Pressurized electro-Fenton for the reduction of the environmental impact of antibiotics

Ángela Moratalla[1], Danyelle M. Araújo[2], Gabriel O. M. A. Moura[3], Engracia Lacasa[4], Pablo Cañizares[1], Manuel A. Rodrigo[1], Cristina Sáez[1*]

[1] Department of Chemical Engineering, Faculty of Chemical Sciences and Technologies, University of Castilla-La Mancha, Edificio Enrique Costa Novella, Campus Universitario s/n, 13005 Ciudad Real, Spain

[2] Faculty of Exact and Natural Sciences, State University of Rio Grande do Norte, Campus Central, Mossoro - RN 59625-620, Brazil

[3] Federal University of Rio Grande do Norte, School of Science and Technology, Natal - RN, 59078-970, Brazil

[4] Department of Chemical Engineering, Higher Technical School of Industrial Engineering, University of Castilla-La Mancha, Edificio Infante Don Juan Manuel, Campus Universitario s/n, 02071 Albacete, Spain

*author to whom all correspondence should be addressed (corresponding author): cristina.saez@uclm.es. Tel.: +34-926-29-53-00 Ext. 6708

ABSTRACT

This work evaluates the performance of a pressurized heterogeneous electro-Fenton (EF) process to transform the antibiotic into compounds that do not promote the appearance of bacteria resistant to antibiotic in the environment. Experimental system consisted of a pressurized non divided microfluidic electrochemical cell equipped with a jet aerator, flow-through electrodes and a fluidized bed of goethite as heterogeneous iron catalyst. Results show that meropenem (model antibiotic) can be degraded by EF and that the degradation rate depends on the gauge pressure applied: the higher is the pressurization, the faster is the abatement of meropenem. The antibiotic effect of the urine is related to meropenem remained in the treated urine, and the contribution of reaction intermediates does not seem to be relevant. The mineralization of the organic load is almost nil. The higher dissolved oxygen concentration of pressurized-EF and thus, the higher hydrogen peroxide generation seems to be the key point to explain the effect of pressure on EF process. Results confirm that moderated pressurized EF process (up to 3 bar) can be satisfactorily used to decrease the chemical risk of synthetic hospital urines, which opens the possibility of an optimized pre-treatment which may help to save cost in the treatment of these hazardous wastes.

Keywords

Antibiotic, urine, antibiotic effect, electro-Fenton, pressure.

1. INTRODUCTION

The presence of antibiotics in aquatic environments, related to its high consumption and the inefficiency of conventional biological processes to remove this type of compounds, is one of the main subjects of environmental concerns nowadays [1, 2]. Because of this, many researchers have focused their studies on the development of technologies for the abatement of this type of pharmaceutical compounds from industrial and treated urban wastewater to prevent their accumulation in the environment. Recently, the focus has been on the treatment of sanitary effluents that are considered one of the main routes of entry of antibiotics into the environment.

During last decade, Electrochemical Advanced Oxidation Processes (EAOPs) have demonstrated their readiness to reach high efficiencies in the degradation of organic compounds, including antibiotics and other pharmaceutics in different aqueous matrixes [3-5]. Among EAOPs, EF process is one of the most effective technologies for achieving fast and complete degradation of target organic pollutants in water [6-8]. This process is based on the continuous electro-generation of hydrogen peroxide by reducing oxygen at the cathode, and the activation of this oxidant throughout its transformation into hydroxyl radicals by the decomposition of H_2O_2 catalyzed by Fe^{2+} through Fenton´s Reaction. Then, the performance of the EF process depends on the electroactivity and selectivity of the cathode to produce H_2O_2. Carbonaceous materials doped with a mixture of carbon black and polytetrafluoroethylene (CB/PTFE) have demonstrated good results in the rapid and efficient production of hydrogen peroxide [4, 9-14]. In addition, the oxygen fed, and the Fe-based catalysts are also considered two key parameters in the development of efficient processes and further scientific effort is still needed to design EF reactors feasible to be scaled and that allow the implementation of the technology at full-scale.

To solve the problem of oxygen feeding, different strategies have been evaluated. In many cases, gas diffusion electrodes (GDE) were used [15]. GDE allows air or oxygen to pass directly through the diffusion layer, but it generally presents a relatively small specific electrode surface area, poor stability, and difficult scalability. Because of this, some authors have studied other alternatives. Pérez et al. [16] reported the use of a jet aerator based on the Venturi effect, which allowed generate air bubbles and supersaturate in oxygen the electrolyte without the need for a compressor. The jet was also used by Yu et al. [17] in a novel jet-type reactor (vertical flow reactor) to enhance the hydrogen peroxide production, getting that the H_2O_2 production was much larger than the traditional gas diffusion cathode (1419 mg dm^{-3} against 684 mg dm^{-3}, respectively) and where the removal of tetracycline hydrochloride with this novel reactor was around 100% (88% of total organic carbon, TOC) within the 60 min of reaction in EF process. Other authors proposed the use of pressurized-EF reactors in which the system was pressurised with air or oxygen to increase the dissolved oxygen concentration, demonstrating that hydrogen peroxide generation can be significantly improved [11, 18, 19]. The obtained results showed that the removal of organics such Acid Orange 7 and maleic acid was accelerated using air-pressurized EF processes [18, 20]. In addition, Klidi et al. [21] reported the treatment of paper mill wastewater by pressurized-EF, improving TOC removal from 48 to 58% when pressure increased from 1 to 10 bar. Similar results were obtained by Ltaïef et al. [19].

With this background, this work tries to go one step further, proposing for the first time the study of the influence of pressurization at bench scale on the performance of a heterogeneous EF process in its application for the degradation of antibiotics in synthetic hospital urine, selected as model of sanitary effluent where drugs are highly concentrated. In this case, the complete mineralization of the organic load is not required, but the decrease of the hazardousness associated to the polluted urine. That is, the aim is to transform the antibiotic into compounds without antibiotic effect that do not promote the appearance of bacteria

resistant to antibiotic in the environment, but not their complete mineralization (which will be cheaper by many other technologies). To do this, meropenem is selected as antibiotic model, which is a broad-spectrum antibiotic of the carbapenem class that is frequently used to treat clinical diseases caused by Gram-negative bacteria such as *Escherichia coli* (*E. coli*) [22] and that is excreted through urine. The experiments are performed in a pressurized microfluidic electrochemical cell equipped with a jet aerator and flow-through electrodes [11], and results are evaluated in terms of meropenem abatement and removal of antibiotic effect.

2. MATERIALS AND METHODS

2.1 Chemicals

Meropenem trihydrate (MRP) was supplied by the Pharmacy Department of the Albacete University Hospital (Spain). Anhydrous sodium sulphate (Na_2SO_4) was purchased from Panreac. Calcium phosphate, diammonium hydrogen phosphate, sodium carbonate, magnesium sulfate, potassium chloride, uric acid, creatinine, and urea were used to make the synthetic urine and supplied by Sigma-Aldrich. The pH of the samples was adjusted using sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH). HPLC grade Methanol, HPLC grade acetonitrile and formic acid (98% from Sigma-Aldrich) were used in the mobile phase. P-dimethylaminobenzaldehyde (from Sigma-Aldrich) and titanium (IV) oxysulfate (1.9-2.1%, from Sigma-Aldrich) were used as indicators of urea and hydrogen peroxide, respectively. Goethite (catalyst grade, 30-50 mesh from Sigma-Aldrich) was used as heterogeneous catalyst for EF tests. All solutions were prepared using double de-ionized water (Millipore Milli-Q system, resistivity: 18.2 MΩ cm at 25 ºC).

2.2 Experimental set-up

As shown in Figure 1a, the experimental setup consists in a microfluidic flow-through cell (MF-FT) with a pressurized-jet aeration (PJA). The tank, the cell and the pipelining are

fabricated from polyvinyl chloride (PVC). The electrolyte (2.7 dm^{-3}) is fed to the cell from the reservoir tank by a Micropump® (GB-P25 J F5 S A head coupled to a DB 380 A 24 V motor with speed control 0-5 V DC supplied by Techma GPM s.l.r.) fixing a flow rate of 140 $dm^3\ h^{-1}$. In addition, it incorporates a fluidized bed of goethite particles connected to the outlet of the electrochemical cell. The fluid velocity throughout the bed is 0.043 m s^{-1}. A heat exchanger is used for control temperature.

In the MF-FT cell, the electrodes are separated by a polytetrafluoroethylene (PTFE) film with an inter-electrode gap of 150 μm. 3D-Mixed Metal Oxide mesh (MMO-$IrO_2Ta_2O_5$) supplied by Tianode® is used as anode. 3D-titanium mesh with a deposition of carbon black (CB, Vulcan® XC72 from cabot corporation) and PTFE (a 60% wt. Teflon® emulsion solution in H_2O, from Sigma-Aldrich) is used as cathode in EF tests. In Electrooxidation (EO) tests, the cathode is replaced by a perforate-plate stainless steel AISI 304. (Figure 1b). The dimensions of the electrodes were 8 x 9.5 cm, with 33 cm^2 corresponding to the wet area. The surface area was 49.5 cm^2 and was estimated by determining the surface/ geometric area ratio [23].

