrodes, a different mechanical design of the electrochemical cell is required, and recently, our group proposed a significantly efficient design in which the concepts of microfluidics and flow-through electrodes were properly merged [1–4,24]

Given the above, this article studies the behavior of 2D, or 3D anodes (MMO-Ti/RuO_2IrO_2) synthesized employing a new heating technique using microwaves [17,25] in the electrolysis and photo-electrolysis of urine polluted with a mixture of antibiotics: Penicillin G (PENG), Meropenem (MEP) and Chloramphenicol (CLP). These electrodes are placed in different electrochemical cells: a conventional single-flow cell (E-cell) for the 2D electrode and a flow-through microfluidic reactor (MF-Reactor) for the 3-D electrode. In the first, the urine flows over the surface of the electrode, while in the second, it percolates through it. Results obtained will help clarify the importance of choosing a suitable electrochemical cell and of appropriate electrodes for the selective oxidation of antibiotics into compounds without antibiotic effect (not complete mineralization) and the reduction of the impact of hospital wastewater on the environment.

2. Experimental

2.1 Chemicals

All compounds used to prepare synthetic urine (urea, creatinine, uric acid, potassium chloride, magnesium sulfate, calcium phosphate, sodium carbonate, and diammonium hydrogen phosphate) were of analytical grade. Penicillin G, meropenem, chloramphenicol, and the reagents used in the mobile phase of the chromatographic measurements (methanol, formic acid, acetone, 2,6-pyridinedicarboxylic acid, and nitric acid) were purchased from Sigma Aldrich®. All chemicals used for analytical measurements were analytical grade and used as received. Ultrapure water (Millipore Milli-Q system, resistivity: 18.2 MΩ cm at 25 ° C) was used to prepare all solutions.

2.2 Experimental set-up

In this work, two e+xperimental configurations were used: a conventional one-chamber single-flow electrochemical cell (later referred to as E-cell) and a microfluidic flow-through reactor (later referred to as MF-Reactor). **Figure 1** shows the layout and details of both cells. Their mechanical details were also shown elsewhere [1–3,5,6,24]. In both configurations, an MMO-Ti/RuO_2IrO_2 electrode prepared using microwave heating was used as an anode, a method previously proposed by Gonzaga and co-authors[17]. The mixture of metal oxides was deposited over a Ti plate (4.0 cm² of geometric area) for use in the E-cell. In the MF-Reactor, the support material was a porous titanium foam (supplied by American elements) with a geometrical area similar to that of the Ti plate. As a cathode, an AISI304 stainless steel mesh was used in both cases. In the MF-Reactor, the inter-electrode gap was 150 μm, trying to improve mass transport limitations.

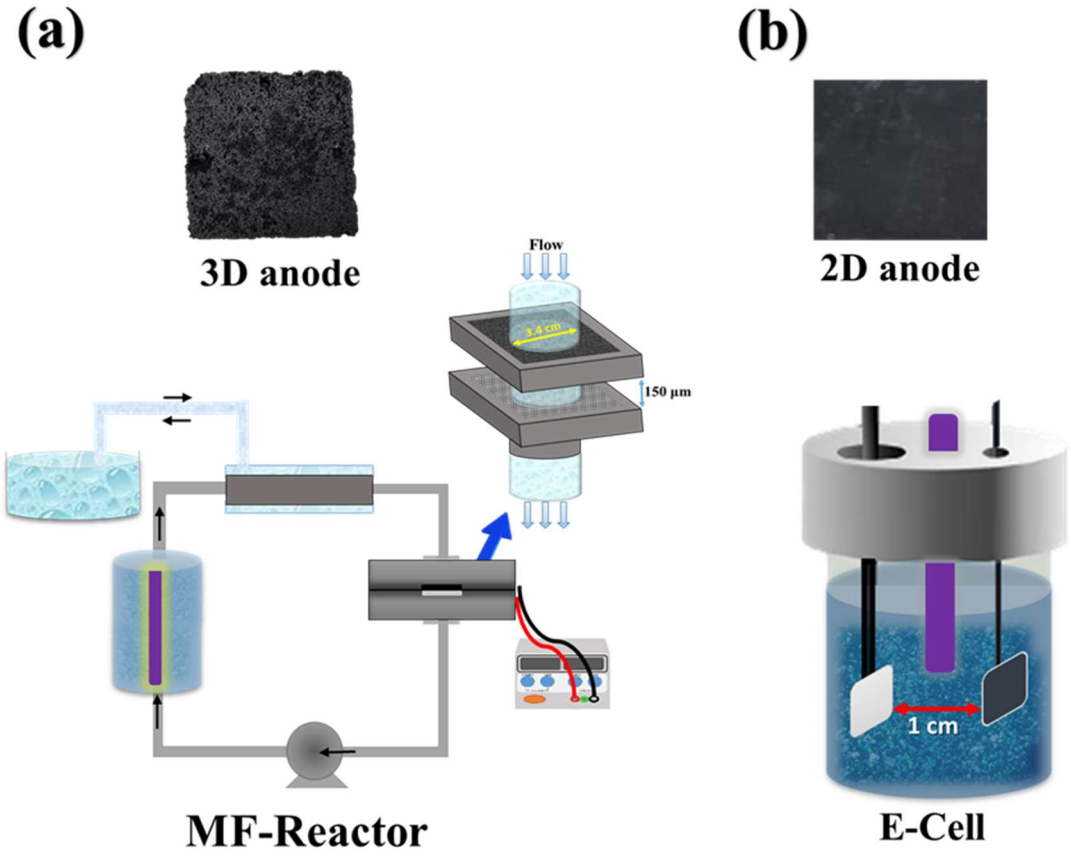

Figure 1. Layout and details of the (a) MF-Reactor and (b) E-Cell where were used the 3-D and 2-D Ti/RuO_2IrO_2 electrodes, respectively.

