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Exploring the use of carbon materials as cathodes in electrochemical advanced oxidation processes for the degradation of antibiotics

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Abstract

Three carbon materials from a varied origin, composition and porosity have been used as cost-effective cathodes in different electrochemical advanced oxidation processes (i.e. anodic oxidation (AO) and electro-Fenton (EF) in homogeneous and heterogeneous catalysis modalities) for the degradation of an antibiotic (e.g., metronidazole). In general, the efficiency towards the pollutant degradation increased as: AO < homogeneous EF < heterogeneous EF. The heterogeneous EF approach with iron pre-loaded in the carbon cathode outperformed the homogenous EF counterpart, despite a lower amount of iron. Reusability tests showed that iron-containing cathodes prepared from samples CQ (carbon obtained upon steam activation) and CB (carbon prepared by H_3PO_4 activation of biomass) were stable over at least three consecutive cycles. The best results were attained for cathode prepared with carbon CQ modified with iron, yielding over 97% removal of metronidazole after 150 min in all three reuses. Such better performance is related to the favorable adsorption of the pollutant on carbon CQ, thereby favoring the close contact between the generated oxidant species and the target antibiotic. The cathode based on carbon CQ was tested for the degradation of a more recalcitrant

antibiotic (sulfamethoxazole) in a real wastewater treatment plant effluent by means of a heterogeneous EF treatment, showing good degradation performance.

Keywords: Electrochemical treatments; Carbon-based cathodes; Boron-doped diamond; Heterogeneous catalyst; Water remediation

1. INTRODUCTION

The upmost challenges for water treatment and water reuse relate to the occurrence of organic matter, pathogens, antimicrobial resistance bacteria and viruses and the so-called contaminants of emerging concern. There is a wide variety of compounds falling under the latter family of pollutants (e.g. pharmaceuticals, personal care products, pesticides or industrial additives), all having in common a poor regulatory status and a lack of in-depth knowledge regarding their fate and toxicity in the environment [1-4]. Among them, antibiotics are one of the most frequently reported as water pollutants, causing increasing concern due to the generation of antimicrobial resistance and alterations in food chains [3,5]. While wastewater treatment plants should be safe barriers against all these pollution threats, owing to their stability and limited biodegradability most of these compounds are not fully eliminated by conventional treatments ending up in recipient waters [5,6]. This points out the need for more efficient and resilient treatment to deal with antibiotics pollution and to assure clean water access for all.

Electrochemical advanced oxidation processes (EAOPs) have gained attraction in this field, thanks to their versatility, easy operation, safety (they are operated under mild conditions of temperature and pressure) and cleanliness (the main reagent is the electron, thus avoiding the addition of hazardous chemicals) [7]. These techniques are based on the in-situ generation of powerful oxidizing agents, mainly the hydroxyl radical, which has demonstrated to be able to

non-selectively attack and mineralize several recalcitrant compounds [8]. Among EAOPs, electro-Fenton (EF) is considered an efficient technique owing to the in-situ generation of H_2O_2 at the cathode via the two-electron oxygen reduction reaction as shown in (r1), and the effective generation of hydroxyl radicals via Fenton's reaction between Fe(II) and the electrochemically generated H_2O_2 (r2) at an optimal pH around 3 [9,10]. The role of the cathode for EF reactions is essential, since it allows the in-situ generation of H_2O_2 (minimizing risk of decomposition), its reduction to render hydroxyl radicals and the regeneration of the Fe(II) species [11]. The role of the anode is also important as to assure a supplementary production of hydroxyl radicals as indicated in (r3); where M represents the anode material and $M(^{\cdot}OH)$ the adsorbed radical [12,13].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad \text{(r1)}$$

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\cdot}OH + OH^- + Fe^{3+} \quad \text{(r2)}$$

$$M + H_2O \rightarrow M(^{\cdot}OH) + H^+ + e^- \quad \text{(r3)}$$

Despite the critical role of the cathode material in EF process, most studies in the literature are mainly focused on the optimization of anode materials possessing a high overpotential for the oxygen evolution reaction for EF process (e.g., boron doped diamond, PbO_2, SnO_2 [7, 14]), with less attention being paid to optimizing the cathode [15]. In this regard, optimal cathode materials should display high conductivity and stability, with high overvoltage for hydrogen evolution reaction, and low catalytic activity for H_2O_2 decomposition [16-18]. Indeed, several types of carbon materials have been tested for EF processes including graphites [19,20], graphite felts [21,22], or reticulated vitreous carbon [23,24] among most commonly used. Among them, carbon felts are most widely used carbon cathodes in EAOP; however, despite the good performance obtained for the degradation of different pollutants, the cost of this material prevents its large scale utilization [25,26]. Indeed, our previous studies on the scaling-up of EF treatments have pointed out that carbon felt cathodes are not adequate in scaled-up

flow systems due to its flexibility, while cathodes prepared upon casting of a powder material and a binder on a titanium mesh support are more robust [27,28]. Some other supports have also been reported in the literature [29,30].

On the other hand, another main drawback on the implementation of EF treatments is the separation of dissolved iron from the solution after the treatment and the removal of the resulting iron sludge [18]. To avoid those issues, the use of natural iron minerals, entrapping iron into organic or inorganic matrixes, or its immobilization in the cathode surface have been proposed [31].

Considering all the above, in this work we have explored the potentialities of low-cost forms of carbon from varied origin, composition and porosity as alternatives to carbon felts for the elaboration of cost-effective cathodes in different EAOPs: AO, homogeneous and heterogeneous EF. The originality of this approach stands in the choice of the low-cost carbon forms and in exploring electrodes fabricated upon casting powders of the carbon materials on a titanium mesh to fabricate compliant and easily scalable cathodes. The selected carbon powders were used as-prepared and after the immobilization of iron using two different protocols. Two wide spread used antibiotics frequently detected in water environments (metronidazole [32] and sulfamethoxazole [33]) were selected as the target pollutants to perform their degradation via the different electrochemical treatments both in synthetic water and in a real wastewater treatment plant effluent. The electrocatalytic performance of the process incorporating low-cost carbon-based cathodes has been analyzed in terms of degradation efficiency of the pollutants, energy consumption compared to typical carbon cathodes and reusability of the electrodes in subsequent cycles. The most performing process has been tested for the degradation of antibiotics in a real wastewater treatment plant effluent.