For cathode preparation, the titanium mesh (from Xian Howah Technology Co., Ltd.) is immersed into boiling hydrochloric acid (HCl, 37% from Scharlab) solution (20% v/v) for 15 min, followed by immersion into boiling oxalic acid (99.5 % from Panreac) solution (10% v/v), and finally it is rinsed with ultrapure water. The CB/PTFE mixture are prepared by dispersing 1 mg mL^{-1} of CB and 5 mg mL^{-1} of PTFE into isopropanol for 2 hours at 50 ºC in an ultrasound bath. After this, titanium mesh is place over plate at 130 ºC and 200 mL of ink is sprayed (100 mL each side). Finally, electrodes are tempered at 360 ºC for 1 h starting from room temperature at a heating rate of 12 ºC min^{-1}. A second layer is deposited on the electrode, repeating the procedure.

Synthetic urine is polluted with 50 mg dm^{-3} of meropenem. Urine consists of a mixture of organic species such as urea, creatinine, uric acid, and inorganic salts (including potassium

chloride, magnesium sulfate, or diammonium hydrogen phosphate). The composition synthetic urine has been reported elsewhere [24]. The initial pH of the solution is adjusted to 3.0. All experiments are carried out under galvanostatic conditions at a current density of 5.0 mA cm^{-2}. The amount of goethite used in the fluidized bed is 10.8 g (it guarantees good fluidization of the goethite particles). In the different tests, the system is pressurized, and tests are carried out at gauge pressures ranging from 0.0 to 3.0 bar. The key of the pressurized system is connecting the intake of the jet aerator to the biphasic reservoir tank. After pressurization, the system is in equilibrium as in the case of jet aerated under room pressure. When liquid flows through the Venturi, a difference of pressure appears between the tank and the throat of the jet serving as the driving force (ΔP) to aspire the gas, but in this case a pressurized liquid-gas mixture is obtained. During the treatment the pressure variance is nil. In any case, any possible overpressure caused by gases generated during the process is removed when the system is momentarily opened for sampling.

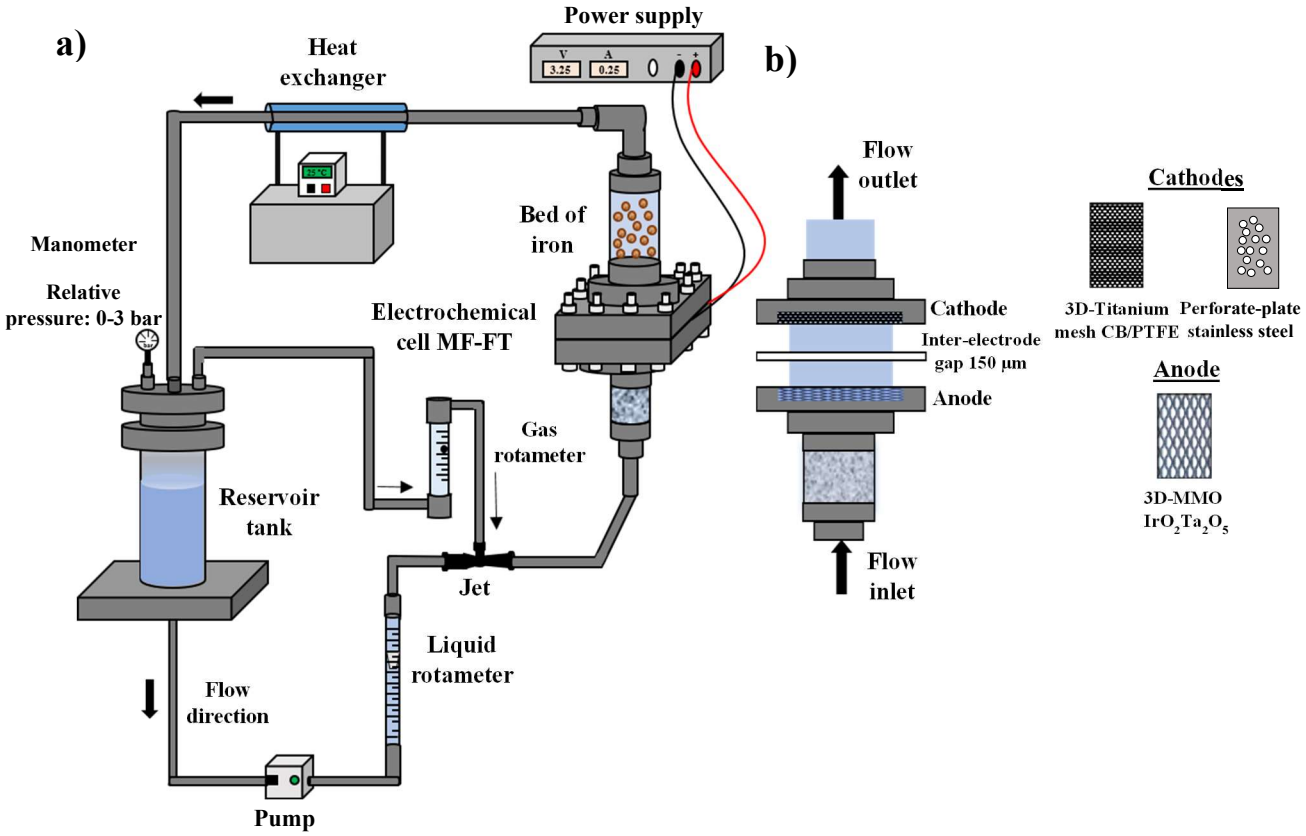


Figure 1. Experimental set-up. a) Complete view, b) diagram of the electrochemical cell MF-FT and electrodes.

2.3 Analytical

Meropenem, intermediates and uric acid concentrations are monitored via High Performance Liquid Chromatography (HPLC) using Agilent 1100 series coupled a DAD detector and a Zorbax Eclipse Plus C18 analytical column (4.6 mm x 100 mm; 3.5 μm). The mobile phases used for the determination of meropenem are 15% acetonitrile and 85% formic acid (0.1%) at a flow rate of 0.6 mL min^{-1} at 300 nm. The injection volume is 20 μL. On the other hand, uric acid is determined by using a mobile phase consisting of 2% acetonitrile and 98% aqueous solution with 0.1% of formic acid, applying a flow rate of 1.0 mL min^{-1}, an injection volume of 20 μL and 292 nm wavelength.

Intermediates are identified on an Agilent 1260 Infinity coupled to an Agilent time-of-flight mass spectromgeter (LC-MS TOF 6230) with and electrospray interface operating under the following conditions: capillary, 3500 V; nebulizer 40 psi; drying gas, 10.0 L/min; gas temperature, 325 ºC; skimmer voltage, 65 V. Mobile phase is composed of 15% acetonitrile and 85% aqueous solution with 0.1% formic acid, and flowed at 0.6 mL min^{-1} through a Zorbax Eclipse Plus C-18 column (4.6 mm x 100 mm; 3.5 μm).

The urea is estimated by a spectrophotometric colorimetric method using a UV-1700 Shimadzu Spectrophotometer according to the previously reported methodologies [25]. Creatinine, anions and cations are determined via ion chromatography (IC) with a Metrohm 930 Compact IC Flex coupled to a conductivity detector. Organic acids are identified by HPLC using a Jasco 2080 Plus equipped with a Hi-Plex H (7.7 mm x 300 mm; 8 μm) with detection at 210 nm. The mobile phase consists of 5 mM H_2SO_4 and the injection volume is 20.0 μL. The hydrogen peroxide concentration is measured by spectrophotometric method, following the concentration of the complex formed between H_2O_2 and Ti^{4+} [26].