For photoelectrolysis and photoelectrolysis in both configurations, a UVC lamp (λ = 254 mm) was placed in the reservoir tank to irradiate 9 W directly in the electrolyte solution (**Figure 1**). During electrolisys and photoelectrolysis the experiments were carried out on a galvanostatic mode at a current density of 30 mA cm^{-2}. A total electrical charge of 6.4 Ah dm^{-3} was passed, which corresponds to 7.24 h or 8 h of operation in the MF-Reactor or E-Cell, respectively. Solutions were recirculated through the reactor using a Micropump® with a flow rate of 140 L h^{-1}. The volume of the solution was 120 mL.

2.3 Physical and electrochemical characterization

The surface morphology of the microwave prepared MMO-Ti/RuO_2IrO_2 was visualized employing a field-emission scanning electron microscope (FE-SEM; Zeiss GeminiSEM 500). The cyclic voltammetry measurements were performed using an Autolab PGSTAT302 N (Metrohm) using a conventional three-electrode cell. The counter electrode was a stainless steel, the Ag/AgCl reference electrode, and a working electrode, which consisted of a microwave-prepared plate or foam. The potential range of 0.0–1.2 V with a scan rate of 20 mV s^{-1}.

2.4 Analytical techniques

The evolution of PENG was quantified by high-performance liquid chromatography (HPLC), with an Eclipse Plus C-18 column (4.6 mm x 100 mm) at 30 °C. A mixture of 50% methanol and 50% acidified water (0.1% formic acid) was used as a mobile phase, flowing at 0.6 mL min^{-1}. The injection volume was 20.0 µL, measured at a wavelength of 220 nm. The mobile phase at 15% acetonitrile and 85% formic 0.1% was used to monitor the MEP concentration, with a flow rate of 0.2 mL min^{-1} and the injection volume was 20 µL. For the CLP, the mobile phase of 50% methanol/50% Milli-Q water was used with a flow rate of 0.6 mL min^{-1}, with an injection volume of 20 µL and a wavelength of 270 nm DAD detection. Besides, the evolution of other organics contained in the urine composition was monitored using HPLC (uric acid), ion chromatography (creatinine), and colorimetric methods (urea) according to previously reported methodologies [7]. Finally, the total organic carbon (TOC) changes were measured using a TOC Multi N/C 3100 Analytik Jena analyzer.

2.5 Antibiotic activity assay

In addition, the antibiotic activity of the treated samples was monitored using a µ-Trac® 4200 (Sy-lab, Austria) that performs the counting of microorganisms. The tests were carried out with two types of bacteria, *E. Coli* and *E. Faecalis*, which were initially placed on agar plates and

incubated at 37 °C. Then, the urine matrix was contaminated with 10^6–10^7 CFU of E. Coli or *E Faecalis*; after contamination, a sample was measured to verify the initial concentration of microorganisms. The treated samples were measured at different concentrations (without dilution, 1:10, 1: 100, and 1: 1000) and kept under stirring and controlled temperatures (37 °C) for 3 h. Finally, the number of microorganisms was measured by the μ-Trac® 4200.

2.6 Performance parameters

The synergistic coefficient (%) was calculated [26] using Eq. (1), where *k* is the kinetic constant calculated for the different single and combined processes studied (electrolysis, photo-electrolysis, and photolysis).

$$\text{Synergy coefficient } (\%) = \frac{k_{Photoelectro} - k_{electro} - k_{photo}}{k_{photo} + k_{electro}} \text{ x } 100 \quad (1)$$

Electric energy per order (EEO) is an important figure of merit and is used to determine the electrical energy (kWh) needed to reduce the concentration of the pollutant by order of magnitude. It can be calculated from Eq. (2) for a batch operation [27] and Eq. (3) for flow-through operation [28], where 38.4×10^{-4} is a conversion factor (1 h / 60 min / 0.4343) [28], E_{cell} (V) is the cell potential, I (A) the applied current, F is the flow (m^3/h), and k is the kinetic constant (min^{-1}).

$$EEO_{Batch} = \frac{\mathbf{38.4 \text{ x } 10^{-4} \, E_{cell} \text{ x I x } 1000}}{\mathbf{V_s \text{ x k}}} \quad (2)$$

$$EEO_{Flow} = \frac{\mathbf{38.4 \text{ x } 10^{-4} \text{x } E_{cell} \text{ x I x } 1000}}{\mathbf{F \text{ x k}}} \quad (3)$$

3. Results and discussion

3.1 Characterization of the 2-D and 3-D electrodes

Figure 2 shows the physical and electrochemical characterization of the developed anodes. In order to obtain a more accurate and complete view of the surface characteristics of the synthesized materials, cyclic voltammetry (CV) was performed in the potential range of 0.2–1.2 V. The voltammetric charge values were obtained from the integration of cyclic voltammograms, which are used as a relative measure of the electrochemically active area of the MMO.