2. MATERIALS AND METHODS

2.1. Reagents

Pharmaceuticals metronidazole and sulfamethoxazole were supplied by Alfa Aesar and Sigma-Aldrich, respectively. Sodium sulfate, iron (II) sulfate heptahydrate, acetic acid, sulfuric acid, acetonitrile and potassium titanium oxide oxalate dihydrate were purchased to Sigma-Aldrich. All aqueous solutions were prepared with Milli-Q water (18.2 MΩ cm).

2.2. Carbon materials

Several carbon materials with varied physicochemical characteristics were selected for the fabrication of the cathodes: sample CB, prepared by chemical activation in H_3PO_4 of biomass at 450 ºC; sample CQ, obtained upon steam activation (ca. 850 ºC) of bituminous coal; sample HC, a hydrochar obtained by hydrothermal carbonization of 0.5 M glucose at 180 ºC in an autoclave (heating rate of 100 ºC h^{-1} for 10 h). Before use, all of the carbon materials were thoroughly washed in distilled water, dried at 60 ºC and stored in a desiccator. More detailed information on the characteristics of the carbon materials have been presented elsewhere (carbon CQ in [34], carbons CB and HC in [35], labeled therein as AC2 and CS, respectively). We herein reintroduce some details on their textural and chemical properties for better comprehension of their performance as cathodes in the different EAOPs investigated. A commercial carbon felt (CF, supplied by Mersen) was also used as cathode for comparison purposes.

2.3. Electrodes manufacturing

The electrodes were prepared as follows: 1) ink preparation: 85 wt.% of the carbon material powders, 10 wt.% of polyvinylidene difluoride (PVDF) as binder and 5 wt.% of carbon black (Superior Graphite Co) as a conductive additive were mixed with some drops of the solvent NMP (1-methyl-2-pyrrolidone); 2) electrode painting: the electrode collector, a 2 x 2 cm titanium foil (GoodFellow, thickness of 0.03 mm), was painted on both sides with the prepared

ink; 3) drying: the electrode was dried overnight at 60 ºC in a vacuum oven. The amount of carbon material deposited on each cathode was accurately weighted.

For the cathodes used in heterogeneous EF assays, iron was added to the electrode using two different approaches: i) immobilization on the carbon material before the preparation of the cathodes, and ii) immobilization on the prepared cathodes. For the first approach, iron was immobilized by adsorption on the porosity of the carbon materials. Briefly, the amount of the carbon powders required for the elaboration of 10 electrodes (ca. 170 mg) were put in contact with 150 mL of a 3.0 mM Fe(II) solution and stirred for 18 h at 150 rpm and 25 ºC. The powders were then filtered, washed with distilled water, dried and used for the elaboration of cathodes as described above. The amount of iron in the supernatant solution was measured and used to calculate the amount of iron adsorbed on the carbon material. For the second approach, the iron was immobilized directly on the prepared cathodes following a similar procedure: the electrodes were immersed in 150 mL of a 0.3 mM Fe(II) solution and stirred for 18 h; afterwards, the electrodes were washed and dried in an oven at 60 °C.

2.4. Electrochemical treatments

The prepared electrodes were tested in two electrochemical treatments: AO and EF. In both cases, assays were performed in an undivided cylindrical stirred-tank reactor containing 150 mL of 0.05 M Na_2SO_4 with 100 mg L^{-1} of metronidazole or sulfamethoxazole, using a 3-electrode cell configuration. The manufactured electrodes (2 x 2 cm) acted as working electrode, a BDD plate of similar dimensions (Niobium substrate 20 x 20 x 2mm, Condias GmbH) was used as counter and Ag/AgCl KCl 3M as reference electrode. Chronoamperometries at a potential of -0.75 V were carried out with a Metrohm Autolab potentiostat/galvanostat (PGSTAT302N). The potential was selected to assure the production of hydrogen peroxide in the electrodes, and a potentiostatic mode was preferred to prevent high currents through the electrodes. The solution was continuously stirred with a magnetic bar

during the electrochemical treatments. Prior starting the electrochemical treatment, the electrodes were immersed in the solution and allowed to equilibrate for 30 min. Additionally, for EF assays, the pH was adjusted to 3.0 with sulfuric acid and air was pumped into the solution during the 30 min before the beginning of the treatment. For EF assays using homogeneous catalysis, 0.25 mM of an iron salt were added to the solution. Aliquots of ca. 2 mL of the solution were withdrawn at specific time intervals to analyze the composition and evaluate the degradation of the pollutants (the effect of volume changes was disregarded considering the volume of the initial solution).

2.5. Electrochemical assays on real wastewater

For best performing carbon cathodes, electrochemical assays were carried out in a real water matrix obtained from a wastewater treatment plant in Guillarei (Spain), spiked with 30 mg L^{-1} of the pollutant: metronidazole or sulfamethoxazole. The main characteristics of the as-received real wastewater are described in Table 1.

Table 1. Main physicochemical characteristics of the real wastewater.

pH	Conductivity (mS cm^{-1})	Chemical Oxygen Demand (mg L^{-1})	Chlorides (mg L^{-1})	Nitrates (mg L^{-1})	Nitrites (mg L^{-1})
6.05	1291	19.5	239.8	8.2	0.01

2.6. Analytical methods

Metronidazole and sulfamethoxazole concentrations were followed by high performance liquid chromatography in an Agilent 1200 apparatus provided with a DAD detector at 320 nm and 266 nm, respectively. The mobile phase (water containing 1.5% of acetic acid and acetonitrile) was pumped at 1 mL min^{-1} through a Zorbax Eclipse XDB-C8 column (4.6 x 150 mm) using a gradient mode. Carboxylic acids generated during the degradation of the pollutants were detected using an ion-exclusion Rezex-ROA-Organic Acid H+ (8%) column at 206 nm and 196

nm (2.5 mM H_2SO_4 mobile phase, 0.5 mL min^{-1}; 60 ºC). The generation of hydrogen peroxide in the EF assays was detected spectrophotometry following the formation of a titanium(IV)-peroxide complex at 400 nm [36]. Briefly, 2 mL of solution were mixed with 0.25 mL H_2SO_4 (1:17), 0.20 mL of 50 g L^{-1} potassium titanium oxide oxalate dihydrate and 0.05 mL of water; the absorbance was measured after 5 min. The amount of iron loaded on the materials and electrodes, as well as the amount lixiviated in the heterogeneous EF assays was determined from the solutions by ICP-OES using a Perking Elmer Optima 4300 DV (CACTI, Universidade de Vigo).