186 The iron concentration in EF tests is measured using an inductively coupled plasma atomic
187 emission spectroscopy in a Varian Liberty RL sequential ICP-AES equipment.
188
189 *2.4 Antibiotic activity assay*
190 The antibiotic activity of initial and final meropenem samples is determined by using
191 Microtrac® 4200 that counts the colony forming units (CFU) per mL. The microorganism used
192 as indicator is *E. coli*. Before antibiotic activity assay, the microorganisms are incubated on
193 plates with a selective agar at 37 ºC for 24 h. Consequently, urine solution without antibiotic
194 is contaminated with 10^7 CFU of E. *coli*. To verify the initial population of *E. coli*, a control
195 sample (blank) is measured. After this, the antibiotic activity assays are conducted in beakers
196 where 5 mL of urine samples taken from the solution under treatment are added to 5 mL of
197 the solution containing the microorganism. It is maintained under continuous agitation for 3
198 h at 37 ºC. Finally, 1 mL is taken to a measurement cell with culture medium and introduced
199 to the equipment to perform the CFU count. Each urine sample is measured by quadruplicate:
200 without dilution and with dilution 1:10, 1:100 and 1:1000.
201
202 **3. RESULTS AND DISCUSSION**
203
204 Figure 2 shows the final concentration of meropenem remained in the urine after 6.0 h (0.6
205 Ah L^{-1} of electric charge passed) of treatment by EF at different pressurization (gauge
206 pressures ranging from 0 to 3 bar). Additionally, the antibiotic effects of the initial and treated
207 urines are also plotted in terms of CFU of *E. coli* per mL. This antibiotic effect is measured
208 indirectly by comparing the effect of addition of the treated and non-treated urine on a culture
209 of *E. coli*: the higher the number of colonies that survive in the urine, the lower the antibiotic
210 capacity of the urine. In all cases, an initial population of 10^7 CFU mL^{-1} of *E. coli* is used, and

each urine sample (taken from the solution under treatment) is measured by quadruplicate (without dilution and up to 1:1000 dilution). Before starting, pH values were adjusted to 7.0 and the oxidants potentially formed during the electrochemical process (such as hydrogen peroxide, hypochlorite…) were neutralized with thiosulfate. As well, a reference test in absence of antibiotic is carried out to confirm that *E. coli* is not sensitive to other compounds naturally present in the urine and, thus, to discard possible interferences. Thus, it is expected that the obtained results only inform about the antibiotic effect of meropenem, and its reaction intermediates generated during treatment. As well, to show the sensitivity of *E. coli* to meropenem in the conditions used in this work, data obtained with the raw polluted urine (without treatment) are also included in the Figure.

As it can be observed, the meropenem contained in the raw urine (50 mg dm^{-3}) can eliminate completely the *E. coli* contained in the testing samples, and only few colonies can survive when 1:1000 dilution of the raw urine is tested. This confirms that *E. coli* can be used as target model bacterium to monitor the antibiotic activity of synthetic urines polluted with meropenem. Regarding urine samples taken after EF treatment, results show that heterogeneous EF can decrease the meropenem concentration as well as the antibiotic effect of the urine. It is important to take in mind that degradation of the raw antibiotic can lead to the formation of species which still have antibiotic capacity, whose discharge into the environment may favour the development of antibiotic resistant cultures in the environment. Additionally, it can be noted that the increase in the gauge pressure influences markedly on the two parameters selected to monitor the treatment tracking: the higher is the gauge pressure applied during the EF, the higher is the removal of meropenem and the higher is the survival of *E. coli*. This direct relationship between the decrease in the concentration of the antibiotic and the survival of *E. coli* is expected because of the antibiotic capacity of the raw molecule. However, this later parameter is more valuable because it informs also about the antibiotic capacity of the degradation products. In comparing the trends of both parameters, it can be

seen that the effect of the pressurization on the removal of meropenem is lower than in the antibiotic effect, suggesting an influence of the formation of intermediates in this later parameter and the necessity of the simultaneous measurement of the two parameters to understand what it is really happening inside the reactor. In this point, it is important to point out that the minimum inhibitory concentration (MIC) of meropenem to *E. coli* is below 2.00 mg dm^{-3} [27] and, therefore, in urine polluted with lower concentrations no effect should be expected and *E. coli* should remain almost unaltered in the urine media. This is observed in the EF carried out at 3 bar of gauge pressure, where the final meropenem concentration is closer to the MIC and some colonies of *E. coli* survives even when sample is not diluted or when 1:10 dilution is used. The higher amount of *E. coli* remaining in the test may indicate that at higher pressures the degradation of the meropenem is more efficient and leads to intermediates that are more oxidized than at lower pressurization and that due to its greater similarity to meropenem still they have an antibiotic effect. Therefore, these results indicate that the use of pressurized system does not only improve the degradation of antibiotics, but it also helps to decrease the chemical risk of the treated urine by contributing to a more efficient degradation of the raw pharmaceutical compound and its conversion into molecules with no antibiotic effect.

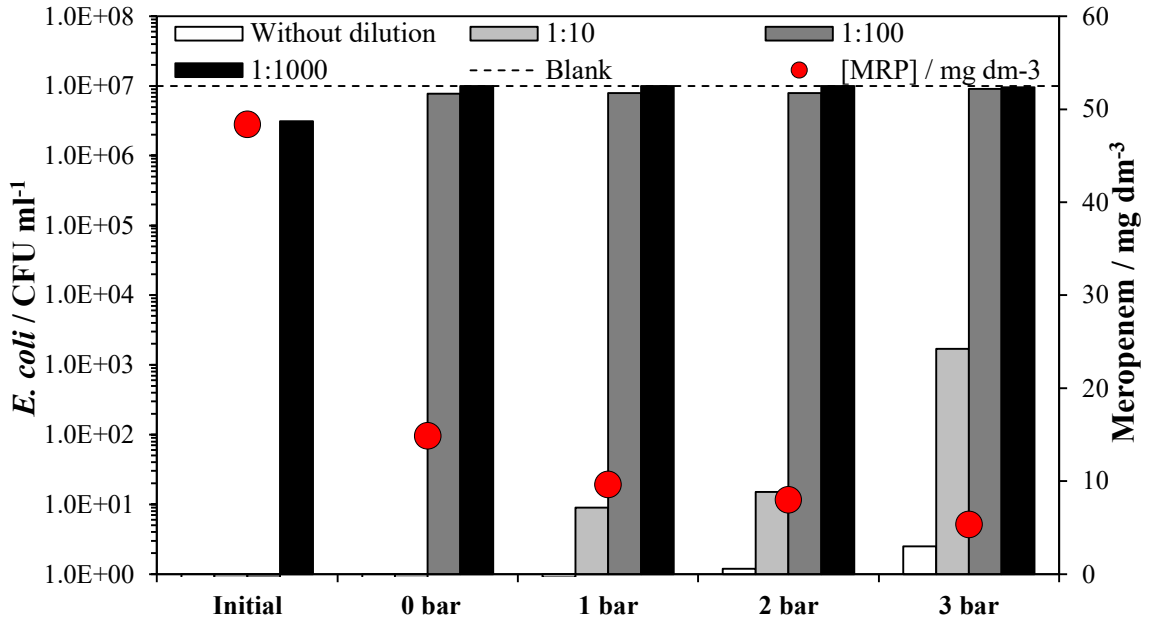


Figure 2. Antibiotic activity (in terms of CFU ml^{-1} of *E. coli*) and remaining meropenem concentration of synthetic urine after EF at different pressurizations. Electric charge passed: 0.6 Ah dm^{-3}. Experimental conditions: j= 5.0 mA cm^{-2}, pH_0= 3.0, $[meropenem]_0$ = 50.0 mg dm^{-3}, [goethite] = 10.8 g.

As mentioned before, urine is a complex media in which organic and inorganic species coexist. These species are biodegradable and/or do not pose a risk to the environment and, thus, they are not considered as target compounds to be oxidized. Therefore, the effort should be focused on the search for efficient and selective processes towards antibiotics. To check this, Figure 3 shows the concentration profile (in terms of mg C L^{-1}) in semilogarithmic scale of meropenem and of the other organic naturally contained in urine: uric acid, creatinine, and urea. The total organic carbon is also shown in the figure, as indicator of the mineralization of the organic load.

As can be observed, meropenem degradation rate increases with the gauge pressure and after passing an electric charge of 0.8 Ah dm^{-3} the meropenem removals are 80.60%, 89.03%,

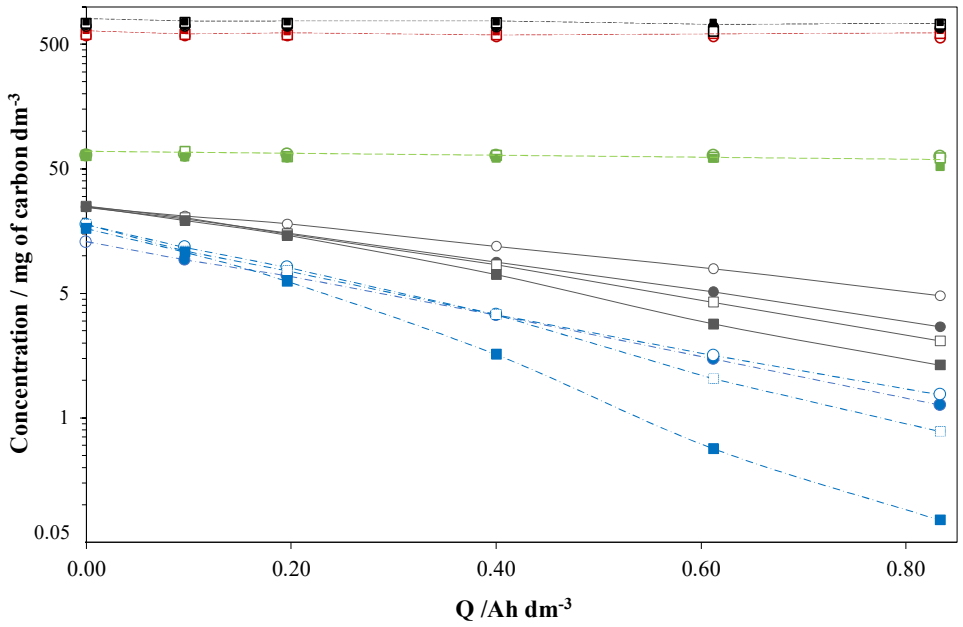
91.6% and 94.64% at gauge pressures of 0.0, 1.0, 2.0 and 3.0 bar, respectively. These decays fit well to a first order kinetics Eq. (1) and kinetic constants are summarized in Table 1, where it is noted the effect of the important effect of the gauge pressure applied (values higher than 70 % when pressure increases from atmospheric pressure to 3 bar of gauge pressure).

$$\mathrm{Ln}\,(C/C_0) = -\,k\cdot t \qquad (1)$$

Table 1. Kinetic constants for meropenem decay by EF process at different overpressures.

