

Scale-up of Ru-based mesh anode for the degradation of synthetic hospital wastewater

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Abstract

This work focuses on the scale up of photoelectrochemical technology for the removal of synthetic urine polluted with meropenem (MP), penicillin G (PG) and chloramphenicol (CL). A conventional mixed electrochemical cell (MEC) with an anode of 4 cm² and a microfluidic flow-through cell (MFC) with an anode of 66 cm² were compared. In both cases, MMO-RuO₂TiO₂ anodes were used and synthetic urines were doped with 50 mgL⁻¹ of each antibiotic (MP, PG, and CL). Same current density and current charge passed were applied. Results demonstrate that photo-electrolysis results attains the efficient removal of MP, PG and CL in the MFC and in the MEC and that removals in the MFC were faster, which was attributed to the improved mechanical design of the cell. In addition, it was confirmed that selective oxidation of antibiotics occurred in both cases, once the complete removal of the three drugs under study was achieved before the removal of the other organics present in the urine. Finally, it was evaluated the removal of the antibiotic effect of the treated effluent with two different bacteria, *E. Coli* and *E. Faecalis* and it was demonstrated that after the PEC treatment there was no residual antibiotic effect, regardless of the system used.

Keywords: Polymedicated urine; antibiotic activity; photo-electrolysis; scaling-up.

1. Introduction

Water pollution with recalcitrant compounds is an important issue, as it has a significant and negative impact on the environment and human health [1]. A relevant topic is the disposal of hospital wastewaters (HWWs), as they are 5-15 times more toxic than urban effluents [2,3]. Additionally, this problem is worsened by the COVID-19 pandemic, as recent studies have reported an increase of up to 45% in the consumption of antibiotics during this period [4].

Hospital urine can be considered as a primary source of not only of drugs but also of pathogens [5]. Typically, these wastes are discharged, together with the other liquids wastes produced in the sanitary facilities, into urban sewers, where they merge with urban wastewater for being then treated by conventional methods in municipal wastewater treatment plants[6]. However, the conventional methods used in these plants are not suitable to remove recalcitrant compounds such as antibiotics, and because of that, the discharge of the effluents of these plants become a major source of this hazardous pollutants in environment [7]. One of the consequences of these ineffective treatments is the emergence of antibiotic-resistant bacteria (ARB) [8], which are becoming a major threat to global health, food security and development according to the World Health Organization (WHO). Therefore, in order to minimize the occurrence of ARBs, it has been suggested as a very promising option to pre-treat hospital urine before disposing it with HWWs, using advanced processes capable of removing antibiotics efficiently by destroying partially this complex molecules [9].

Among these methods, electrochemical technology appears as an advantageous alternative and it has been widely studied in the recent years [10–13]. Several recent studies have focused on the configuration of the cell [14–16] and the material of the anode [17–19]. Regarding cell configuration, there are two widely studied systems: the mixed electrochemical cell (MEC) and the microfluidic flow-through cells (MFC). MEC is a system widely used in

lab-scale studies while for large scale applications, it is preferred the use of flow cells, where the design of the cell allows to reach higher mass transport coefficients and, hence, a much higher efficiency in the degradation of the pollutants. This becomes an important advantage if considering that low concentration of pollutants in this treatment becomes a handicap, as processes are mass-transport controlled [20]. Related to the optimized design of the flow cells, a critical element to be studied is the distance between the electrode materials, since the distance affects the ohmic drop and, hence, to the energy consumed[17]. Thus, the smaller is the distance between the electrodes, the lower is the cell potential and, consequently, the operating costs of this treatment [21] [25]. In this context, a previous work of our group [22] reported excellent performance of microfluidic reactors with micro-gap spacing for the treatment of a soil washing effluent (with low conductivity) polluted with organic compounds. These results were later validated with other types of wastes [23,24].

Considering this background, this work focuses on the initial stage of the scaling up of an important problem: the treatment of urine excreted by polymedicated patients, as well as the evaluation of competitive oxidation between antibiotics and the organic compounds contained in the urine. Thus, three technologies will be used for the treatment of polymedicated urine: photolysis, electrolysis (EC), and photo-electrolysis (PEC). Furthermore, it aims to increase the scale-up of a promising anodic material using it in MEC and MFC. The anode performance was investigated by evaluating the removal of Meropenem (MP), Penicillin G (PG), and Chloramphenicol (CL) in an extremely complex matrix: synthetic urine. In addition, the feasibility of combination with UVC irradiation was evaluated. The volume of the irradiated area and the current density were kept fixed, in both systems, for a better understanding of the increasing scale of the system.

2. Experimental

Chemicals. The antibiotics (PG, CL, and MP), urea, creatinine, uric acid, and inorganic salts employed were of analytical grade (>98% purity) and purchased from Sigma-Aldrich. **Table 1** shows details of synthetic urine media based on the composition given by Dbira et al. [26,27], as well as the concentration of the antibiotics studied in this research. Acetonitrile, methanol and formic acid used for the mobile phase of HPLC were purchased from Sigma-Aldrich. All aqueous solutions were prepared using high-purity water Millipore Milli-Q system, resistivity >18 M Ω .