Total organic carbon (TOC) measurements were recorded on the solutions in a Hach Lange analyser. However, due to the occurrence of interferences arising most from the salinity of the solution, most of experimental TOC values were not consistent (e.g., experimental TOC values corresponding to the initial solution were much higher than the nominal value considering the well-known initial concentration of metronidazole). Hence, the mineralization of the pollutant was evaluated considering the experimental data obtained from the quantification of the remaining pollutant in solution and of the carboxylic acids detected by HPLC, through a TOC balance indicator ($TOC_{balance}$) estimated following Eq. (1). The extent of mineralization has been discussed in terms of the decay of $TOC_{balance}$ compared to the initial concentration of pollutant (expressed in mg C L^{-1}).

$$TOC_{balance} = Amount\ pollutant\ \left(\frac{mg\ C}{L}\right) + Amount\ Carboxylic\ Acids\ \left(\frac{mg\ C}{L}\right) \quad (1)$$

2.7. Characterization of the electrodes

The porosity of the carbons and electrodes was determined by gas adsorption (N_2 at 77 K) in a volumetric analyzer (Micromeritics); before the analysis, the samples were outgassed at 120 ºC for 12 h. The gas adsorption isotherms were used to calculate the specific surface area using the

Brunauer–Emmet–Teller equation, the total pore volume at a relative pressure of 0.99, and the micropore volume using the Dubinin–Radushkevich formulism. The surface pH of the carbon materials and electrodes was measured in aqueous suspension (ca. 0.4 g of carbon powders in 20 mL of distilled water) and allowing equilibration for 24 h. Thermogravimetric analysis of the carbons and electrodes was recorded in a thermobalance (NETZSCH STA 409 DC). About 5 mg of sample were heated up to 1000 ºC (10 ºC min^{-1}) under a constant argon flow (100 mL min^{-1}). SEM images of the electrodes were acquired in a (FEG) SEM Nova NanoSEM 450, operated at 24 kV, with integrated EDX system (EDAX TEAM™) to perform elemental composition analysis on the region of interest. Before and after the electrochemical treatments, a cyclic voltammetry of the cathodes was recorded between -0.8 V and +0.8 V *vs.* Ag/AgCl KCl 3M (scan rate of 50 mV s^{-1}).

2.8. Energy consumption evaluation

The specific energy consumption per unit mass of removed pollutant (EC_{150min}) was determined after 150 min of electrochemical treatment as shown in Eq. (3), where U is the applied cell voltage (V), I the average current intensity (A), t the time (h), V the solution volume (L) and $\Delta C_{pollutant}$ the difference in the pollutant concentration (mg L^{-1}). Due to the different pollutant conversion in the studied cathodes, the energy consumption (EC x%) was also calculated at a given pollutant removal in terms of kWh m^{-3} as indicated in Eq. (4), where X% represents the percentage of pollutant conversion (e.g., 40 % and 60 %).

$$EC_{150\,min}(kWh\,g^{-1}) = \frac{U \cdot I \cdot t}{V \cdot \Delta C_{pollutant}} \quad (3)$$

$$EC\ x\%\ (kWh\,m^{-3}) = \frac{U \cdot I \cdot t}{V} \quad (4)$$

3. RESULTS AND DISCUSSION

In the following sections, the performance of the prepared carbon electrodes will be compared to that of a carbon felt cathode for the degradation of metronidazole. The performance has been discussed in terms of catalytic degradation efficiency of the pollutants and energy consumption. Data from synthetic water will be first discussed; best performing electrode and electrochemical treatment will be further explored for the degradation of sulfamethoxazole in a real wastewater effluent.

3.1. Anodic oxidation and homogeneous electro-Fenton

3.1.1. *Degradation of metronidazole*

Figure 1 shows the degradation of metronidazole following AO (HC and CB electrodes) and EF treatments (HC, CQ and CB electrodes). The AO treatment for carbon CQ is not included since this material contains traces of iron in its ashes (corresponding to a 1 wt.% iron content) [34], thus a Fenton reaction is expected to take place during the treatment. For comparison purposes, the EF assay on the commercial CF cathode has been included.

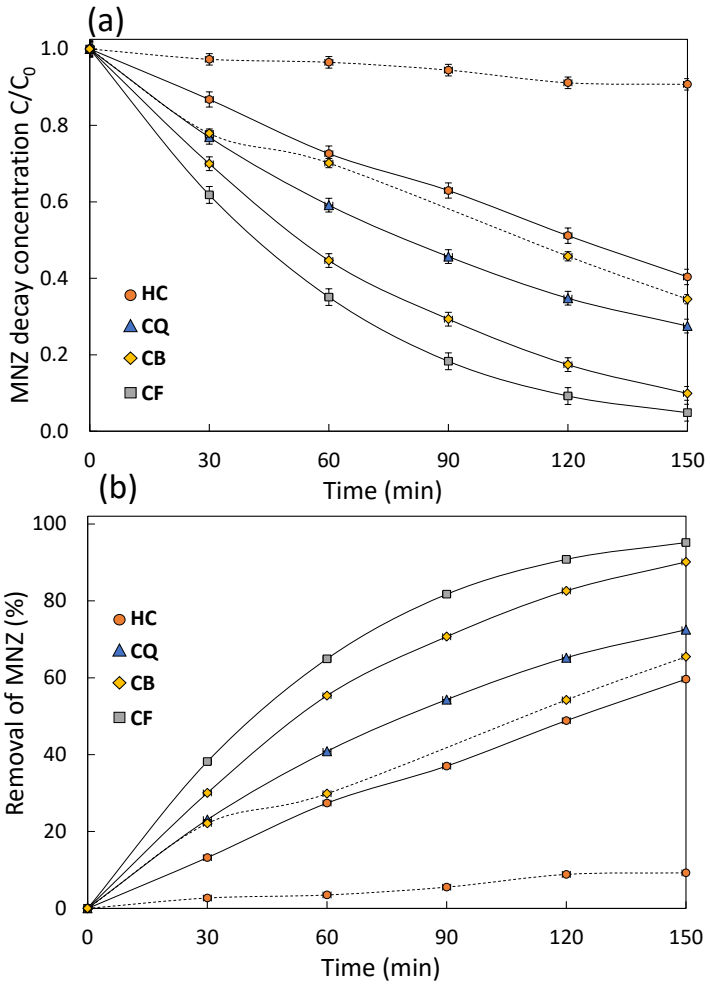


Figure 1. Degradation kinetics of metronidazole by AO (dashed lines) and EF (solid lines) treatments using different carbon materials as cathodes; BDD as anode, 0.05 M Na_2SO_4 electrolyte, 100 mg L^{-1} of metronidazole, applied potential -0.75 V vs Ag/AgCl. Experimental data is shown as: (a) relative decay concentration of MNZ, and (b) removal percentage.