Process	k_{MRP} / min^{-1}	R^2
EF 0.0 bar	0.0033	0.9965
EF 1.0 bar	0.0045	0.9982
EF 2.0 bar	0.0050	0.9964
EF 3.0 bar	0.0057	0.9916

Uric acid is also quickly oxidized. This was also observed in previous studies in which electrochemical oxidation of synthetic urine was tested [28] and where it was pointed out that this compound decomposes rapidly by light [29]. This can explain its faster depletion during both electrochemical treatments. Regarding urea and creatinine, they are present in higher concentration than uric acid and meropenem, and their concentrations almost remain constant regardless of the gauge pressure applied. This agrees with the almost nil mineralization observed, explained by the much higher concentration of these species in urine.



284

285 **Figure 3**. Influence of the overpressure on degradation of TOC, meropenem and organic
286 compounds present in the synthetic urine in semilogarithmic scale as function of the applied
287 electric charge during the EF tests. Experimental conditions: j= 5.0 mA cm^{-2}, pH_0= 3.0,
288 $[meropenem]_0$ = 50.0 mg dm^{-3}, [goethite] = 10.8 g. Symbols: ○ 0.0 bar, ● 1.0 bar, □ 2.0 bar,
289 ■ 3.0 bar. Colours: ■ Urea, ■ TOC, ■ Creatinine, ■ Meropenem, ■ Uric acid.

290

291 Figure 4 shows the trend of M1 ($C_{16}H_{27}N_3O_5S$), the main aromatic intermediate detected in
292 the reaction system during EF process at the four pressures tested and identified by LC-MS
293 (further data about this species are given below). Its concentration (expressed in terms of
294 chromatographic area) increases with the gauge pressure applied and this agrees with the faster
295 degradation of meropenem observed previously. Additionally, at a gauge pressure of 3 bar it
296 attains a maximum value for 0.4 Ah dm^{-3} of electric charge passed and then it stars to decrease.
297 That is, it behaves as reaction intermediate. In the EF at atmospheric pressure, this decrease
298 is not observed. In this case, the degradation of meropenem is slower and around 20% of the
299 initial meropenem still remains in the solutions after passing 0.8 Ah dm^{-3} of electric charge.
300 Simultaneously, the formation of short-chain carboxylic acids is also observed, and their

trends are shown in Figure 5. As it is shown, a mixture of carboxylic acids is formed during the treatment and their concentrations increase with the electrical charge passed. Among them, propionic acid and acetic acid are the compounds accumulated in higher concentration in the reaction system, and their concentrations depend significantly on the experimental conditions: higher gauge pressures applied seem to favour their formation.

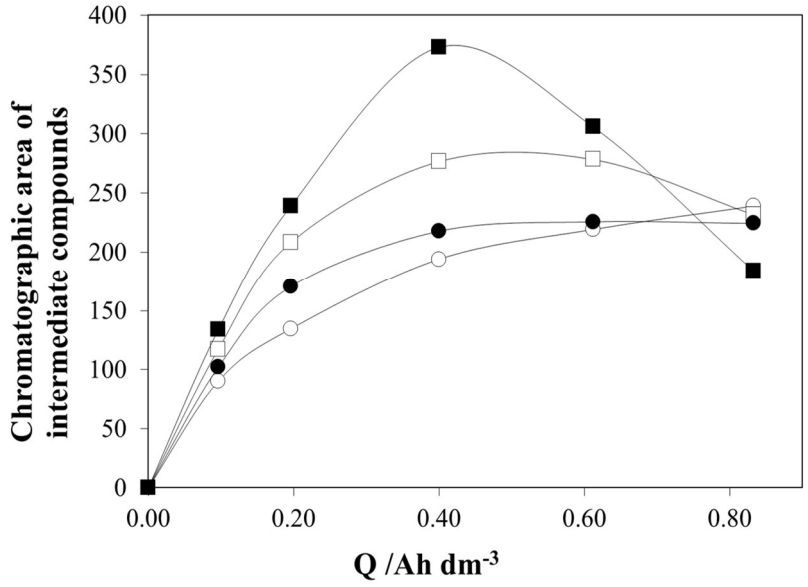
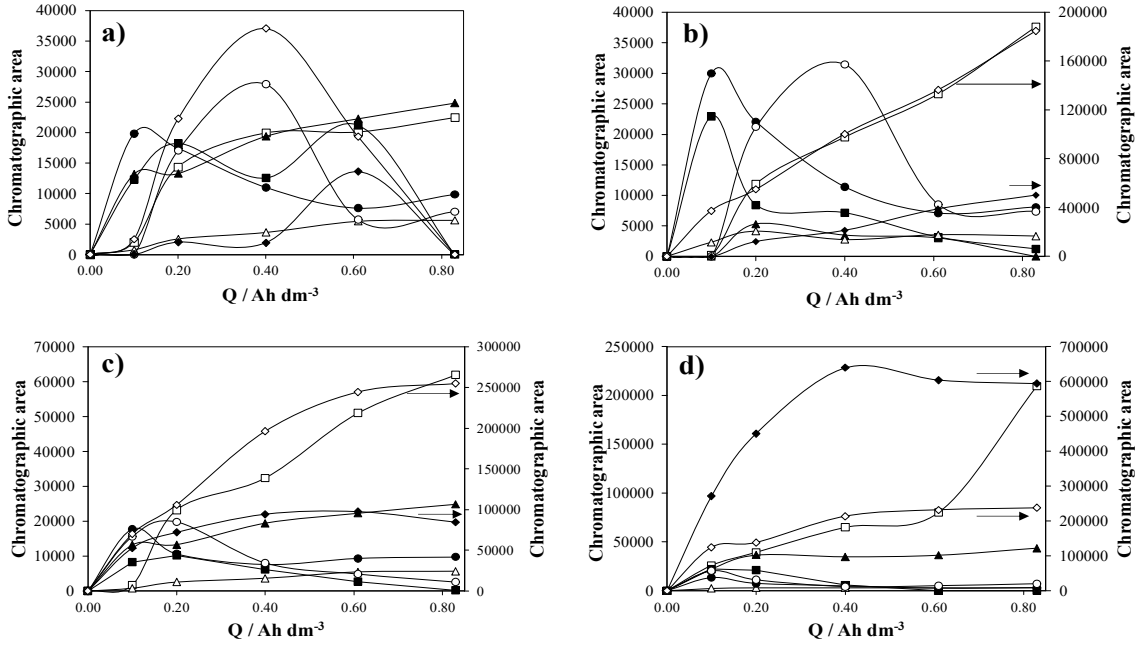


Figure 4. Chromatographic area of aromatic intermediate compounds as function of the applied electric charge during the EF ~~Electro-Fenton~~ process at different overpressures. ○ 0 bar, ● 1.0 bar, □ 2.0 bar, ■ 3.0 bar. Experimental conditions: j= 5.0 mA cm^{-2}, pH_0= 3.0, $[meropenem]_0$ = 50.0 mg dm^{-3}, [goethite] = 10.8 g.