Table 1. Information of the synthetic urine and antibiotics

Compound	Molecular formula	Concentration (mg L ⁻¹)
Urea	CH ₄ N ₂ O	3333.0
Creatinine	C ₄ H ₇ N ₃ O	166.6
Uric acid	C ₅ H ₄ N ₄ O ₃	50.0
Potassium chloride	KCl	1000.0
Magnesium sulfate	MgSO ₄	170.0
Calcium phosphate	(Ca) ₃ (PO ₄) ₂	28.3
Sodium carbonate	Na ₂ CO ₃	166.7
Diammonium hydrogen phosphate	(NH ₄) ₂ HPO ₄	83.3
Meropenem	C ₁₇ H ₂₅ N ₃ O ₅ S	50.0
Penicillin G	C ₁₆ H ₁₈ N ₂ O ₄ S	50.0
Chloramphenicol	C ₁₁ H ₁₂ Cl ₂ N ₂ O ₅	50.0

Experimental setup. In this study, two experimental systems were used: MEC and MFC. The synthesis scheme of the anodes, as well as the configurations of the systems are described in detail elsewhere [22,28,29]. The anode used in MEC was a metal mixed oxide (MMO) plate

(Ru_{0.3}Ti_{0.7}O₂) with 4.0 cm² of geometric area and cathode stainless steel AISI304. In the MFC, it was used a mesh anode of the same composition, with 66 cm², cathode stainless steel AISI304 and between the electrodes a Teflon separator of 150 μm. The anodes used in this work were synthesized according to Santos *et al.* [28] methodology. In order to compare the systems equally, the processes were carried out to remove the antibiotics in urine polluted with MP, CL and PG, 50 mg L⁻¹ of each. Thus, the same current density (30 mA cm⁻²), and electric charge (6.4 A h L⁻¹) were used to ensure similar operational conditions. Because of that, it is worthy to inform that the experiments conducted using the MFC lasted 7.17 h, while 8 h were needed for the MEC experiments to pass the same charge applied. In the experiments carried out in the MFC, the solution passes through the electrodes using a Micropump[®] (GB-P25 J F5 S, with head coupled to a DB 380 A 24 V motor with speed control 0–5 V DC powered by Techma GPM SLr) a fixed flow rate of 140 L h⁻¹. The volume used was 2.25 L for the MFC and 0.15 L for the MEC. In the photolysis and PEC experiments, a UVC lamp (λ = 254 nm) was used to irradiate 9 W directly to the electrolyte solution.

Analytical techniques. The high-performance liquid chromatography (HPLC) was used with an Eclipse Plus C-18 column (4.6 mm x 100 mm) at 30 °C and an injection volume of 20 μL. To identify the PG antibiotic, the mobile phase was 50% methanol and 50% acidified water (with 0.1% formic acid), flow of 0.6 mL min⁻¹ at a wavelength of 220 nm. To follow the evolution of MP, the mobile phase was 15% acetonitrile and 85% formic (0.1%), with a flow of 0.2 mL min⁻¹. CL was quantified using the mobile phase of 50% methanol and 50% Milli-Q water with a flow rate of 0.6 mL min⁻¹ and DAD detection wavelength of 270 nm. Additionally, the monitoring of other organics contained in the urine composition was carried out using HPLC for monitored of uric acid (UA), ion chromatography for creatinine (CR) and colorimetric methods for urea (UR), according to previously reported methodologies [30].

Finally, changes in total organic carbon (TOC) were measured using a TOC Multi N/C 3100 Analytik Jena.

Physical Characterization. The surface morphology of the plate and mesh anode was visualized using a field emission scanning electron microscope (FE-SEM; Zeiss GeminiSEM 500) with 500x magnification.

Antibiotic activity assay. Finally, the antibiotic activity of the samples treated by EC or PEC were analyzed with a μ -Trac[®] 4200 (Sy-lab, Austria) that performs the counting of microorganisms. The analyzes were performed with two different types of bacteria, *E. Coli* and *E. Faecalis*. Initially, the bacteria were placed on agar plates and incubated at 37 °C. Subsequently, the urine matrix was contaminated with $\sim 10^7$ colonies forming units (CFU) of *E. Coli* and *E. Faecalis* and after contamination a sample was measured to check the initial concentration of microorganisms. The treated samples were measured in different concentrations (without dilution, 1:10, 1:100 and 1:1000) and kept under agitation and controlled temperature (37 °C) for 3 h. Finally, the CFU was measured by μ -Trac[®] 4200.

3. Results and Discussion

Scanning electron microscopy (SEM) measurements were carried out to analyze the morphology of the anodes, as well as to confirm whether the change in its form (one anode in plate and the other in mesh) and in the size by the increase of the substrate (from 4 to 66 cm²) brings great changes. It is observed in the SEM images (**Figure 1**) that both surfaces under study have similar morphologies with homogeneous and compact film, which is an advantage of caused by the rapid heating/cooling rate of the method [31]. It is still possible to observe the presence of some cracks, which is typically attributed to the difference in the coefficients of thermal expansion of the substrate and the formed film [32]. Finally, the morphology of both

anodes are similar, where it can be concluded that the increase in size and changes in form of the substrate does not modify the morphology of the deposited film.

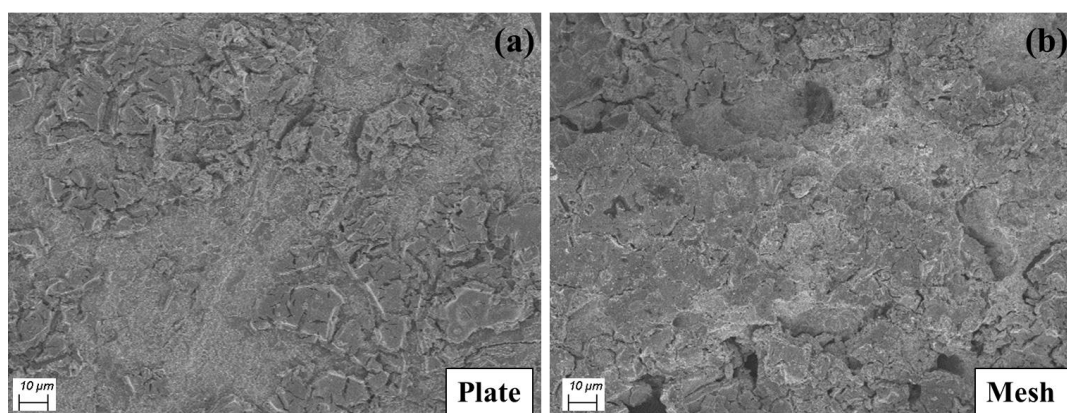


Figure 1: SEM images of the anodes in different substrates with a magnification of 500× magnification for the deposited film of $\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ in (a) Ti Plate and (b) Ti mesh.