As it can be observed, the AO treatment was less efficient than the EF, regardless the material used as cathode. The removal of metronidazole obtained after 150 min of AO was ca. 9 and 65 % using HC and CB cathodes, respectively. A considerable improvement was obtained for the EF treatment in both materials, with removal values reaching 60 and 90 %, for HC and CB, respectively. Regarding the EF assays, a larger metronidazole removal was obtained for the CF (95 %), followed by CB (90 %), CQ (72 %) and HC (60 %). However, it should be noted that despite the similar dimensions of all the cathodes (2 x 2 cm), the thickness of the CF electrode

(0.5 cm) is larger than that of herein prepared cathodes (150 μm on each side of collector). Hence, in practice the CF electrodes have roughly 15 times more mass (as contact surface) than the cathodes prepared with carbons CQ, CB and HC. Therefore, a more adequate comparison of the performance should be done by normalizing the removal of metronidazole vs the mass of the carbon material in the cathode. The normalized data is compiled in Table 2, showing that the degradation is 10 times more efficient for the cathodes prepared with carbons CQ, CB and HC when the performance if normalized vs the mass of the electrodes. In this regard, it should be considered that the mass and dimensions of the electrodes are important parameters to be considered for a potential scale up; the mass is important as it also affects the amount of pollutant adsorbed.

The specific energy consumption of the process using these cathodes was calculated considering the charge applied to the electrodes; the comparison of the specific energy consumption was made on the basis of the total reaction time (150 min) and expressed per mass of metronidazole degraded (W h g^{-1}). As seen in Table 2, $EC_{150\ min}$ for MNZ of reaction was reduced by 60 % with cathodes CQ and HC compared with CF. However, due to the different pollutant conversion in the studied cathodes, the energy consumption was also calculated for selected percentage of metronidazole removal ($EC_{40\ \%}$ and $EC_{60\ \%}$). It can be seen that for achieving the same percentage of removal, the energy consumption is still favorable to the cathodes prepared with carbons CQ and HC. Furthermore, if a preliminary cost analysis is performed considering the price of the pristine carbon materials needed to manufacture the electrodes, herein proposed carbons (CB, CV) clearly outperform CF. In this regard, despite the manufacture of the electrodes would need to be optimized (e.g., ink formulation, binder, percolator, support) before a rigorous economic analysis, the large difference in both the performance and the cost of the raw carbon materials can be used as a good indicator to

demonstrated the potential of carbon materials CQ, CB and HC for their use as cathodes in EF treatments.

Table 2. Specific metronidazole removal after 150 min of treatment, calculation of the energy consumption in the EF treatment with the studied cathodes and cost of the carbon materials.

	HC	**CQ**	**CB**	**CF**
Absolute MNZ removal at 150 min (mg MNZ)	8.94	10.87	13.52	14.27
Specific MNZ removal at 150 min (mg MNZ/mg carbon)	1.21	0.82	0.84	0.069
$EC_{150\ min}$ (Wh g^{-1} MNZ)	0.583	0.597	-	1.463
$EC_{40\ \%}$ MNZ (kWh m^{-3})	0.022	0.023	-	0.030
$EC_{60\ \%}$ MNZ (kWh m^{-3})	0.035	0.037	-	0.058
Cost of carbon material (US$ kg^{-1})[a]	-	100	100	700

[a] Material's costs estimated from commercial suppliers -purchase of low quantities-

The different performance in the EF reaction of those carbon materials might be partially explained in terms of their physicochemical features; a summary of selected parameters is compiled in Table 3. Both carbons CB and CQ present a marked nanoporous character with high specific surface areas; this is expected to favor the generation of hydrogen peroxide during the EF reaction owing to a higher density of exposed active sites and an enhanced diffusion of the species involved in the two-electron ORR [16]. The electrogenerated hydrogen peroxide can be activated not only by means of the Fenton reaction, but also at the surface of these nanoporous carbons that would act as electron-transfer catalysts to produce hydroxyl radicals and hydroperoxy radicals via reaction (r4) and (r5) [16,37]. The contribution of those radicals formed within the pores and at the surface of these cathode materials could improve the degradation of metronidazole.

$$AC + H_2O_2 \rightarrow AC^+ + OH^- + {}^{\cdot}OH \quad \text{(r4)}$$

$$AC^+ + H_2O_2 \rightarrow AC + H^+ + HO_2^{\cdot} \quad \text{(r5)}$$

Furthermore, the adsorption of metronidazole in the micropores of these nanoporous carbons used as cathodes is expected to have a beneficial effect in the abatement of the pollutant due to

an enhanced transfer of the reactive species towards the target molecule, owing to the close proximity between metronidazole and the active sites at the carbon's surface where hydrogen peroxide is generated and activated to form radicals [16]. In this regard, it should be reminded that the cathodes were immersed in the solution of the pollutant for 30 min before the electrochemical treatment, allowing the adsorption in the porosity of the carbons.

Table 3. Main textural parameters of the carbon materials obtained from N_2 adsorption/desorption isotherms at -196 °C, and surface pH.

Material	**S_{BET} ($m^2\ g^{-1}$)**	**$V_{TOTAL\ PORES}$ ($cm^3\ g^{-1}$)[a]**	**$V_{MICROPORES}$ ($cm^3\ g^{-1}$)[b]**	**Surface pH**
CF	25	0.022	0.01	8.5
CB	1280	1.06	0.23	2.2
CQ	1033	0.52	0.42	8.9
HC	10	0.02	0.004	3.5