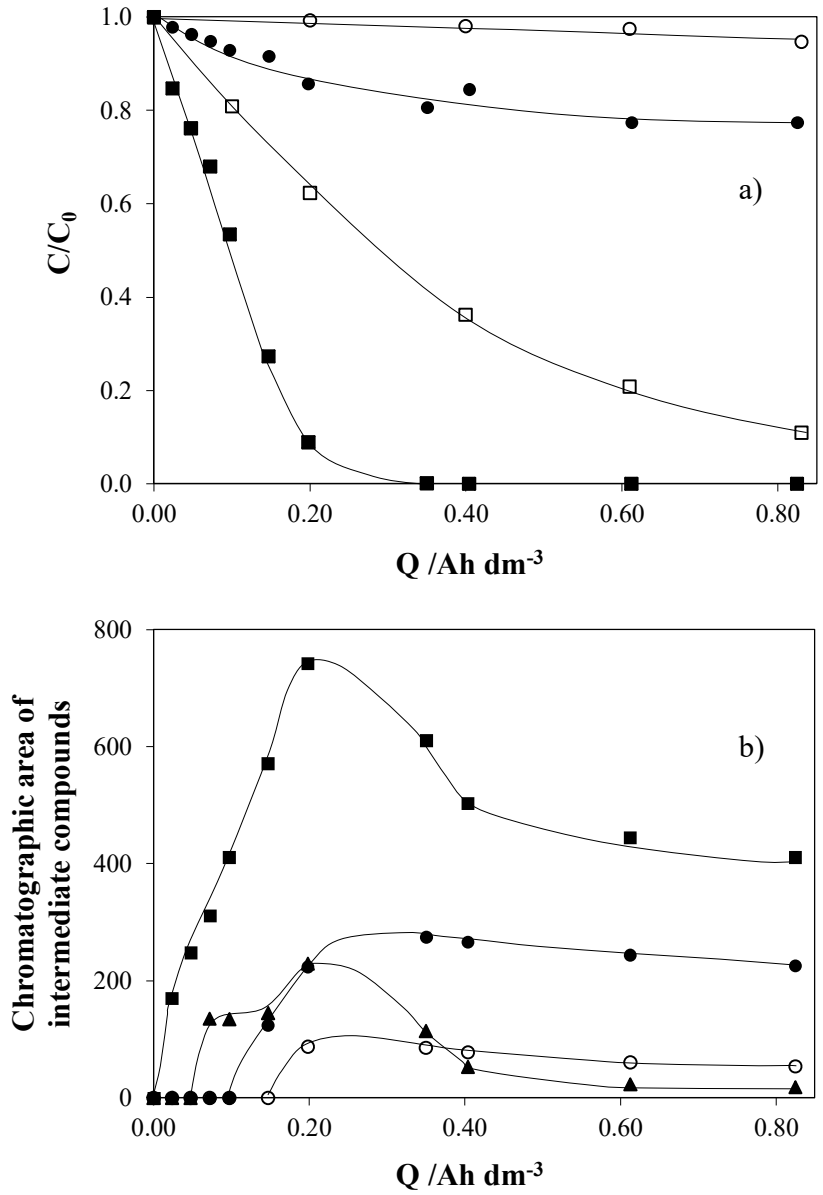
313

314 **Figure 5**. Evolution of carboxylic acids concentration during EF process ~~Electro-Fenton test~~
315 at different overpressures. a) 0.0 bar, b) 1.0 bar, c) 2.0 bar and d) 3.0 bar. □ Oxalic Acid, ■
316 Maleic acid, ▲ Oxamic acid, Δ Malonic acid, ● Succinic acid, ○ Formic acid, ♦ Acetic acid,
317 ◊ Propionic acid. Experimental conditions: j= 5.0 mA cm^{-2}, pH_0= 3.0, $[meropenem]_0$ = 50.0
318 mg dm^{-3}, [goethite] = 10.8 g.

319

320 In this point, it is important to remark that the great variety of inorganic and organic species
321 in urine (which are in higher concentration than meropenem) makes difficult the analysis and
322 identification of its degradation intermediates by HPLC, and the formation of some of them
323 can be masked. To clarify this point, additional tests were carried out in perchloric acid, using
324 the same initial antibiotic concentration and ionic conductivity of the reaction media (Figure
325 6). As can be observed, the degradation of meropenem is more efficient in perchloric acid and
326 0.4 Ah dm^{-3} of electric charge is enough to attain the complete removal of the antibiotic. This
327 confirms that in urine media there is a competitive oxidation and that electrons supplied are
328 not only use for the meropenem degradation, but for the oxidation of other compounds

contained in the solution including organics and inorganics. The oxidation of these ions can lead to the formation of oxidants (such as hypochlorite, peroxosulfate or peroxodiphosphate) that can contribute to the degradation (mediated oxidation) or recombine with each other [30] without contributing to mediated oxidation. The complete mineralization of meropenem is also promoted and up to 20 % of TOC removal is attained in perchloric media after 8.0 h of treatment. This indicates that meropenem is rapidly oxidized but further reaction time is required to attain the complete conversion of the organic load to carbon dioxide. That is, the accumulation of reaction intermediates should take place. Part b of Figure 6 shows the main aromatic intermediates detected and accumulated in the system during the degradation of meropenem by EF process in perchloric acid media at a gauge pressure of 1 bar. Four aromatic intermediates were identified by LC-MS (Table 2). As in the case of EF of urine, M1 ($C_{16}H_{27}N_3O_5S$) is the main intermediate which can be generated by hydrolysis of the aromatic nitrile group. Comparing chromatographic area, the maximum concentration attained in perchloric acid (data shown in Figure 6b) is higher than those monitored in urine media (data shown in Figure 4), indicating that hydrolysis should be faster in perchloric acid, and this can explain the rapid decay observed in meropenem concentration. Additionally, M2 ($C_{16}H_{25}N_3O_4S$), M3 ($C_{17}H_{27}N_3O_6S$), M4 ($C_{10}H_{19}NO_4$) and M5 ($C_{15}H_{27}N_3O_4S$) were also identified. Wang et al. [31] also identified the intermediates M1 ($C_{16}H_{27}N_3O_5S$), M2 ($C_{16}H_{25}N_3O_4S$), M4 ($C_{10}H_{19}NO_4$) and M5 ($C_{15}H_{27}N_3O_4S$) during the photocatalytic removal of meropenem. In the case of urine medium, M1 ($C_{16}H_{27}N_3O_5S$) was the only intermediate detected by HPLC, but M2 ($C_{16}H_{25}N_3O_4S$) and M3 ($C_{16}H_{25}N_3O_4S$) were also detected by LC-MS. In any case, analyzing these results together with those shown in Figure 2, these intermediates do not seem to present antibiotic effect and then their discharge to the sewerage system may not lead to serious environmental problems neither promote the appearance of bacteria resistant to antibiotic.

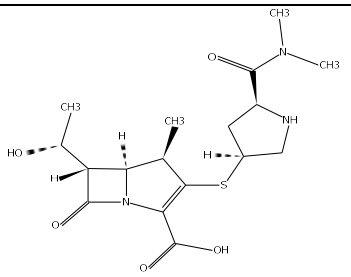
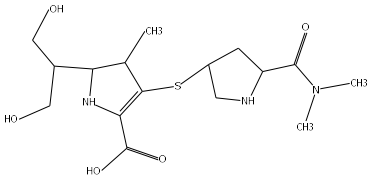
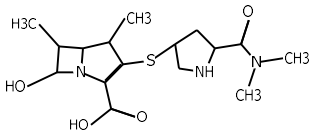
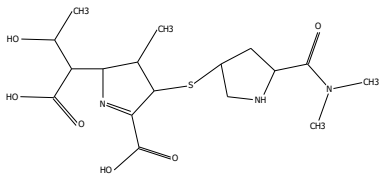
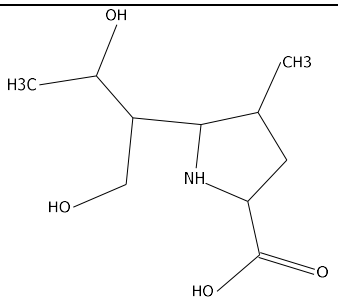
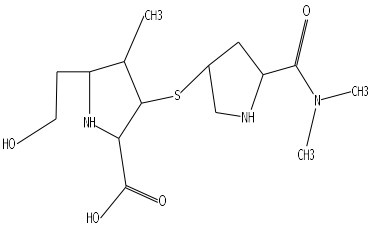


354

355 **Figure 6.** a) Meropenem (■, □) and TOC removal (●, ○) as function of the applied electric
356 charge during the EF of meropenem in urine (empty symbols) and perchloric acid (full
357 symbols) media pressurized at 1.0 bar of gauge pressure. b) Chromatographic area of the
358 aromatic intermediates formed during the EF of meropenem in perchloric acid media at 1 bar
359 of overpressure. ■ M1 ($C_{16}H_{27}N_3O_5S$), ▲ M2 ($C_{16}H_{25}N_3O_4S$), ○ M3 ($C_{17}H_{27}N_3O_6S$), ● M4
360 ($C_{10}H_{19}NO_4$). Experimental conditions: j= 5.0 mA cm^{-2}, pH_0= 3.0, $[meropenem]_0$ = 50.0 mg
361 dm^{-3}, [goethite] = 10.8 g.

362

363 **Table 2.** Analytes identified, structure and m/z.