Figure 2 shows the removal of 50 mg L^{-1} of each antibiotic (MP, PG, and CL) during EC and PEC in a complex matrix, the synthetic urine. The degradation experiments were carried out in two different systems: MEC and MFC. All results were compared with the removal obtained by single photolysis. As result, it is possible to observe that after 8 h of treatment, less than 10% of each antibiotic in the synthetic urine is degraded by photolysis. Opposite, the electrochemical techniques are much more efficient, regardless of the system used. In electrolysis, after 8 h of reaction with an applied charge of 6.4 A h L^{-1} , removal of all antibiotics was higher than 60% using the MEC and 63% with the MFC. As for photo-electrolysis, the removals increases up to 75% for MEC and 88% for the MFC applying the same electric charge. Hence, the more realistic design of the MFC, with much lower interelectrode gaps, shows important improvements and this increases in size does not only non enworsen but promote the removal of the antibiotics from the urine[22,28].

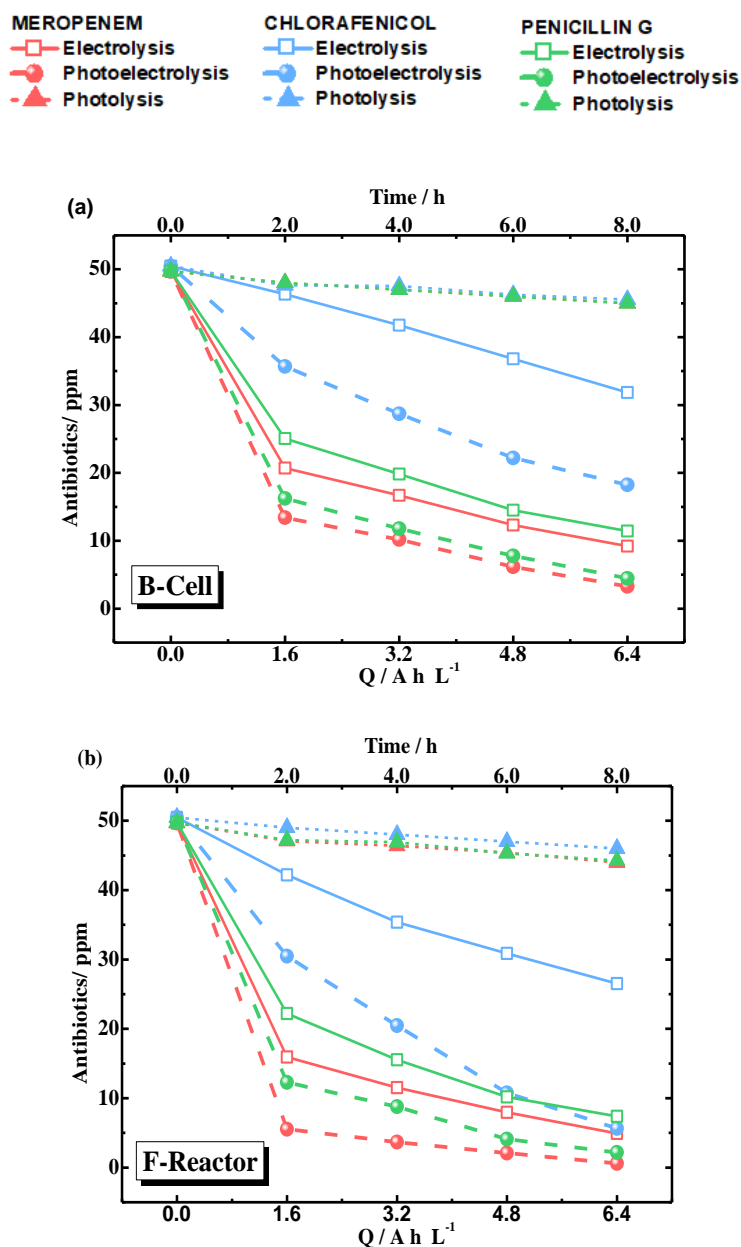


Figure 2: Degradation of MP, PG and CL during photolysis, electrolysis, and photoelectrolysis of synthetic urine solutions in the (a) MEC and (b) MFC. Current density applied in electrochemical processes: 30 mA cm^{-2} . UV-light power applied in irradiated processes: 9 W.