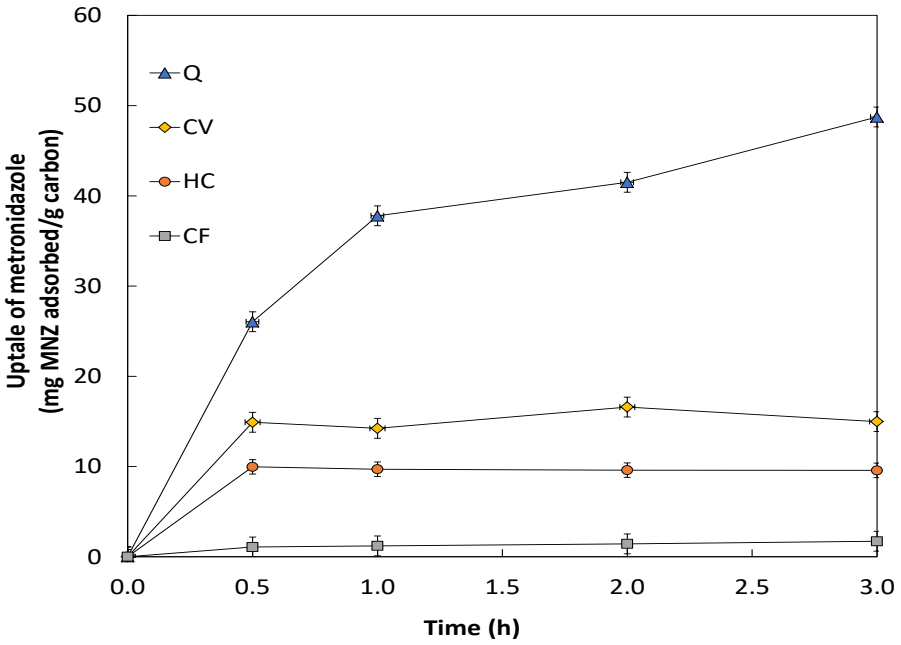
[a] Total pore volume evaluated at 0.99 of relative pressure

[b] Micropore volume evaluated by Dubinin Radushkevich method

Indeed, previous to the electrochemical treatment, the adsorption capacity of metronidazole on the different carbon materials was explored by putting them in contact with a solution of the target pollutant and analyzing the concentration at periodic intervals. The obtained data (Figure 2) revealed a high uptake of metronidazole in carbon CQ, followed by CB and HC.

The uptake of metronidazole in the carbon felt was considerably lower. The high uptake of metronidazole on carbon CQ is expected due to the large micropore volume of the material and its low functionalization (Table 3). Aromatic compounds are usually well retained in carbon adsorbents of such characteristics due to dispersive π-π interactions [38,39]. For carbon HC, the low uptake is due to its poor porosity; in the case of carbon CB, the low adsorption capacity despite favorable porous features (micropore volume) is associated to its hydrophilic nature (see surface pH in Table 3) owing to a high amount of O-surface functionalities of the carbon (ca. 20 wt.% oxygen content); this is known to favor the competitive adsorption of water in the nanopores, and to have a marked withdrawal character on the π electronic density of the carbon, thereby decreasing the dispersive interactions with the pollutant.

Figure 2. Adsorption capacity of metronidazole on the carbon materials used as cathodes



(ca.150 mL, 100 mg L^{-1} metronidazole, 50 mM Na_2SO_4, pH 3).

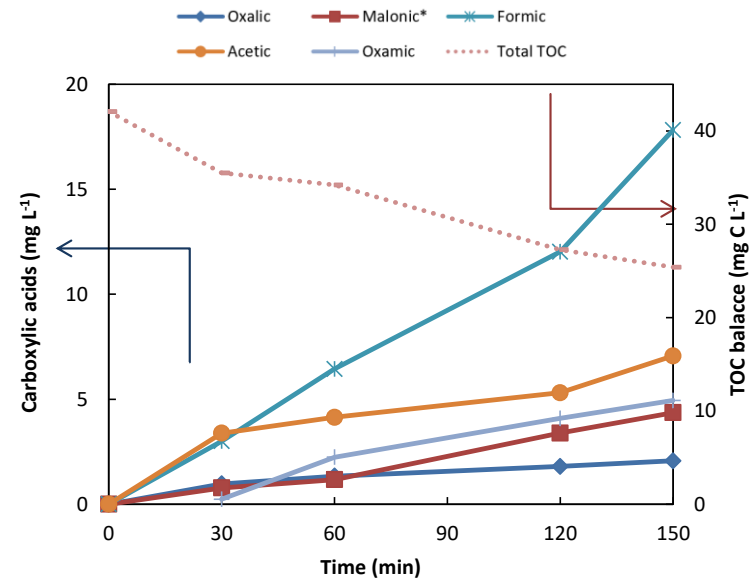
It should be pointed out that the uptake obtained after 3 h corresponds to the adsorption of ca. 3-1 % of the amount of metronidazole in the solution for the electrodes CQ and CB/ HC during

the electrochemical reactions (both AO and EF). This confirms that the pollutant removal observed during the electrochemical treatments (ca. 150 min) is mainly due to its degradation by means of the AO and EF reactions, and that the removal due to non-degradative adsorption contributes to a much lower extent.

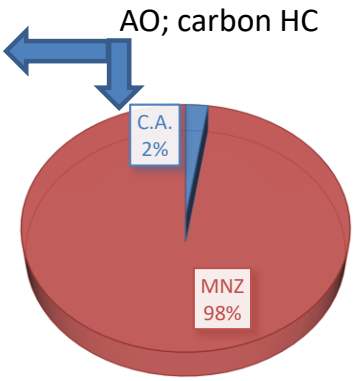
3.1.2. *Carboxylic acids detected during the treatment*

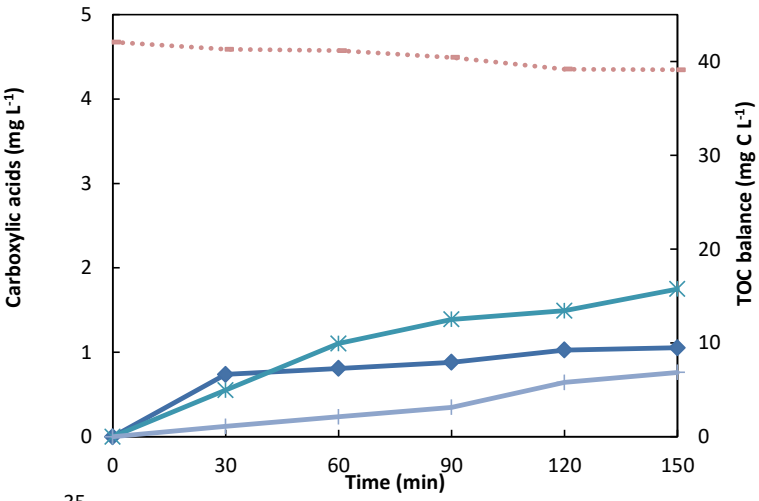
The formation of degradation intermediates during the electrochemical treatments was investigated by HPLC. Several carboxylic acids (Figure 3) were detected throughout the treatments (i.e. oxalic, oxamic, acetic, formic and malonic/glyoxylic -these two acids coeluted, thus calculations were done assigning the peak to malonic acid-). These are typical intermediates obtained in EAOPs and represent the previous steps to complete mineralization of the pollutant [40,41]. The amounts of those carboxylic acids detected during the AO and EF treatments on the studied carbons are represented in Figure 3. The identified organic acids are in line with those reported in the literature for the degradation of metronidazole by other oxidation techniques [42,43].