	Formula	m/z	Feasible structure
Meropenem	$C_{17}H_{25}N_3O_5S$	383.15149	
M1	$C_{16}H_{27}N_3O_5S$	373.16714	
M2	$C_{16}H_{25}N_3O_4S$	355.15658	
M3	$C_{17}H_{27}N_3O_6S$	401.16206	
M4	$C_{10}H_{19}NO_4$	217.13141	
M5	$C_{15}H_{27}N_3O_4S$	345.17223	

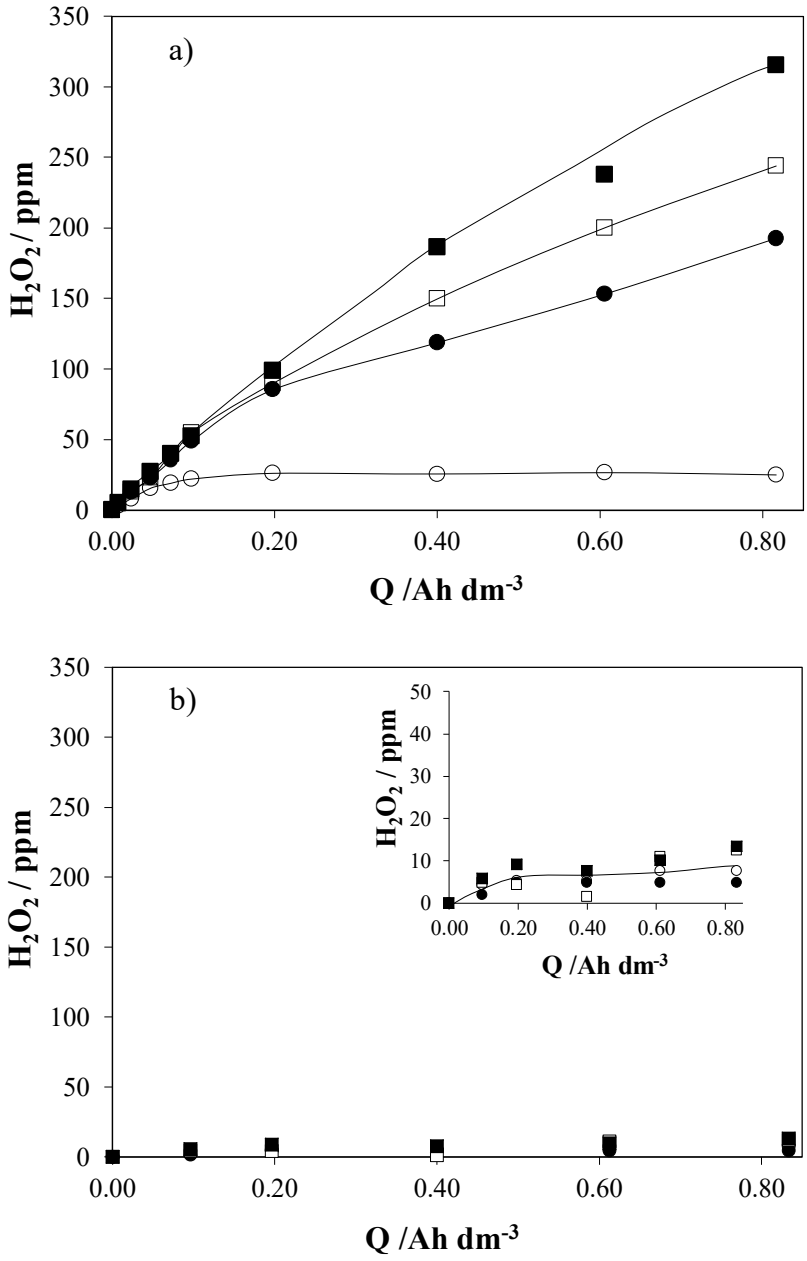
364

The positive effect of gauge pressure on meropenem degradation by EF may be related to the contribution of direct and mediated oxidation mechanisms promoted in the electrochemical system. As it is known, the generation of hydroxyl radicals via Fenton's reaction, Eq. (2) depends on the concentration of hydrogen peroxide [19]. H_2O_2 is generated mainly by reduction of O_2 on the cathode according to Eq. (3). Its generation rate depends on the current intensity and electrode material, and it is often limited by the solubility of oxygen in water [11]). Then, the addition of oxygen is key for a fast and efficient electro-generation of hydrogen peroxide. As explained before, the experimental set up used in this work is equipped with a jet aerator which was tested in previous works for the electro-generation of H_2O_2 [16, 32]. Results confirmed that the aerator based on venturi effect helps to super-saturate the solution with oxygen even at atmospheric pressure. Additionally, it is important to take in mind that the solubility of oxygen in water increases with pressure (linearly in the range studied) according to Henry's Law. Then, the amount of dissolved oxygen in the liquid treated is expected to be much higher at 3 bar, and therefore the electro-generation of hydrogen peroxide should be promoted.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+}\ OH^- + {}^{\cdot}OH \quad (2)$$

$$O_2 + 2H^+ + 2\ e^- \rightarrow H_2O_2 \quad (3)$$

To confirm this, additional tests were carried out in urine media, without organic load and in absence of catalyst, to prevent the fast decomposition of the electrogenerated hydrogen peroxide. Figure 7a shows the changes in the concentration of hydrogen peroxide with the applied electric charge at different gauge pressures applied (0.0, 1.0, 2.0 and 3.0 bar) when applying a current density of 5.0 mA cm^{-2}. Additionally, Figure 7b shows the remaining concentration of hydrogen peroxide during the EF tests of meropenem in urine media at different gauge pressures applied.



390

391 **Figure 7.** a) Concentration of hydrogen peroxide generated as function of the applied electric
392 charge at different overpressures in the absence of iron catalyst and organic compounds
393 present in the urine. b) Concentration of hydrogen peroxide remain in the system during the
394 EF of meropenem in urine media. Experimental conditions: j= 5.0 mA cm^{-2}, pH_0= 3.0,
395 [meropenem]$_0$ in EF tests = 50.0 mg dm^{-3}, [goethite] in EF tests = 10.8 g. ○ 0.0 bar, ● 1.0 bar,
396 □ 2.0 bar, ■ 3.0 bar

As can be observed, hydrogen peroxide concentration increases with the applied electric charge and gauge pressure. The maximum amounts obtained are 24.99, 192.61, 244.01 and 315.37 mg dm^{-3}, for 0.0, 1.0, 2.0 and 3.0 bar, respectively. Two regions are observed in the generation of hydrogen peroxide regardless of the gauge pressure applied. Initially, hydrogen peroxide increases rapidly but its concentration starts to stabilize from a given electric charge passed. This indicates that other parasitic reactions occur such as its self-decomposition (Eq. 4), or its oxidation to oxygen in the anode (Eq. 5) or reduction to water in the cathode (Eq. 6) [11, 18, 33]. Initially, the rate of these side reactions is low because of the low hydrogen peroxide concentration but after that, they start to be relevant, and the generation rate is no longer linear. Then, the plateau zone attained indicates that formation and decomposition reaction rates balance.

$$H_2O_2 \rightarrow H_2O + 1/2\ O_2 \quad (4)$$

$$H_2O_2 - 2e^- \rightarrow O_2 + 2H^+ \quad (5)$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (6)$$

At atmospheric pressure, the accumulation reaches the plateau after passing 0.1 Ah dm^{-3}. However, for gauge pressures applied of 1.0, 2.0 and 3.0 bar, the oxygen concentration is high enough to guaranty a higher generation rate in comparison with decomposition ones and 0.8 Ah dm^{-3} are not enough to attain this plateau. In comparing these results with the concentration of hydrogen peroxide during EF processes (part b of Figure 7), it can be observed that in all cases the residual concentration is low (around 10-15 ppm) and negligible differences are observed with the gauge pressure applied. Then, regardless of the H_2O_2 generated, this oxidant seems to be rapidly activated and this can help to explain the better results obtained in pressurized-EF where the amount of hydrogen peroxide generated and activated should be higher. Additionally, it is important to mention that leaching does not seem to be favored with gauge pressure and in any case soluble iron species are detected in the media.

Besides cathodic generation of hydrogen peroxide, the anodic reaction can also contribute to the overall degradation process and the effect of gauge pressure applied on it should be also checked. Figure 8 shows the degradation of meropenem in urine media during electrooxidation in the same cell, but without aeration, at atmospheric pressure and with 1.0 bar of gauge pressure. As it can be observed, electrochemical oxidation is also improved working at 1 bar and around 14 % extra of meropenem is oxidized during the test. Oxygen produced during the anodic oxidation of water (typically the non-desired side reaction) can be more efficiently dissolved into the liquid in treatment and, hence, a higher amount of oxygen is available on the cathode for the generation of hydrogen peroxide.