Similar results were found by Perez and co-authors [22], where they compared two different reactors, one flow by and the other microfluidic flow for the electrochemical oxidation of a pesticide. When using the microfluidic flow-through reactor the electrical charge necessary

for mineralization of the pesticide, was 10 times lower than in the flow-by reactor. The reduction of the energy required for the mineralization of the organic compound was attributed to a 70% higher mass transfer coefficient of the microfluidic flow-through system. Decay of antibiotics were fitted to pseudo-first order kinetics (Eq. 1) and values are plotted in **Figure 3**, where the constants obtained in the MFC are seen to be almost double of those achieved in the MEC, despite the same current density is applied and the same electric charge is passed. This results highlight the significance of a good mechanical design of the cell in the scaleup [22,28,33].

$$\ln \frac{C}{C_0} = k \cdot t \quad (1)$$

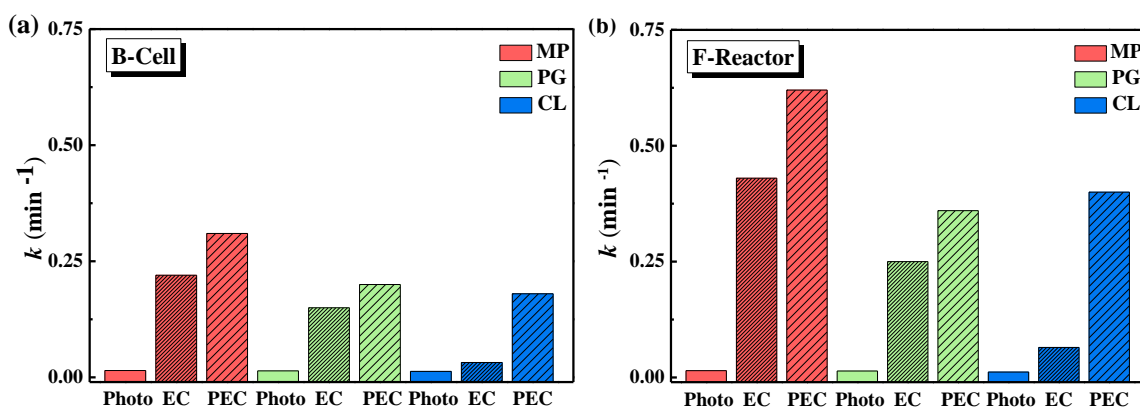


Figure 3: Pseudo-first-order degradation rate constants for: (a) MEC and (b) MFC.

It is important to note that the urine matrix is extremely complex, containing several organic compounds, such as urea (UR), creatinine (CR) and uric acid (UA), in concentrations which are even higher than the antibiotics concentration [27]. These organics can be oxidized in the treatment, competing directly with the oxidation of antibiotics, thus reducing the efficiency of the desired processes [34,35]. Thus, in the **Figure 4**, it is shown the decay of the organic components of urine (UR, UA, and CR) during the 8 h of the processes. Note that photolysis does not eliminate any of the organics present in the urine composition. On the other

hand, when the EC or PEC processes are applied, it is clear that regardless of the system, the UA decreases about 40%, while the CR and UR reduces in about 30% and 10%, respectively.

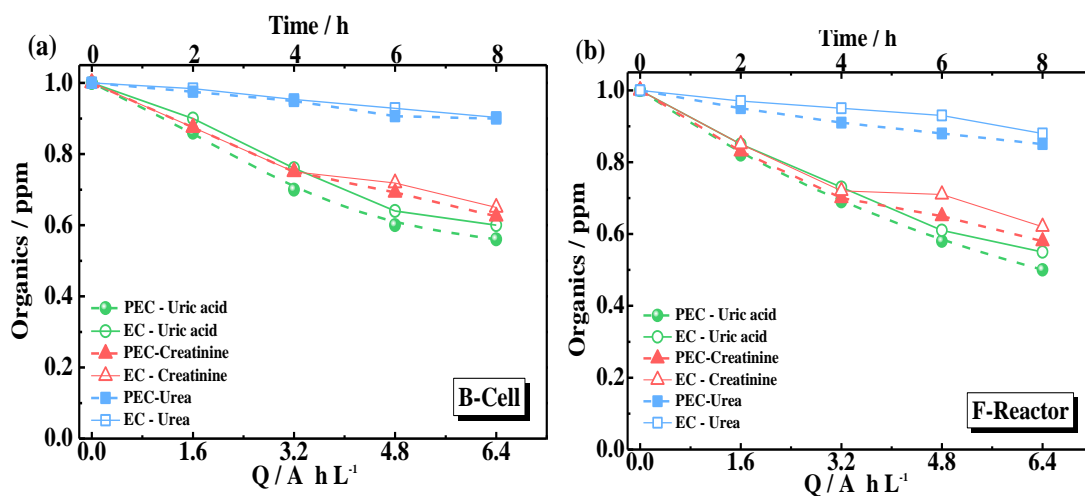


Figure 4: Changes in the concentration of UR, CR, and UA during the electrolysis or photoelectrolysis in the (a) MEC and (b) MFC. Current density applied in electrochemical processes of 30 mA cm^{-2} and UV-light power applied in irradiated processes: 9 W .

Therefore, it can be affirmed that UR, UA and CR are present at high concentrations at the end of all processes, in both systems, indicating that among the organics present in the medium, the oxidation of antibiotics is favored [36]. Therefore, we can conclude that the use of MMO in electrochemical processes, using low applied current, is highly promising for the selective oxidation that highly dangerous organic compounds [37,38].

The total organic carbon (TOC) have also been monitored to inform mineralization capacity of the processes in both systems studied. As result, **Figure 5a** shows the TOC removal and **Figure 5b** kinetics rate constant achieved after 8 h and 6.4 A h L^{-1} of charge applied to treatments with EC and PEC with two different systems (MEC and MFC). Note that regardless of the system used, the PEC process has a greater TOC removal than the EC (~40 and 30% removal, respectively), but still has relevant TOC concentrations. This is because a large part of the TOC contained in urine polluted with MP, PG and CL comes from UR (approximately

666 mg L⁻¹ of C) [27] and this does not reach removals greater than 10%, as seen in **Figure 4**. Thus, the data obtained for UR decay directly corroborate with the final TOC value. This result may give new possibilities to arise development of selective degradation technologies for the treatment of hospital wastewater.