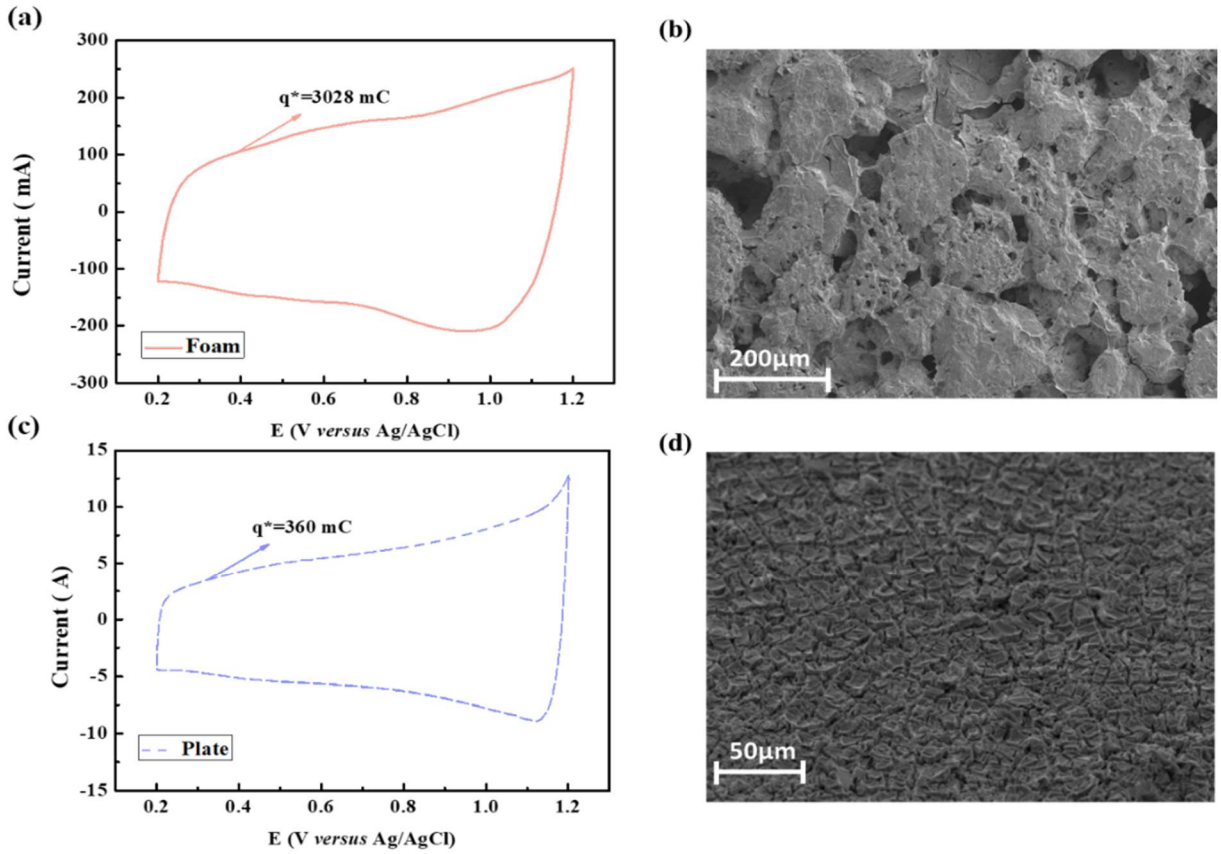

Figure 2. Cyclic voltammetry curves obtained at a scan rate of 20 mV s^{-1} using the anodes (a) Ti foam and (c) Ti plate; scanning electron microscopy (SEM) images of anodes (b)Ti foam and (d) Ti plate.

The voltammetric charge calculated, from Figure 2a, for the foam electrode is 3208 mC, being around 10-fold greater than that of the Ti plate electrode (Figure 2b) for the same geometric area tested. As it is known [27], the larger the electroactive area, the higher the number of active

sites, and consequently, the better the electrocatalytic activity. Thus, the anode with Ti foam as a substrate could display an enhanced electrocatalytic activity associated with its larger electrochemically active area.

Figures 2b and 2d show the SEM images acquired for the anodes synthesized in this study. Both electrodes are covered by homogeneous thin films, with high adherence since that handling does not produce detachments of film. Likewise, we observe that the substrate structure of the Ti foam (Figure 2b) is highly porous and that the deposition of the oxides did not obstruct the pores, thereby giving an anode with a larger surface area. The Ti plate (Figure 2d) has a coating with a typical "cracked mud" morphology resulting from the different expansion rates during the calcination process. Similar results were found in several studies [17,18,29–31] focused on the synthesis of MMO anodes, where cracked mud aspect was also found in the electrode surface morphology. This outcome corroborates with the CV data, where the Ti foam has a greater voltammetric active area than the Ti plate.

3.2 Degradation of antibiotics by electrolysis and photo-electrolysis

Figure 3 shows the removal of PENG, MEP, and CLP achieved during photolysis, electrolysis, and photo-electrolysis in urine polluted with 50 mg L^{-1} of each antibiotic and treated in the MF-Reactor and E-cell. The experiments were carried out in galvanostatic mode at 30 mA cm^{-2}. The decay results were plotted as a function of the concentration of pharmaceuticals, and the reaction kinetics are plotted on a semi-logarithmic scale.