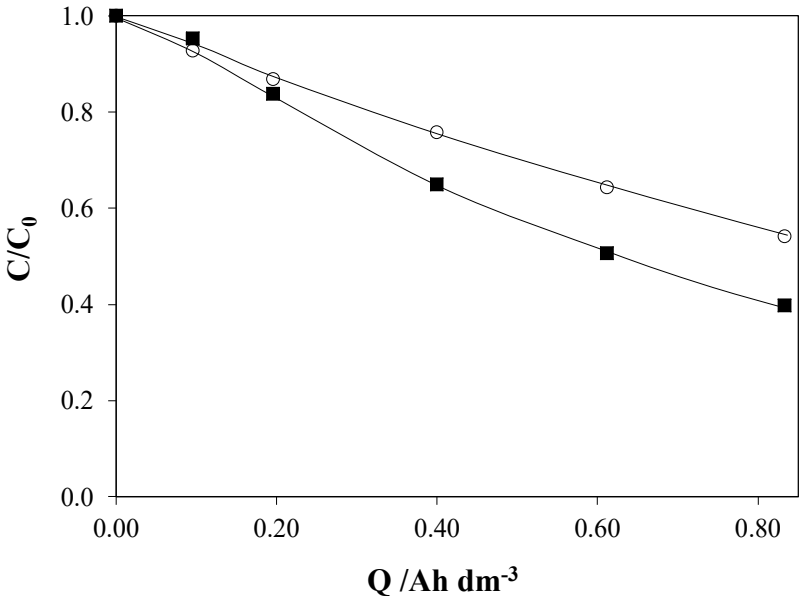


Figure 8. Meropenem removal as function of the applied electric charge during the electrooxidation of synthetic urine. Experimental conditions: j= 5.0 mA cm^{-2}, pH_0= 3.0, $[meropenem]_0$ = 50.0 mg dm^{-3}. (○) atmospheric pressure, (■) pressurized with 1.0 bar of gauge pressure.

Hence, from the obtained results it can be concluded that the use of pressurized EF reactors can allow to increase the efficiency of EF processes, and that it can be satisfactorily used to degrade selectivity antibiotics in urine media. Pressurized EF has been previously tested in the recent years [9, 18, 21, 34] but these works employed very different electrochemical reactors (mixed tanks cells) and they were focused on the improvement of the mineralization of the process using up to 10 and 30 bar of gauge pressure. Table 3 summarizes the experimental conditions and the main results reported previously in literature. The direct comparison of these results is not an easy task due to the different experimental conditions tested, aqueous matrix, electrodic material used, catalyst used, or electrical charge passed. In any case, as for the knowledge of the authors, this is the first time in which the use of moderated pressurized EF has been satisfactorily tested to decrease the chemical risk of hospital effluents.

462 **Table 3.** Experimental conditions and the main results reported previously in literature

Process	Conditions	Target	Initial concentration	Results	Kinetic constant	Ref.
Homogeneous EF	Microfluidic Flow-Through reactor at atmospheric pressure. *Anode:* 3D-Boron Doped Diamond (BDD) mesh *Cathode:* modified 3D-Aluminium foam (Al) with CB/PTFE or modified 3D-RVC foam with CB/PTFE. *Current density:* 10 mA cm^{-2} *Electrolyte:* 7 mM Na_2SO_4 at pH 3, Fe^{2+} (0.5 mM).	Clopyralid	100.0 mg dm^{-3}	3D-Al-CB/PTFE: 100% removal (0.44 Ah dm^{-3}) 3D-RVC-CB/PTFE: 100% removal (0.90 Ah dm^{-3})	-	[35]
EO or Homogeneous EF	Two types of electrochemical cells: Commercial flow-by and Microfluidic Flow-Through reactor. Atmospheric pressure. *Anode:* 3D-BDD mesh *Cathode:* Stainless Steel (EO) or modified 3D-Aluminium foam with CB/PTFE (EF). *Current density:* 10 mA cm^{-2} *Electrolyte:* soil washing fluids at pH 3, *Catalyst in EF tests*: Fe^{2+} (0.5 mM)	Clopyralid	400 g of soil polluted with 100 g kg^{-1} with 1.0 dm^3 of water	<u>Commercial flow-by:</u> Electrooxidation: 80% removal (6.0 Ah dm^{-3}) <u>Microfluidic Flow-Through reactor:</u> Electrooxidation: 80% removal(4.0 Ah dm^{-3}) Electro-Fenton: 80% removal (0.4 Ah dm^{-3})	-	[36]
Heterogeneous EF	Microfluidic Flow-Through reactor at atmospheric pressure. *Anode:* BDD mesh *Cathode:* modified titanium mesh with CB/PTFE. 6 g of iron (Fe^{3+}) containing alginate beads *Current:* 0.12 and 0.25 A *Electrolyte:* 0.05 M Na_2SO_4 at pH 3.	Clofibric acid	10.0 mg dm^{-3}	0.12 A~100% removal (8h) 0.25 A~100% removal (8h)	0.009 min^{-1} (0.12 A) 0.014 min^{-1} (0.25 A)	[32]

Homogeneous EF	Undivided high-pressure stainless-steel cell Pressurised system. *Anode: Ti/IrO_2-Ta_2O_5* *Cathode: compact graphite* *Electrolyte:* 35 mM Na_2SO_4 at pH 3 *Catalyst*: 0.5 mM $Fe(SO)_4$ at pH 3 *Current:* 110 mA *Range of gauge pressures*: 0, 3, 6 and 11 bar	Acid Orange 7	0.43 mM	0 bar: 48 % removal of TOC 3 bar: 54 % removal of TOC 6 bar: 63 % removal of TOC 10 bar: 74 % removal of TOC	-	[18]
Homogeneous EF	Undivided high-pressure stainless-steel cell Pressurised system *Anode*: DSA® *Cathode*: carbon felt *Current density*: 20 mA cm^{-2} *Electrolyte:* real paper mill wastewater at pH 3 *Catalyst*: Fe^{2+} 0.5 mM *Range of gauge pressures*: 0 and 10 bar	Real wastewater	115.0 mg dm^{-3} TOC	0 bar: 48 % removal of TOC (5h) 10 bar: 58 % removal of TOC (5h)	-	[21]
Homogeneous EF	Undivided high-pressure stainless-steel cell Pressurised system *Anode*: Ti/IrO_2-Ta_2O_5 *Cathode*: carbon felt *Current density*: 10 mA cm^{-2} *Electrolyte:* 50 mM Na_2SO_4 at pH 3 *Catalyst*: Fe^{2+} 0.5 mM *Range of gauge pressures*: 0 and 30 bar	Maleic Acid	0.70 mM	0 bar: 40 % removal (2h) 30 bar: 90 % removal (4h)	-	[9]
Homogeneous or heterogeneous EF	Undivided high-pressure stainless-steel cell Pressurised system with oxygen *Anode*: Ti/IrO_2-Ta_2O_5 *Cathode*: carbon felt *Current density*: 20 mA cm^{-2} *Electrolyte:* 0.1 M Na_2SO_4 at pH 3 *Catalyst*: Fe^{2+} (0.05 M), pyrite (1.0 g L^{-1}) and chalcopyrite (0.5 g L^{-1}) *Range of gauge pressures*: 1 and 10 bar	Caffeic Acid	100.0 mg dm^{-3}	$\underline{Fe^{2+}}$: 1 bar: 30% removal of TOC (2h) 10 bar: 58% removal of TOC (2h) $\underline{Pyrite}$: 1 bar: ~40% removal of TOC (2h) 10 bar: ~58% removal of TOC (2h) $\underline{Chalcopyrite}$: 1 bar: ~48% removal of TOC (2h) 10 bar: ~74% removal of TOC (2h)	-	[19]

Heterogeneous EF	Microfluidic Flow-Through reactor. Pressurised system. *Anode*: 3D-MMO-$IrO_2Ta_2O_5$ mesh *Cathode*: Modified 3D-titanium mesh with CB/PTFE. 10.8 g of goethite. *Current density*: 5 mA cm^{-2} *Electrolyte*: Urine at pH 3 *Range of gauge pressures*: 0 to 3 bar	Meropenem	50.0 mg dm^{-3}	0 bar: 80.60 % removal 1 bar: 89.03 % removal 2 bar: 91.60 % removal 3 bar: 94.64 % removal	0.0033 min^{-1} (0 bar) 0.0045 min^{-1} (1 bar) 0.0050 min^{-1} (2 bar) 0.0057 min^{-1} (3 bar)	This work

4. CONCLUSIONS

From this work, the following conclusions can be drawn:

- Meropenem can be degraded by EF in system in which jet aerator, microfluid flow through cell and iron bed are implemented. The abatement of meropenem is related to the antibiotic effect (quantified using *E. coli* as target bacterium) remained in the treated urine but it cannot fully explain the decay in the antibiotic capacity of the treated urine.
- The mineralization is almost nil during EF of polluted urine at 5.0 mA cm^{-2} using goethite as heterogeneous catalyst. Increasing pressurization is not relevant in terms of TOC removal but it favours the progress of the degradation as it is demonstrated with the accumulation of carboxylic acids in the treated urine. In addition, it has a positive effect on the losing of antibiotic capacity of the treated urine, which is explained in terms of the higher progress of the oxidation reached.
- The positive effect of the pressurization on EF is related to the higher hydrogen peroxide generation in pressurized systems, which in turn is explained in terms of the higher oxygen concentration that can be attained. Additionally, the anodic oxidation is also favoured because the formation of oxygen from the non-desired water oxidation provides of oxygen to the cathode for the effective production of hydrogen peroxide.