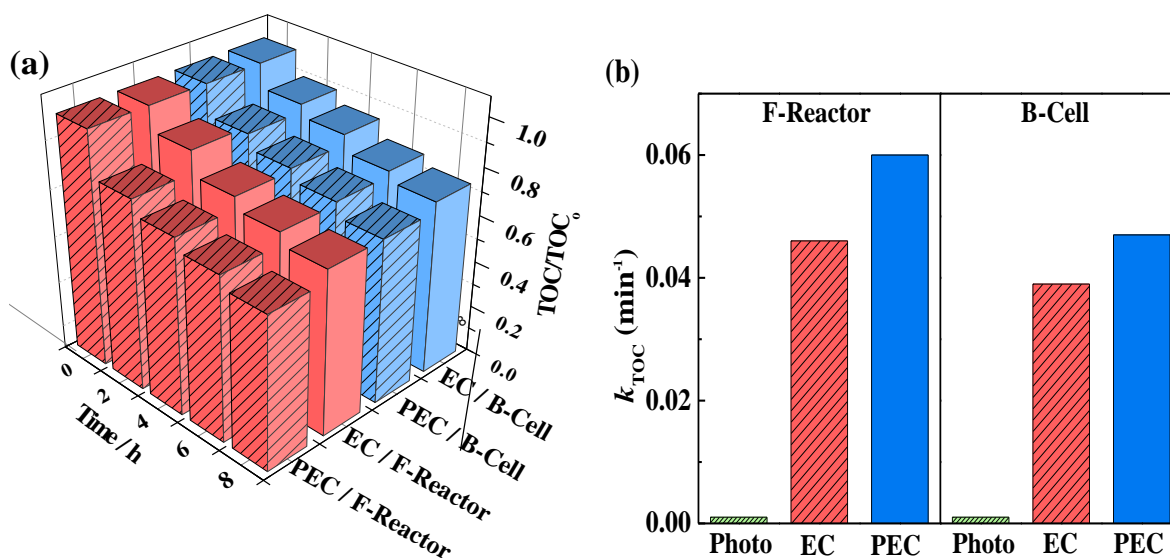


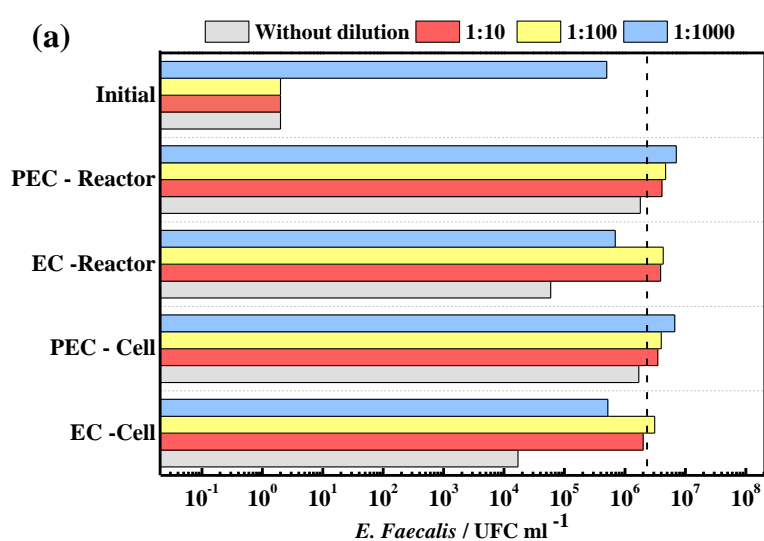
Figure 5: (a) TOC removal on the different processes (EC and PEC) in B- and MFC. (b) TOC kinetics rate constant. Conditions: current density 30 mA cm⁻², TOC initial 800 mg L⁻¹.

As can be seen for TOC kinetics rate constant (**Figure 5b**), PEC in MFC also appears as the better system due to the faster kinetics. Despite other substances in the complex matrix are responsible to contribute to the TOC, which make it the kinetics slow, PEC leads to better outcomes, mainly in the MFC

At this point, it is important to consider that these results only confirm the removal of antibiotics (MP, PG and CL), but do not inform about the remaining dangerousness of the treated urine, which may be associated with the presence of highly toxic substances (antibiotic and/or by-products) such as biologically active organic compounds or inorganic species [36,39,40]. Therefore, it is necessary to use techniques based on biological indicators to assess the hazardousness of urine before and after treatment [41]. Therefore, to clarify this point, in addition to the physical-chemical characterization, it is necessary to use a specific method to

monitor the antibiotic resistance of the urine treated using microorganisms as the target bacteria. According to previous research by this group [30], this method can be used with different types of antibiotics, but the selection of the target bacteria depends directly on the type of antibiotic and its mechanism of action. Since in these studies we analyzed a urine that was polymedicated with MP, PG and CL, we used two different types of bacteria, *E. Faecalis* and *E. Coli*. From the results achieved in the microbiological method, and analyzing together with the physical-chemical characterization, it will be possible to determine optimal conditions to reduce the risk of hospital wastewaters.

Thus, after treatment, the urine was mixed with a pure culture of *E. faecalis* (10^6 CFU mL^{-1}) or *E. Coli* (10^7 CFU mL^{-1}) after 3 h of contact at 37°C , it was possible to quantify the amount of CFU remaining in the solution with $\mu\text{-Trac}^{\text{®}}$ 4200. **Figure 6** shows the analysis of the antibiotic effect of polymedicated urines, before and after treatment. We can observe that regardless of the system used, urine treated with PEC has no antibiotic effect. On the other hand, those treated with EC, presented a low antibiotic effect, since in both bacteria the CFU concentration went from 10^6 - 10^7 to 10^5 (just an order of magnitude).