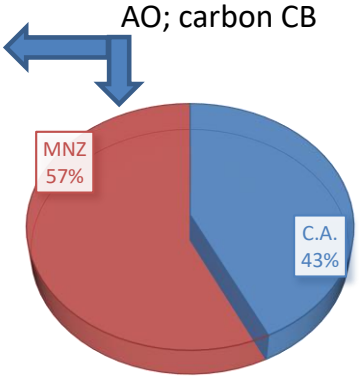
The general sequence for the degradation of MNZ through electrochemical processes has been proposed to proceed through subsequent N-denitration and hydroxyethyl cleavage reactions triggered by the presence of oxygen reactive species (hydroxyl radicals, hydrogen peroxide) and the formation of short alkyl chain carboxylic acids (Figure S1). The detection of oxamic and malonic acids as intermediates is in agreement with these reactions, and the predominance of formic and acetic acids (over all detected carboxylic acids) the confirms the advanced stage of the metronidazole mineralization.

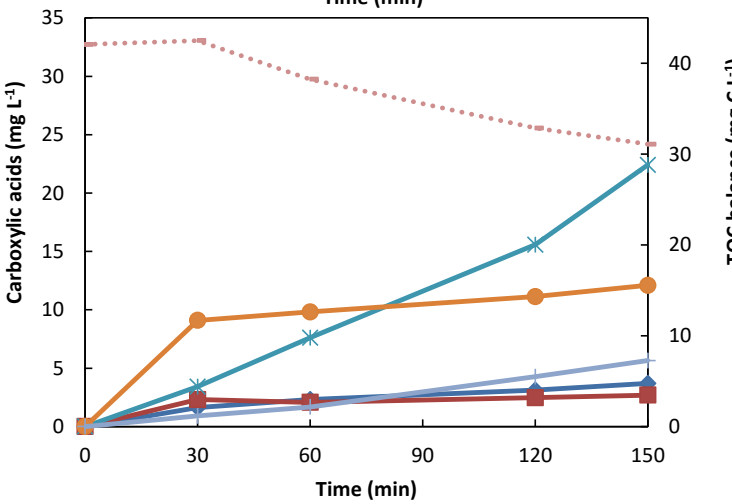


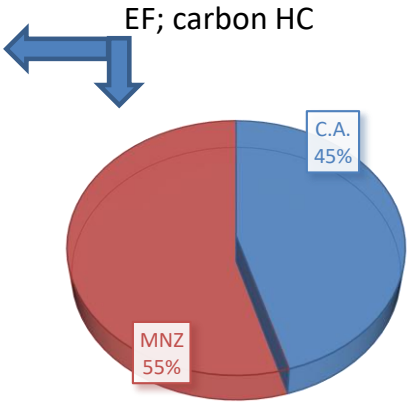
$TOC_{balance}$ speciation at 150 min











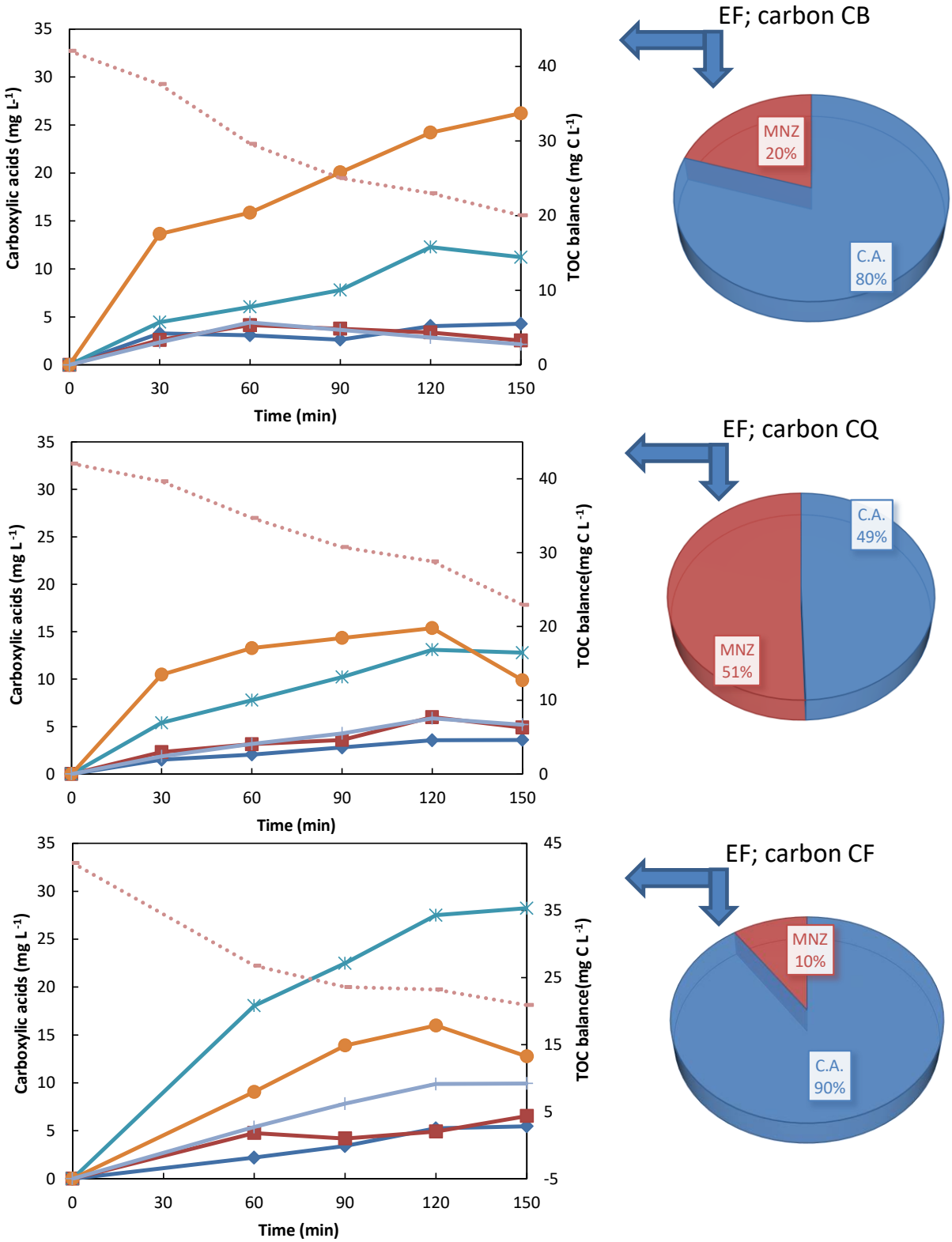


Figure 3. (left) Concentration of carboxylic acids and TOC $_{balance}$; (right) speciation of TOC$_{balance}$ (fraction of unreacted pollutant and carboxylic acids) at 150 min in AO and EF treatments with the studied cathodes. * Malonic and glyoxylic acids coeluted; calculations were done assigning the detected peak to malonic acid. Errors are below 3% in all measurements; error bars are not added to the plots for clarity.