For photolysis, regardless of the reactor configuration used, no decrease in antibiotic concentrations is observed, indicating that this single technology is unsuitable for removing antibiotics and consequently for their mineralization. Regarding electrolysis, good removal of antibiotics was achieved (at least 70%). Finally, in photo-electrolysis, the removals were more accentuated (82%–100%). However, a critical point is the configuration of the reactor. The MF-

Reactor noticeably promotes faster and larger removal of target contaminants. The key point for this behavior is that the Ti foam is three-dimensional, possessing pores that provide an enhanced contact surface than the Ti plate, and consequently, it has a pronounced electroactive area (see Fig. 2). This effect corroborates with the data obtained in the electrode CVs (**Figure 2**), confirming that the higher is the electroactive area, the higher is the electrocatalytic activity toward the removal of the pollutants.

Besides, the MF-Reactor configuration allows exploring two fundamental points: the micro inter-electrode gap (which reduces the ohmic resistance of the system) and the percolation associated with the flow-through configuration (which increases the anode contact surface). Therefore, the greater electroactive area in contact with the polymedicated urine results in efficient degradation using the MF-Reactor. Similar results were found by Perez and collaborators [32] once compared a commercial cell flow with a microfluidic flow-through reactor in the electrochemical degradation of clopyralid. The energy needed to mineralize 100-ppm clopyralid reduced 15-fold when used the flow-through reactor. This improvement was attributed to both a greater surface area and a 70% higher mass transfer coefficient.

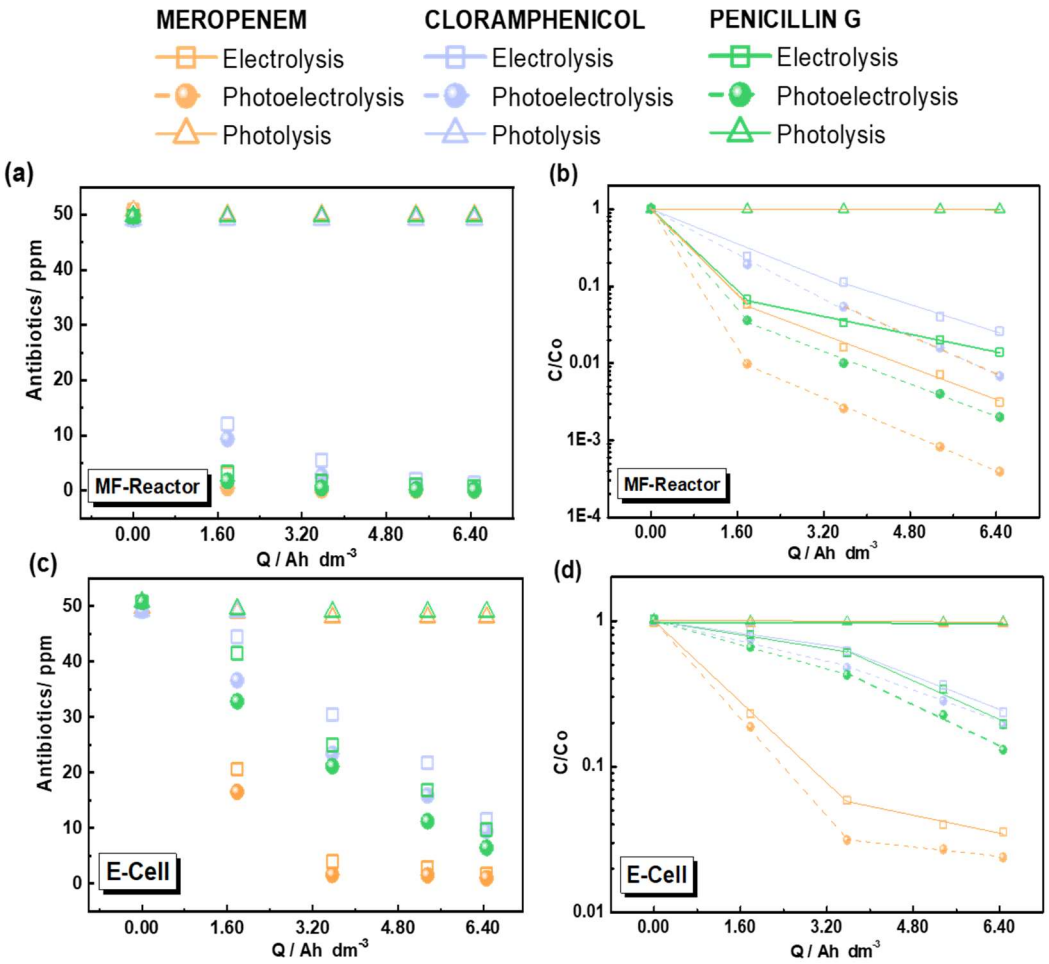

Figure 3. Removal of antibiotics in synthetic urine using (a) Microfluidic flow-through reactor (c) Electrochemical cell and kinetics decay as a function of treatment time by different processes (b) Microfluidic flow-through reactor (d) Electrochemical cell.

Figures 3b and **3d** show the kinetics decays for the removal of the pharmaceuticals studied here. All cases adjust well to pseudo-first-order kinetics. The kinetic constants adjusted from experimental data are shown in Table 1. For photolysis, regardless of the reactor configuration used, there is only one behavior with extremely slow reaction speed, which justifies the low or negligible removal of the antibiotics. For electrolysis and photo-electrolysis, two behaviors with different tangents are distinguishable, indicating different antibiotic removal rates. This behavior has been previously reported in the literature, and it can indicate the coexistence of more complex processes (parallel reactions) and the competitive oxidation between the different organic

compounds contained in the urine [11]. It is observed that the first zone is the fastest, and consequently, the most efficient. The second zone has a slower rate, which probably corresponds to the competition for oxidants produced during the reaction between the antibiotics and their intermediates [33].