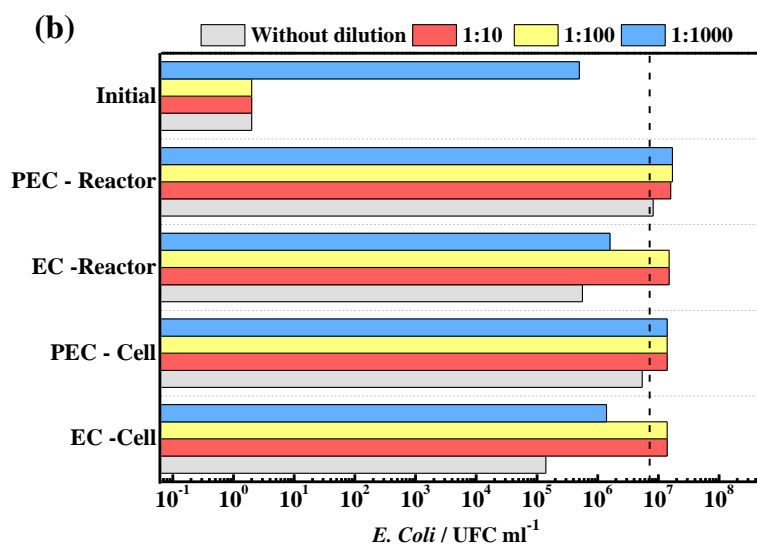


Figure 6. Antibiotic effect in terms of (a) *E. Faecalis* and (b) *E. Coli* survival measured after the EC and PEC in both systems (MEC and MFC). Electric charge passed: 6.4 A h L⁻¹.

These results confirm the suitability of the technology: the disposal of treated urine in the environment should not have any adverse effects other than typical urban wastewater. Moreover, the results obtained in this test corroborates with the main conclusion obtained in the previous studies: The PEC is efficient to reduce the dangerousness of hospital urine. In addition, these results allows to remark that the increase in the size of the equipment (and also in the mechanical design of the cell) improves operating results even taking into account the high scaleup ratios evaluated (more than 15) as the volumes of synthetic hospital wastewater treated increase from 0.15 to 2.25L and the anode size from 4 and 66 cm².

4. Conclusion

From this research, the following conclusions can be drawn:

- Meropenem, Penicillin G and Chloramphenicol have been efficiently degraded using electrolysis and photo-electrolysis, while single photolysis is not able to degrade any of the target antibiotics;

- Better results with the MFC as compared with the MEC, that indicate that the scale-up was successfully performed using the same operational parameters in both systems. The large scaleup ratio (over 15) supports the necessity of evaluating new reactor designs during the scaling up.
- PEC is the best technology to decrease the antibiotic activity of hospital urine polluted with MRP, PG and CL.
- Anodes used in both systems showed high selectivity for the target antibiotics removal which are contained in a complex water matrix where other organic and inorganic substances are present.
- Findings reported in the present work are very important in the context of the treatment of polluted water with antibiotics, which are of special concern on the topic of avoid ecotoxicological risks, mainly related to antibiotic resistant bacteria.

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5. References

- [1] G. Ren, M. Zhou, M. Liu, L. Ma, H. Yang, A novel vertical-flow electro-Fenton reactor

for organic wastewater treatment, *Chem. Eng. J.* 298 (2016) 55–67. doi:10.1016/j.cej.2016.04.011.

[2] P. Verlicchi, M. Al Aukidy, E. Zambello, What have we learned from worldwide experiences on the management and treatment of hospital effluent? - An overview and a discussion on perspectives, *Sci. Total Environ.* 514 (2015) 467–491. doi:10.1016/j.scitotenv.2015.02.020.

[3] P. Verlicchi, A. Galletti, L. Masotti, Management of hospital wastewaters: The case of the effluent of a large hospital situated in a small town, *Water Sci. Technol.* 61 (2010) 2507–2519. doi:10.2166/wst.2010.138.

[4] A.K. Murray, The Novel Coronavirus COVID-19 Outbreak: Global Implications for Antimicrobial Resistance, *Front. Microbiol.* (2020). doi:10.3389/fmicb.2020.01020.

[5] N.A. Khan, S. Ahmed, I.H. Farooqi, I. Ali, V. Vambol, F. Changani, M. Yousefi, S. Vambol, S.U. Khan, A.H. Khan, Occurrence, sources and conventional treatment techniques for various antibiotics present in hospital wastewaters: A critical review, *TrAC - Trends Anal. Chem.* (2020). doi:10.1016/j.trac.2020.115921.

[6] D. Mao, S. Yu, M. Rysz, Y. Luo, F. Yang, F. Li, J. Hou, Q. Mu, P.J.J. Alvarez, Prevalence and proliferation of antibiotic resistance genes in two municipal wastewater treatment plants, *Water Res.* (2015). doi:10.1016/j.watres.2015.09.010.

[7] R.K. Langbehn, C. Michels, H.M. Soares, Antibiotics in wastewater: From its occurrence to the biological removal by environmentally conscious technologies, *Environ. Pollut.* (2021). doi:10.1016/j.envpol.2021.116603.

[8] L. Proia, A. Adriana, S. Jessica, B. Carles, F. Marinella, L. Marta, B.J. Luis, P. Servais, Antibiotic resistance in urban and hospital wastewaters and their impact on a receiving

freshwater ecosystem, *Chemosphere*. (2018). doi:10.1016/j.chemosphere.2018.04.163.

[9] M. Herraiz-Carboné, S. Cotillas, E. Lacasa, P. Cañizares, M.A. Rodrigo, C. Sáez, Enhancement of UV disinfection of urine matrixes by electrochemical oxidation, *J. Hazard. Mater.* (2021). doi:10.1016/j.jhazmat.2020.124548.