ACKNOWLEDGEMENTS

Financial support from Junta de Comunidades de Castilla-La Mancha (JCCM), European Union (European Regional Development Fund), and 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 is also gratefully acknowledged through the projects EQC2018-004469-P and EQC2018-004240-P.

REFERENCES

[1] H. Wang, H. Xi, L. Xu, M. Jin, W. Zhao, H. Liu, Ecotoxicological effects, environmental fate and risks of pharmaceutical and personal care products in the water environment: A review, Science of The Total Environment, 788 (2021) 147819.

[2] U. Szymańska, M. Wiergowski, I. Sołtyszewski, J. Kuzemko, G. Wiergowska, M.K. Woźniak, Presence of antibiotics in the aquatic environment in Europe and their analytical monitoring: Recent trends and perspectives, Microchemical Journal, 147 (2019) 729-740.

[3] I. Sirés, E. Brillas, M.A. Oturan, M.A. Rodrigo, M. Panizza, Electrochemical advanced oxidation processes: today and tomorrow. A review, Environmental Science and Pollution Research, 21 (2014) 8336-8367.

[4] W. Wang, Y. Li, Y. Li, M. Zhou, O.A. Arotiba, Electro-Fenton and photoelectro-Fenton degradation of sulfamethazine using an active gas diffusion electrode without aeration, Chemosphere, 250 (2020) 126177.

[5] H. Pourzamani, N. Mengelizadeh, H. Mohammadi, N. Niknam, B. Neamati, R. Rahimi, Comparison of electrochemical advanced oxidation processes for removal of ciprofloxacin from aqueous solutions, Desalination and Water Treatment, 113 (2018) 307-318.

[6] E. Brillas, I. Sirés, M.A. Oturan, Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton's Reaction Chemistry, Chemical Reviews, 109 (2009) 6570-6631.

[7] P.V. Nidheesh, R. Gandhimathi, Trends in electro-Fenton process for water and wastewater treatment: An overview, Desalination, 299 (2012) 1-15.

[8] I. Sirés, E. Brillas, Upgrading and expanding the electro-Fenton and related processes, Current Opinion in Electrochemistry, 27 (2021) 100686.

[9] 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, Electrochimica Acta, 273 (2018) 447-453.

[10] F. Yu, M. Zhou, X. Yu, Cost-effective electro-Fenton using modified graphite felt that dramatically enhanced on H_2O_2 electro-generation without external aeration, Electrochimica Acta, 163 (2015) 182-189.

[11] J.F. Pérez, J. Llanos, C. Sáez, C. López, P. Cañizares, M.A. Rodrigo, Towards the scale up of a pressurized-jet microfluidic flow-through reactor for cost-effective electro-generation of H_2O_2, Journal of Cleaner Production, 211 (2019) 1259-1267.

[12] G.d.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, Journal of Electroanalytical Chemistry, 871 (2020) 114291.

[13] R.R. Kalantary, M. Farzadkia, M. Kermani, M. Rahmatinia, Heterogeneous electro-Fenton process by Nano-Fe3O4 for catalytic degradation of amoxicillin: Process optimization using response surface methodology, Journal of Environmental Chemical Engineering, 6 (2018) 4644-4652.

[14] 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.

[15] V.S. Pinheiro, E.C. Paz, L.R. Aveiro, L.S. Parreira, F.M. Souza, P.H.C. Camargo, M.C. Santos, Mineralization of paracetamol using a gas diffusion electrode modified with ceria high aspect ratio nanostructures, Electrochimica Acta, 295 (2019) 39-49.

[16] J.F. Pérez, J. Llanos, C. Sáez, C. López, P. Cañizares, M.A. Rodrigo, The jet aerator as oxygen supplier for the electrochemical generation of H_2O_2, Electrochimica Acta, 246 (2017) 466-474.

[17] F. Yu, Y. Chen, Y. Pan, Y. Yang, H. Ma, A cost-effective production of hydrogen peroxide via improved mass transfer of oxygen for electro-Fenton process using the vertical flow reactor, Separation and Purification Technology, 241 (2020) 116695.

[18] O. Scialdone, A. Galia, C. Gattuso, S. Sabatino, B. Schiavo, Effect of air pressure on the electro-generation of H_2O_2 and the abatement of organic pollutants in water by electro-Fenton process, Electrochimica Acta, 182 (2015) 775-780.

[19] A.H. Ltaïef, S. Sabatino, F. Proietto, S. Ammar, A. Gadri, A. Galia, O. Scialdone, Electrochemical treatment of aqueous solutions of organic pollutants by electro-Fenton with natural heterogeneous catalysts under pressure using Ti/IrO_2-Ta_2O_5 or BDD anodes, Chemosphere, 202 (2018) 111-118.

[20] 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, Electrochimica Acta, 248 (2017) 169-177.
[21] N. Klidi, F. Proietto, F. Vicari, A. Galia, S. Ammar, A. Gadri, O. Scialdone, Electrochemical treatment of paper mill wastewater by electro-Fenton process, Journal of Electroanalytical Chemistry, 841 (2019) 166-171.
[22] E.A. Agudelo, S.A. Cardona G, Advanced Oxidation Technology (Ozone-catalyzed by Powder Activated Carbon - Portland Cement) for the Degradation of the Meropenem Antibiotic, Ozone: Science & Engineering, 43 (2021) 88-105.
[23] 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, Chemical Engineering Journal, 351 (2018) 766-772.
[24] S. Dbira, N. Bensalah, P. Cañizares, M.A. Rodrigo, A. Bedoui, The electrolytic treatment of synthetic urine using DSA electrodes, Journal of Electroanalytical Chemistry, 744 (2015) 62-68.
[25] S. Cotillas, E. Lacasa, C. Sáez, P. Cañizares, M.A. Rodrigo, Disinfection of urine by conductive-diamond electrochemical oxidation, Applied Catalysis B: Environmental, 229 (2018) 63-70.
[26] G. Eisenberg, Colorimetric Determination of Hydrogen Peroxide, Industrial & Engineering Chemistry Analytical Edition, 15 (1943) 327-328.
[27] E.C.o.A.S. Testing, "The European Committee on Antimicrobial Susceptibility Testing. Breakpoint tables for interpretation of MICs and zone diameters. Version 11.0, 2021.
[28] 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, Science of The Total Environment, 725 (2020) 138430.
[29] M. Herraiz-Carboné, S. Cotillas, E. Lacasa, P. Cañizares, M.A. Rodrigo, C. Sáez, Enhancement of UV disinfection of urine matrixes by electrochemical oxidation, Journal of Hazardous Materials, (2020) 124548.
[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, Science of The Total Environment, 736 (2020) 139536.
[31] J. Wang, B. Gao, M. Dou, X. Huang, Z. Ma, A porous g-C3N4 nanosheets containing nitrogen defects for enhanced photocatalytic removal meropenem: Mechanism, degradation pathway and DFT calculation, Environmental Research, 184 (2020) 109339.
[32] V. Poza-Nogueiras, Á. Moratalla, M. Pazos, Á. Sanromán, C. Sáez, M.A. Rodrigo, Towards a more realistic heterogeneous electro-Fenton, Journal of Electroanalytical Chemistry, 895 (2021) 115475.
[33] E. Petrucci, A. Da Pozzo, L. Di Palma, On the ability to electrogenerate hydrogen peroxide and to regenerate ferrous ions of three selected carbon-based cathodes for electro-Fenton processes, Chemical Engineering Journal, 283 (2016) 750-758.
[34] N. Hamdi, F. Proietto, H. Ben Amor, A. Galia, R. Inguanta, S. Ammar, A. Gadri, O. Scialdone, Effective Removal and Mineralization of 8-Hydroxyquinoline-5-sulfonic Acid through a Pressurized Electro-Fenton-like Process with Ni−Cu−Al Layered Double Hydroxide, ChemElectroChem, 7 (2020) 2457-2465.
[35] J.F. Pérez, J. Llanos, C. Sáez, C. López, P. Cañizares, M.A. Rodrigo, On the design of a jet-aerated microfluidic flow-through reactor for wastewater treatment by electro-Fenton, Separation and Purification Technology, 208 (2019) 123-129.
[36] M. Rodríguez, M. Muñoz-Morales, J.F. Perez, C. Saez, P. Cañizares, C.E. Barrera-Díaz, M.A. Rodrigo, Toward the Development of Efficient Electro-Fenton Reactors for Soil Washing Wastes through Microfluidic Cells, Industrial & Engineering Chemistry Research, 57 (2018) 10709-10717.