Due to the interferences present in the solution, the experimental determination of the total organic content of the solutions was not reliable (see experimental section). Thus, the extent of the mineralization was evaluated from the $TOC_{balance}$ indicator, that corresponds to the sum of unreacted metronidazole and the total amount of carboxylic acids quantified by HPLC and expressed in mg C L^{-1} (dotted line in Figure 3). The speciation of the $TOC_{balance}$ (fraction of unreacted metronidazole and total amount of carboxylic) is shown in the charts on the right in Figure 3).

Data analysis revealed that the EF processes were not only more efficient towards the degradation of metronidazole (Figure 1) but also in terms of a greater degree of mineralization of the pollutant estimated by the evolution of $TOC_{balance}$. For the AO reaction with cathode HC, the total amount of organic acids was considerably lower than that of the EF process with the same system (e.g., malonic acid and acetic acid were not detected), with a final $TOC_{balance}$ value of 39.1 mg C L^{-1} (ca. 7% of TOC elimination) after AO compared to 31.1 mg C L^{-1} (TOC removal of 26%) for the EF reaction. Furthermore, carboxylic acids accounted only for ca. 2% of the $TOC_{balance}$ remaining at the end of the AO treatment (the other 98% corresponding to metronidazole), rising up to 45% in the EF process. This confirms the more advanced stage of metronidazole mineralization in the EF process with cathode HC, despite a low overall performance.

Regarding cathode CB, short-chain organic acids were also accumulated at the end of the AO reaction. In contrast, for the EF process, the concentration of some acids reached a maximum and started to decrease within the 150 min of reaction. This indicates that metronidazole degradation intermediates are also degraded to some extent upon the electrochemical reaction (Figure 3), thus suggesting a greater degree of mineralization. This was also corroborated by the $TOC_{balance}$ abatement (52 vs.40 % for EF and AO, respectively) and the larger contribution of organic acids to the final TOC (80 vs. 43 % for EF and AO, respectively). The performance

of the cathodes in terms of mineralization in the EF reactions followed the trend: CB > CQ > HC, corresponding to a decay in the $TOC_{balance}$ of 52 % > 48 % > 26 %, respectively (Figure 3). This trend is in agreement with the removal of metronidazole discussed above. The analysis of the $TOC_{balance}$ speciation at the end of the EF treatment for the studied cathodes revealed a higher mineralization extent with carbon CB (ca. 20 % of $TOC_{balance}$ is attributed to metronidazole, compared to 51 % and 55 % for CQ and HC cathodes, respectively).

In the case of the commercial CF the decay in $TOC_{balance}$ (ca. 50 %) was very similar to that achieved with material CB (ca. 53 %) after 150 min of treatment, as shown in Figure 3. However, in terms of final TOC distribution, the CF cathode showed a better performance, with only a 10 % corresponding to metronidazole compared to 20 % for the case of CB.

This might be explained by the larger amount of carbon material present in the CF cathode (ca. 15 times more, as discussed above due to the differences in thickness of the electrodes) compared to the cathodes prepared from CQ, CB and HC. In sum, these results demonstrate the ability of the cathodes prepared from low cost carbons -particularly CQ and CB- to participate in the degradation and mineralization of metronidazole through an EF process, achieving performances close to that of a commercial carbon felt commonly used for this reaction. Their performance is expected to improve by the incorporation of iron in the cathode; this will be discussed in the following sections.

3.2. Heterogeneous electro-Fenton

3.2.1. *Heterogeneous catalysis*

The performance of the cathodes was also investigated in a heterogeneously catalyzed EF process for the degradation of metronidazole. For this, iron as catalyst was incorporated to the cathodes so as to boost the generation of hydroxyl radicals by the reaction of hydrogen peroxide

in the presence of iron species. The iron was incorporated to the low-cost carbon materials upon immobilization on either the powders of the carbon materials before the fabrication of the cathodes (this procedure will be referred to as “pre”), or directly on the cathodes (this procedure will be referred to as “post”). The carbon felt was not further used for the immobilization of iron, since our previous works have shown that carbon felts are not the best candidates for a potential scaling up of the process [27,28].

The electrocatalytic performance of the series of electrodes prepared following the “pre” procedure is shown in Figure 4. As seen, the degradation of metronidazole increased in the order: HC < CB < CQ, with removal values after 150 min of ca. 70 %, 91 % and 98 %, respectively. When compared with the outcome of the homogeneous EF assays (Figure 1), it is clear that the conversion of the pollutant has been improved with the incorporation of iron in the materials for the cathodes prepared with HC and CQ carbons, with a remarkable boost for the latter material from 72 % to 98 % (Table S1 summarizes the degradations achieved with the different EAOPs applied, to facilitate the comparison). Conversely, for CB cathode, the incorporation of iron in the carbon before the preparation of the cathodes did not show any significant enhancement in the conversion of metronidazole compared to the performance of the electrode in the homogeneous EF process (ca. 90 % degradation).

It should be noted that the amount of iron loaded in each carbon material was different (about 0.015, 0.033 and 0.061 mg Fe/mg carbon for HC, CB and CQ, respectively), while it was constant for the homogeneous EF process (2.09 mg Fe in 150 mL). Considering the mass of carbon used in the preparation of the cathodes, the iron content of the electrodes was 0.23, 0.65 and 0.95 mg Fe, for HC, CB and CQ, respectively (much lower than the amount available for the homogeneous EF process). It should also be mentioned that this amount of iron decreased significantly for all the electrodes upon consecutive electrocatalytic tests (Table 4); this will be further discussed in Section 3.2.2.