[10] W. Yang, M. Zhou, N. Oturan, Y. Li, M.A. Oturan, Electrocatalytic destruction of pharmaceutical imatinib by electro-Fenton process with graphene-based cathode, *Electrochim. Acta.* 305 (2019) 285–294. doi:10.1016/j.electacta.2019.03.067.

[11] D. Dionisio, A.J. Motheo, C. Sáez, P. Cañizares, M.A. Rodrigo, Competitive Anodic Oxidation of Methyl Paraben and Propylene Glycol: Keys to Understand the Process, *ChemElectroChem*. (2019). doi:10.1002/celec.201801332.

[12] H. Pourzamani, N. Mengelizadeh, Y. Hajizadeh, H. Mohammadi, Electrochemical degradation of diclofenac using three-dimensional electrode reactor with multi-walled carbon nanotubes, *Environ. Sci. Pollut. Res.* (2018). doi:10.1007/s11356-018-2527-8.

[13] E.A. Serna-Galvis, A.L. Giraldo-Aguirre, J. Silva-Agredo, O.A. Flórez-Acosta, R.A. Torres-Palma, Removal of antibiotic cloxacillin by means of electrochemical oxidation, TiO₂ photocatalysis, and photo-Fenton processes: analysis of degradation pathways and effect of the water matrix on the elimination of antimicrobial activity, *Environ. Sci. Pollut. Res.* 24 (2017) 6339–6352. doi:10.1007/s11356-016-6257-5.

[14] D.A.C. Coledam, J.M. Aquino, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, Influence of chloride-mediated oxidation on the electrochemical degradation of the direct black 22 dye using boron-doped diamond and β -PbO₂ anodes, *Quim. Nova.* 37 (2014) 1312–1317. doi:10.5935/0100-4042.20140219.

[15] G. Ren, M. Zhou, P. Su, W. Yang, X. Lu, Y. Zhang, Simultaneous sulfadiazines

degradation and disinfection from municipal secondary effluent by a flow-through electro-Fenton process with graphene-modified cathode, *J. Hazard. Mater.* 368 (2019) 830–839. doi:10.1016/j.jhazmat.2019.01.109.

[16] Y. Jiao, L. Ma, Y. Tian, M. Zhou, A flow-through electro-Fenton process using modified activated carbon fiber cathode for orange II removal, *Chemosphere.* 252 (2020) 126483. doi:10.1016/j.chemosphere.2020.126483.

[17] W. Wu, Z.-H. Huang, T.-T. Lim, Recent development of mixed metal oxide anodes for electrochemical oxidation of organic pollutants in water, *Appl. Catal. A Gen.* 480 (2014) 58–78. doi:10.1016/j.apcata.2014.04.035.

[18] X. Li, H. Li, M. Li, C. Li, D. Sun, Y. Lei, B. Yang, Preparation of a porous boron-doped diamond/Ta electrode for the electrocatalytic degradation of organic pollutants, *Carbon N. Y.* 129 (2018) 543–551. doi:10.1016/j.carbon.2017.12.052.

[19] G.O.S. Santos, K.I.B. Eguiluz, G.R. Salazar-Banda, C. Saez, M.A. Rodrigo, Photoelectrolysis of clopyralid wastes with a novel laser-prepared MMO-RuO₂TiO₂ anode, *Chemosphere.* 244 (2020). doi:10.1016/j.chemosphere.2019.125455.

[20] X. Zhu, J. Ni, J. Wei, P. Chen, Scale-up of B-doped diamond anode system for electrochemical oxidation of phenol simulated wastewater in batch mode, *Electrochim. Acta.* 56 (2011) 9439–9447. doi:10.1016/j.electacta.2011.08.032.

[21] C.A. Martínez-Huitle, O. Scialdone, M.A. Rodrigo, Electrochemical water and wastewater treatment, 2018. doi:10.1016/C2016-0-04297-3.

[22] J.F. Pérez, J. Llanos, C. Sáez, C. López, P. Cañizares, M.A. Rodrigo, Development of an innovative approach for low-impact wastewater treatment: A microfluidic flow-through electrochemical reactor, *Chem. Eng. J.* (2018). doi:10.1016/j.cej.2018.06.150.

- [23] J.F. Pérez, S. Sabatino, A. Galia, M.A. Rodrigo, J. Llanos, C. Sáez, O. Scialdone, Effect of air pressure on the electro-Fenton process at carbon felt electrodes, *Electrochim. Acta.* 273 (2018) 447–453. doi:10.1016/j.electacta.2018.04.031.
- [24] J.F. Pérez, A. Galia, M.A. Rodrigo, J. Llanos, S. Sabatino, C. Sáez, B. Schiavo, O. Scialdone, Effect of pressure on the electrochemical generation of hydrogen peroxide in undivided cells on carbon felt electrodes, *Electrochim. Acta.* 248 (2017) 169–177. doi:10.1016/j.electacta.2017.07.116.
- [25] J.F. Pérez, J. Llanos, C. Sáez, C. López, P. Cañizares, M.A. Rodrigo, A microfluidic flow-through electrochemical reactor for wastewater treatment: A proof-of-concept, *Electrochem. Commun.* (2017). doi:10.1016/j.elecom.2017.07.026.
- [26] S. Dbira, N. Bensalah, A. Bedoui, P. Cañizares, M.A. Rodrigo, Treatment of synthetic urine by electrochemical oxidation using conductive-diamond anodes, *Environ. Sci. Pollut. Res.* 22 (2015) 6176–6184. doi:10.1007/s11356-014-3831-6.
- [27] S. Dbira, N. Bensalah, P. Cañizares, M.A. Rodrigo, A. Bedoui, The electrolytic treatment of synthetic urine using DSA electrodes, *J. Electroanal. Chem.* 744 (2015) 62–68. doi:10.1016/j.jelechem.2015.02.026.
- [28] G. de O.S. Santos, I.M.D. Gonzaga, A.R. Dória, A. Moratalla, R.S. da Silva, K.I.B. Eguiluz, G.R. Salazar-Banda, C. Saez, M.A. Rodrigo, Testing and scaling-up of a novel Ti/Ru_{0.7}Ti_{0.3}O₂ mesh anode in a microfluidic flow-through reactor, *Chem. Eng. J.* 398 (2020). doi:10.1016/j.cej.2020.125568.
- [29] G. de O.S. Santos, K.I.B. Eguiluz, G.R. Salazar-Banda, C. Saez, M.A. Rodrigo, Testing the role of electrode materials on the electro-Fenton and photoelectro-Fenton degradation of clopyralid, *J. Electroanal. Chem.* (2020). doi:10.1016/j.jelechem.2020.114291.