Furthermore, it is worth considering that, when using the MF-Reactor, the reaction rate is much faster (from 2–4 times) than when using the E-cell. This fact can be explained in terms of the configuration of the reactor and the anode used. The MF-Reactor has a configuration that allows the electrodes to have a microdistance [16]. This micro-gap decreases the ohmic resistance of the system and consequently increases mass transport [32]. In general, very small distances (in this case, micrometers) between the electrodes spontaneously enhance the mass transport of pollutants towards the electrode surfaces [34]. Additionally, since the 3-D anode allows the flow through it, the contact surface increases compared with the 2-D anode , in addition to decreasing the accumulation of gases within the interelectrodic range. The importance of this information is highlighted, since the ohmic resistance does not only depend on the gap between the electrodes, but also on the fluid dynamics within it [32]. Another relevant explanation for the increase in mass transport in the flow-through configuration is the local turbulence induced by the 3D electrode used in the MF-reactor [35].

Regardless of the system configuration, integrated photo-electrolysis removes antibiotics more efficiently than photolysis and electrolysis, indicating that mediated oxidation is important to increase the efficiency of the process. Mechanisms for understanding this improved efficiency have been previously studied [7]. The oxidants electrogenerated on anodes surfaces are transformed into highly oxidant radicals by UV irradiation, therefore extending the oxidation from the proximity of the surface of the electrodes to the bulk of the treated wastewater. Additionally, the combination of electrochemical and UV light processes generates synergism for removing the three antibiotics, affecting 3-fold more positively when using the MF-Reactor,

for all antibiotics (Table 1). The improvement of efficiency after adding UVC light can be justified by forming massive chlorine and hydroxyl radicals through homolytic reactions of ions present in the urine [36].

Table 1: Kinetic constants observed for antibiotics decays and the synergistic coefficient on MF-Reactor and E-cell.

		Kinetic contants												**Synergistic coefficient (%)**						
		Meropenem				*Penicillin G*				*Chloramphenicol*				MRP			PenG		CLP	
		k_1	R^2	k_2	R^2	k_1	R^2	k_2	R^2	k_1	R^2	k_2	R^2	Z_1	Z_2	Z_1	Z_2	Z_1	Z_2	
MF-Reactor	Ph	0.0001	1	–	–	0.001	0.99			0.0001	1	–	–	22	77	63	13	28	42	
	EC	0.59	1	0.13	0.99	0.61	0.98	0.23	0.99	0.25	0.99	0.19	0.99							
	PhEC	0.72	1	0.23	0.99	1.02	0.99	0.26	0.99	0.32	0.99	0.27	0.99							
E-cell	Ph	0.0001	1	–	–	0.001	1	–		0.0001	1	–	–	20	9	13	8	27	14	
	EC	0.15	0.99	0.14	0.98	0.31	0.98	0.11	0.96	0.15	0.98	0.12	0.99							
	PhEC	0.19	0.99	0.16	0.98	0.37	0.98	0.12	0.98	0.17	0.99	0.13	0.97							

On the other hand, **Figure 4** shows the removal of other organics contained in the urine composition (urea, creatinine, and uric acid) and TOC after passing 6.4 Ah dm^{-3} of electric charge with a current density of 30 mA cm^{-2}. Note that these organics (urea, creatinine, and uric acid) remain in the solutions in highly relevant concentrations after treatment using all the configurations and processes tested here. It indicates that the competitive oxidation of antibiotics is favored [37–39] over creatine, urea, and acid uric. In light of these results, the use of MMO seems to be promising for selective treatments where electrochemical processes are used to reduce the concentration of dangerous pharmaceuticals (which occurred with a low current charge and, consequently, lower operating cost) [33].

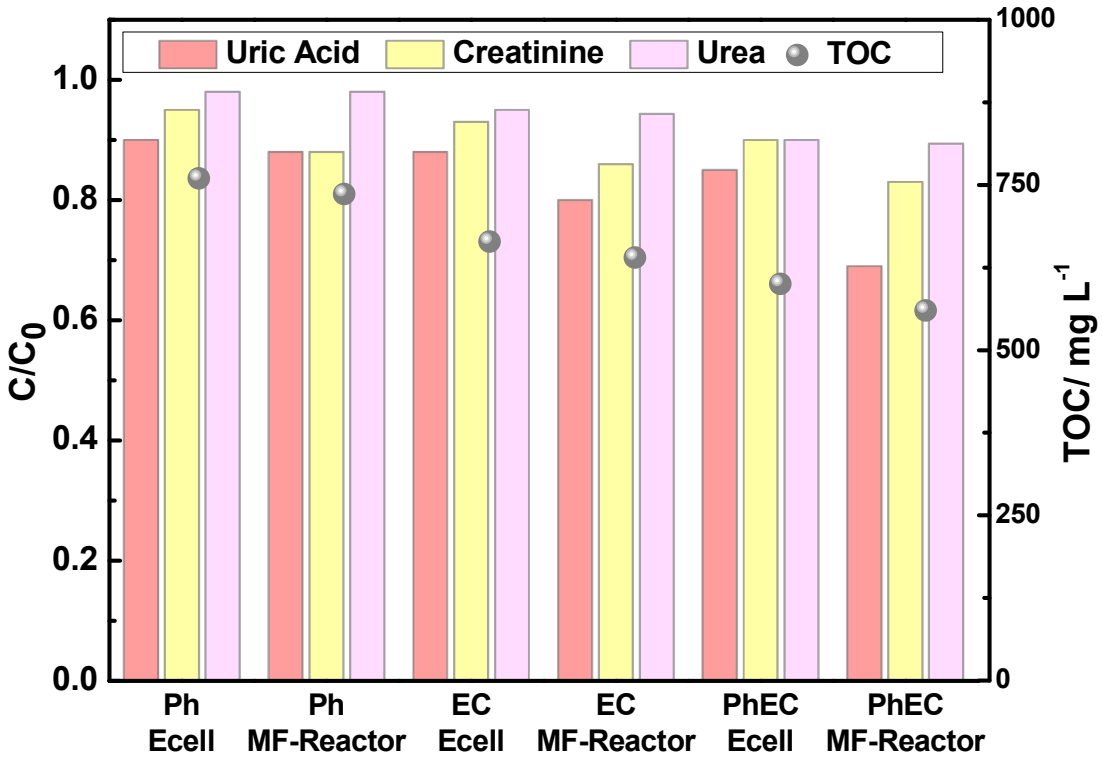

Figure 4. Removal of TOC, uric acid, urea, and creatinine during the electrolysis and photoelectrolysis of PENG, MRP, and CLP solutions in urine media. The electric charge passed was 6.4 Ah dm^{-3} at 30 mA cm^{-2}. TOC_0: 800 mg L^{-1}

When using the E-cell, TOC removals of 17% and 25% are achieved by electrolysis and photo-electrolysis, respectively. Whereas by using MF-Reactor, removals of 20 and 30% are achieved by applying electrolysis and photo-electrolysis, respectively.

In addition, another essential point to be highlighted is the micro-gap between the electrodes, which reduces the ohmic resistance observed in the MF-Reactor, which can reduce operating costs [40,41]. Besides, the use of UVC light favors the activation of oxidants in the bulk solution, transforming them into radical species [42–44].

However, it is worthwhile to consider that monitoring only the decay of compounds and TOC is not enough to assess the risk of accumulation of antibiotics in the environment because intermediates formed during the oxidation may have antibiotic behavior. Because of that, in this work, the antibiotic resistance of treated and untreated polymedicated urine solutions was assessed by exposure to two types of bacteria, a gram-positive (*Enterococcus Faecalis*) and a gram-negative (*Escherichia Coli*) [45]. Particularly, *E. Faecalis* bacteria are intrinsically resistant to many commonly used antimicrobial agents but exhibit sensitivity to penicillin, whereas *E. Coli* has a high sensitivity to chloramphenicol and meropenem. Therefore, the information acquired from both microbiological tests can be a valuable indicator of the antibiotic effect of urine after treatments. **Figure 5** shows the results obtained for these antibiotic resistance tests, in which each sample was measured in four dilutions (without dilution, 1:10, 1:100, and 1:1000) [46]. When the urine still contains an antibiotic effect, a CFU decrease should be observed, which indicates the high ecotoxicity risk of the urine sample. The antibiotic effect of the treated urine is still high after electrolysis due to the presence of antibiotics (regardless of the bacteria or anode used) that still deactivates the bacteria (from 10^7 to 10^5 CFU mL^{-1}). Conversely, the population of *E. Faecalis* and *E. Coli* is practically unaffected when the urine is treated by photo-electrolysis (the bacterial population remains around 10^7 CFU mL^{-1}) for MF-Reactor.

Therefore, this result indicates a low risk of ecotoxicity for this sample; thereby, its release into the environment can occur without adverse impacts.