- [30] I.M.D. Gonzaga, A. Moratalla, K.I.B. Eguiluz, G.R. Salazar-Banda, P. Cañizares, M.A. Rodrigo, C. Saez, Influence of the doping level of boron-doped diamond anodes on the removal of penicillin G from urine matrixes, *Sci. Total Environ.* (2020). doi:10.1016/j.scitotenv.2020.139536.
- [31] G.O.S. Santos, L.R.A. Silva, Y.G.S. Alves, R.S. Silva, K.I.B. Eguiluz, G.R. Salazar-Banda, Enhanced stability and electrocatalytic properties of Ti/RuIr_{1-x}O₂ anodes produced by a new laser process, *Chem. Eng. J.* 355 (2019) 439–447. doi:10.1016/j.cej.2018.08.145.
- [32] A.R. Dória, I.M.D. Gonzaga, G.O.S. Santos, M. Pupo, D.C. Silva, R.S. Silva, M.A. Rodrigo, K.I.B. Eguiluz, G.R. Salazar-Banda, Ultra-fast synthesis of Ti/Ru_{0.3}Ti_{0.7}O₂ anodes with superior electrochemical properties using an ionic liquid and laser calcination, *Chem. Eng. J.* 416 (2021) 129011. doi:10.1016/j.cej.2021.129011.
- [33] G.R.P. Malpass, R.S. Neves, A.J. Motheo, A comparative study of commercial and laboratory-made Ti/Ru_{0.3}Ti_{0.7}O₂ DSA?? electrodes: “In situ” and “ex situ” surface characterisation and organic oxidation activity, *Electrochim. Acta.* 52 (2006) 936–944. doi:10.1016/j.electacta.2006.06.032.
- [34] S. Cotillas, E. Lacasa, M. Herraiz, C. Sáez, P. Cañizares, M.A. Rodrigo, The Role of the Anode Material in Selective Penicillin G Oxidation in Urine, *ChemElectroChem.* 6 (2019) 1376–1384. doi:10.1002/celec.201801747.
- [35] S. Cotillas, E. Lacasa, C. Sáez, P. Cañizares, M.A. Rodrigo, Removal of pharmaceuticals from the urine of polymedicated patients: A first approach, *Chem. Eng. J.* 331 (2018) 606–614. doi:10.1016/j.cej.2017.09.037.
- [36] I.M.D. Gonzaga, A. Moratalla, K.I.B. Eguiluz, G.R. Salazar-Banda, P. Cañizares, M.A. Rodrigo, C. Saez, Novel Ti/RuO₂IrO₂ anode to reduce the dangerousness of antibiotic polluted urines by Fenton-based processes, *Chemosphere.* 270 (2021).

doi:10.1016/j.chemosphere.2020.129344.

[37] S. Cotillas, E. Lacasa, C. Sáez, P. Cañizares, M.A. Rodrigo, Electrolytic and electro-irradiated technologies for the removal of chloramphenicol in synthetic urine with diamond anodes, *Water Res.* 128 (2018) 383–392. doi:10.1016/j.watres.2017.10.072.

[38] M. Herraiz-Carboné, S. Cotillas, E. Lacasa, Á. Moratalla, P. Cañizares, M.A. Rodrigo, C. Sáez, Improving the biodegradability of hospital urines polluted with chloramphenicol by the application of electrochemical oxidation, *Sci. Total Environ.* (2020). doi:10.1016/j.scitotenv.2020.138430.

[39] P. Villegas-Guzman, S. Oppenheimer-Barrot, J. Silva-Agredo, R.A. Torres-Palma, Comparative Evaluation of Photo-Chemical AOPs for Ciprofoxacin Degradation: Elimination in Natural Waters and Analysis of pH Effect, Primary Degradation By-Products, and the Relationship with the Antibiotic Activity, *Water. Air. Soil Pollut.* 228 (2017). doi:10.1007/s11270-017-3388-3.

[40] I.M.D. Gonzaga, A. Moratalla, K.I.B. Eguiluz, G.R. Salazar-Banda, P. Cañizares, M.A. Rodrigo, C. Saez, Outstanding performance of the microwave-made MMO-Ti/RuO₂IrO₂ anode on the removal of antimicrobial activity of Penicillin G by photoelectrolysis, *Chem. Eng. J.* (2021). doi:10.1016/j.cej.2021.129999.

[41] S.D. Jojoa-Sierra, J. Silva-Agredo, E. Herrera-Calderon, R.A. Torres-Palma, Elimination of the antibiotic norfloxacin in municipal wastewater, urine and seawater by electrochemical oxidation on IrO₂ anodes, *Sci. Total Environ.* 575 (2017) 1228–1238. doi:10.1016/j.scitotenv.2016.09.201.