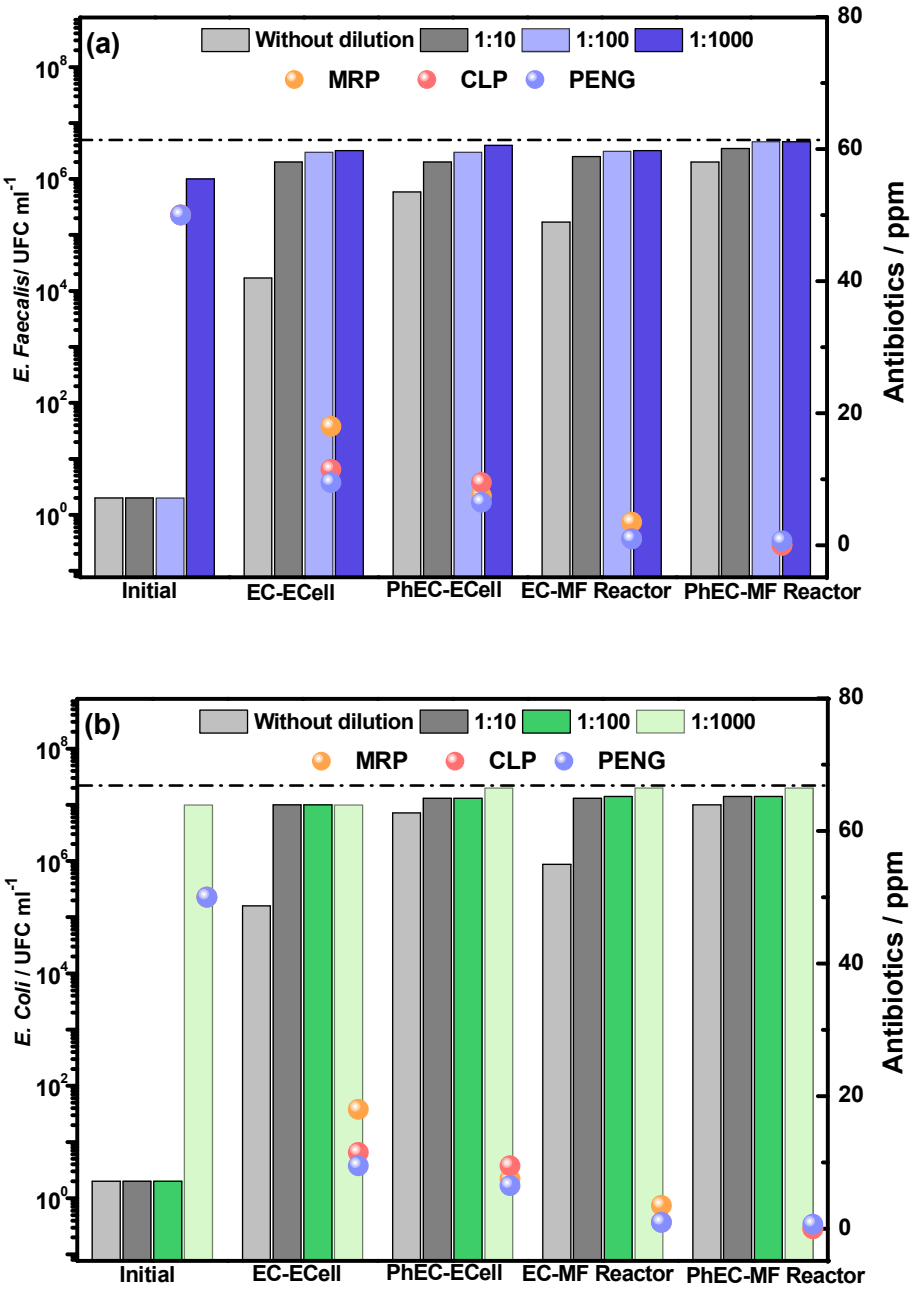

Figure 5. Antibiotic effect (bars) in terms of E. Faecalis (a) and E. Coli (b) survival measured after the electrolysis and photo-electrolysis of PENG (●), MRP (●), and CLP (●) in urine mediaThe electric charge passed was 6.4 Ah dm^{-3}.

As another critical operational characteristic, the electrical energy to reduce the concentration of antibiotics by one order of magnitude (EEO) was calculated for Ecell (**Figure 6a**) and MF-Reactor (**Figure 6b**). The EEO is lower (~1.5 times) when PhEC is used, irrespective of the configuration used. However, when comparing the E-cell and MF-Reactor, it is clear that the electrical consumption to oxidize pollutants is about 3 times lower in the MF-Reactor. This behavior can be attributed to the primary factors: the 3D morphology of the anode (largest active area) and the improved mass transport and decreased ohmic resistance associated with the innovative reactor design (micro distance between the anode and cathode).

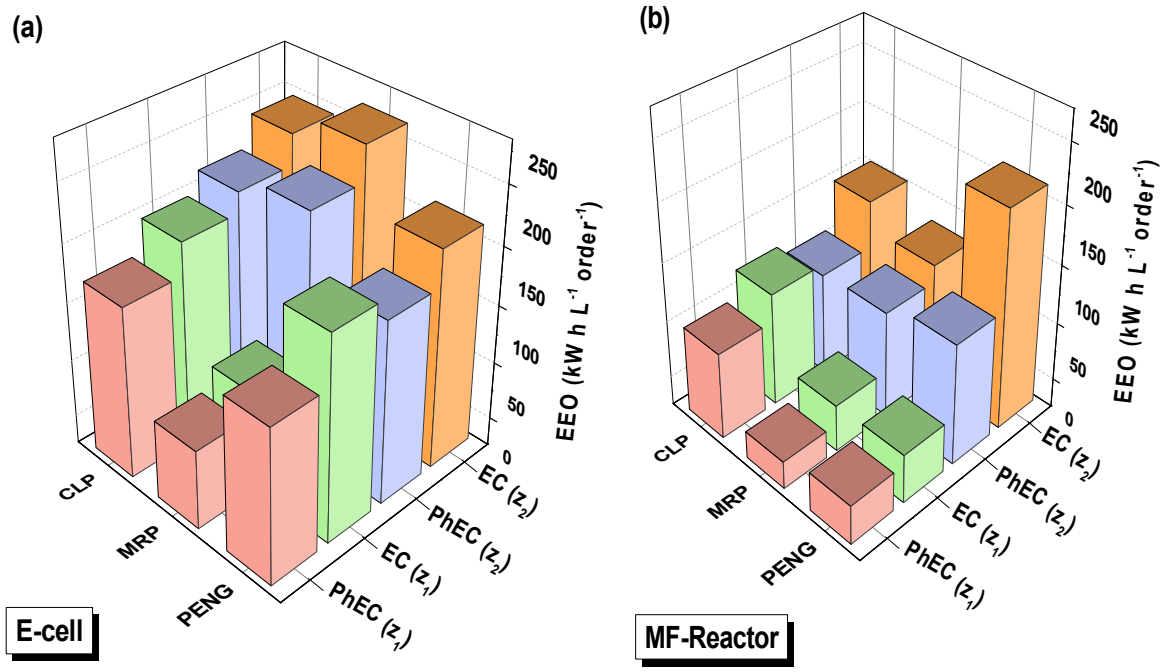

Figure 6. Electrical energy by one order of magnitude consumed to reduce the concentration of PEN G, MRP, and CLP. (a) Data for the E-cell and (b) data for the MF-Reactor.

The results obtained in this study were compared with previous research in the literature in which the degradation of antibiotics in the urine matrix using AOP was evaluated. Comparing these different studies is a complex task since the research uses different experimental conditions

tested, such as the antibiotics under study, the electrode material used, the reaction time, and the current density.

Table 2 gives an overview of both the experimental conditions and the main results found. All works listed use electrochemical oxidation (EO) to degenerate one or more antibiotics in a highly complex matrix, urine. Antonin et al. [47] the degradation of 100 mL of 0.245 mM of the antibiotic ciprofloxacin in urine matrix using a DDB or Pt anode. The EO process with DDB was considered the most efficient treatment, obtained the removal of ciprofloxacin and 98% of mineralization after 6 h of electrolysis.

Similar results were reported by Herraiz-Carboné et al. [24] during electrolysis of urine solutions containing chloramphenicol: the antibiotic is removed after 6 h of treatment at 1.25 mA cm^{-2}. Besides, there was a 74% decrease in toxicity and a 60% increase in biodegradability after treatment. These results are in agreement with those obtained during the electrolysis or photoelectrolysis of MRP, CLP, and PENG. However, the system configuration appears to be a key parameter in removing antibiotics (major kinetics and removal) and in the removal of antibiotic resistance (as shown in Figs. 3 and 5). Thus, the results of our study once more confirm the excellent performance of the MF-Reactor configuration and the efficiency of the 3D anode for treating hospital wastewater.

Table 2. Comparison of the performance antibiotics degradations in urine matrix

Antibiotics	AOP	Parameters	Results	Reference
Ciprofloxacin	EO	t = 6 h j = 66 mA cm^{-2} C_0 = 0.245 mM *Anode* = DDB or Pt	96% ciprofloxacin removal and 98% mineralization after 6 h	[47]
Tetracycline	EO	t = 3 h j = 10–40 mA cm^{-2} C_0 = 200 mg L^{-1} *Anode*= $Ti/Ru_{0.3}Ti_{0.7}O_2$	50% tetracycline removal	[39]

Cephalexin	EO	t = 2 h j = 6 mA cm^{-2} C_0 = 0.86 mM *Anode:* Ti/RuIr	80% Cephalexin removal and 56% activity antibiotic removal	[8]
Norfloxacin	EO	t = 3 h j = 6.53 mA cm^{-2} C_0 = 125 µM *Anode:* Ti/IrO_2	60% Norflaxacin removal and more than 6 h for complete removal of antibiotic activity	[9]
Cefazolin	EO	t = 8 h j = 0.5 mA cm^{-2} C_0 = 100 µM *Anode:* Pt	60% Cefazolin removal	[48]
chloramphenicol	EO	j = 1.25–5 mA cm^{-2} C_0 = 100 mg L^{-1} *Anode:* DDB or RuO_2	100% chloramphenicol removal and 60% increase in biodegradability	[24]
Ibuprofen and Cloxacillin	EO	j = 100 or 1000 A m^{-2} C_0 = 10 mg L^{-1} *Anode:* DDB	100% antibiotic removal	[11]
Meropenem, chloramphenicol and Penicillin G	EO; PhEC	t =7.24 h j = 30 mA cm^{-2} C_0 = 50 mg L^{-1} *Anode:* Foam or plate (Ti/RuO_2IrO_2)	~100% antibiotic removal and complete removal of antibiotic activity	*This work*

4. Conclusions

Based on the results obtained from this research, the following conclusions are drawn:

- Simple photolysis is inefficient in removing the antibiotics studied here, regardless of the configuration used. However, valuable-positive synergisms are obtained by irradiating UVC light to electrochemical processes, which are explained in terms of the activation of electrogenerated oxidants in solution.

- MMO-RuO_2IrO_2 electrodes, produced in this work by a novel microwave heating technique, have demonstrated outstanding features for the treatment of pollutants contained in urine.

- The reactor design is of extreme significance for the treatment process efficiency. The cell equipped with the 3D anode proved to be extremely efficient in removing antibiotics. This behavior was directly related to the greater electroactive area of the anode and the flow-

through configuration of the reactor, which increased the contact area and improved the mass transport, consequently favoring the degradation of organic compounds.

-The lower interelectrode gap is also a great advantage obtained with the use of 3-D electrodes that leads to cheaper treatment processes. The MF-Reactor can degrade antibiotics more quickly and consume lower energy.

- The photo-electrolysis with MMO is one of the best technologies to decrease the ecotoxicity risk of hospital urine wastes polluted with PENG, CLP, and MRP.

Acknowledgments

Financial support from Junta de Comunidades de Castilla-La Mancha (JCCM), European Union (European Regional Development Fund), and the Ministry of Science and Innovation through the projects SBPLY/17/180501/000396 and PID2019-110904RB-I00 are gratefully acknowledged. The Spanish Ministry of Economy, Industry, and Competitiveness and the European Union (project EQC2018-004469-P) are also gratefully acknowledged. Brazilian agencies CNPq (304419/2015-0, 305438/2018-2, and 311856/2019-5), CAPES (88882.365553/2018-01 and 88881.190029/2018-01), and FAPITEC/SE are also gratefully acknowledged.

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