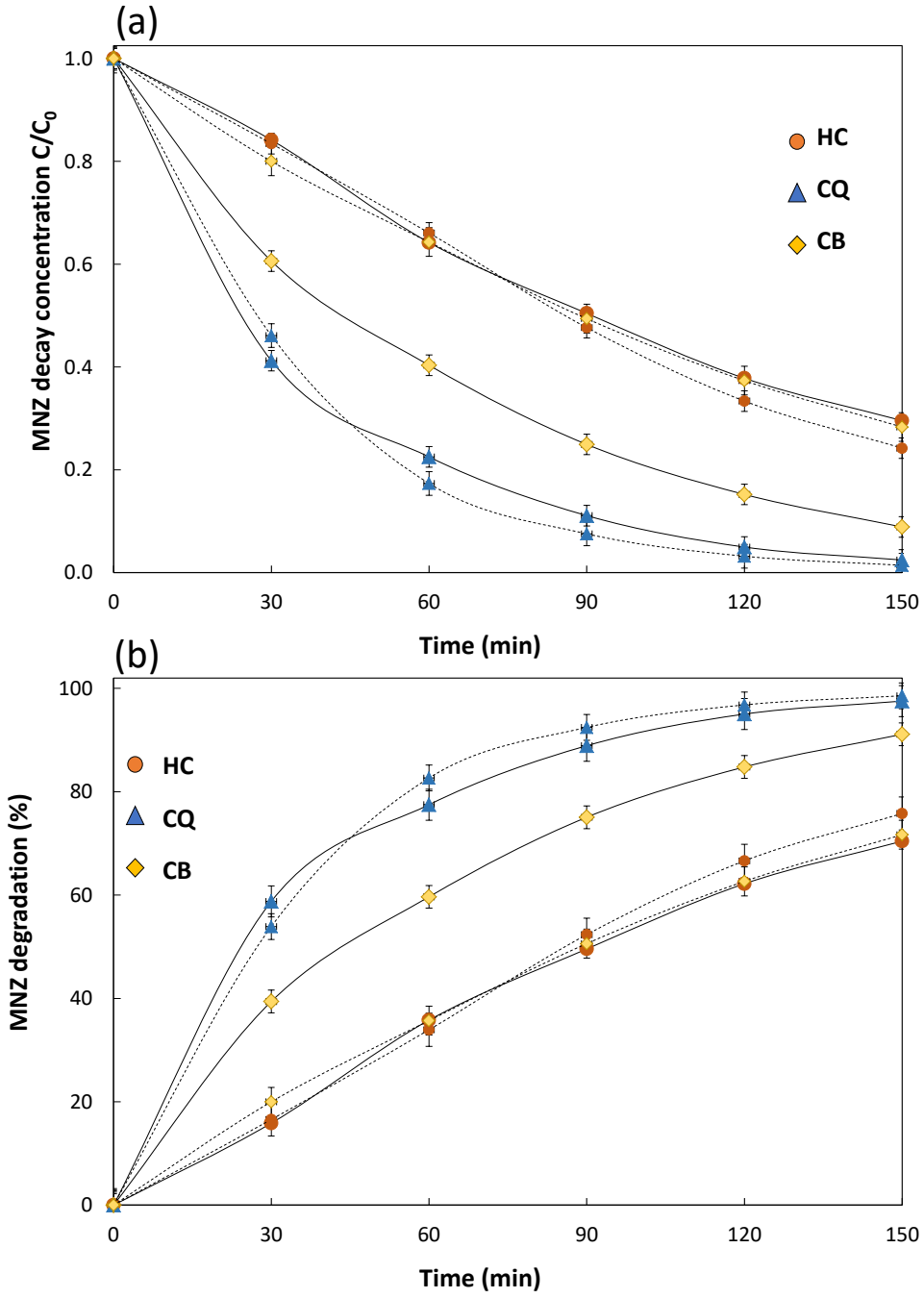


Figure 4. Degradation kinetics of metronidazole by heterogeneous EF treatment using two approaches for the catalyst immobilization in the cathodes prepared with different carbon materials: solid lines: "pre" series; dashed lines: "post" series. BDD as anode, 0.05 M Na_2SO_4 electrolyte, 100 mg L^{-1} of metronidazole, applied potential -0.75 V vs Ag/AgCl. Experimental data is shown as: (a) relative decay concentration of MNZ, and (b) removal percentage.

Interestingly, the degradation of metronidazole on the "pre" CQ cathode was roughly 10 % higher than that of "pre" CB cathode, even after several cycles. As the content of iron in the cathodes after the first cycle was similar, this result seems to indicate that the iron content is in excess in the cathodes and that it cannot account for the difference performance of the carbon materials. This could be attributed to the differences in the adsorption capacity of metronidazole (Figure 2). Indeed, since the iron is immobilized in the carbon materials' surface, the radical species are not generated at the bulk solution (as in the homogenous EF process) but at the carbon cathode's surface. Since the pollutant is also retained on the porosity of the carbon cathodes, this is expected to favor the contact with the radical species, resulting in a faster and enhanced electrocatalytic performance.

The electrocatalytic performance of the series of electrodes prepared following the "post" methodology is shown in Figure 4. The amount of iron incorporated in the electrodes by the "post" methodology was 0.15, 0.32 and 0.45 mg Fe for cathodes HC, CB and CQ, respectively. These are lower amounts of iron compared to the "pre" series, which indicates that the uptake of iron is reduced when the immobilization is carried out in the electrodes (most likely due to the presence of PVDF binder, which confers a hydrophobic character to the electrodes). Regarding the EF reaction, the conversion of metronidazole attained with "post" CQ and HC was similar to that using the "pre" methodology: 99 % and 76 %, respectively. Conversely for CB cathode, the degradation of metronidazole was considerably reduced (ca. 72 % removal), reaching an even lower value than that obtained for homogeneous catalysis (Figure 1). This poor performance could be attributed to the high lixiviation of iron observed for this material during the first electrocatalytic test.

The lixiviation studies of the cathodes showed that the iron leaching was slightly lower for the "post" electrodes (varying from 0.001 to 0.004 mmol Fe) than for the "pre" series (varying from 0.001 to 0.009 mmol Fe). A similar finding has often been reported in the literature for several

heterogeneous EF treatments ([31] and references therein). The leaching of iron implies that a mixed mechanism involving both homogeneous and heterogeneous EF catalysis would occur. However, it is important to highlight that the amount of iron lixiviated to the solution corresponds to iron concentrations between 0.006-0.061 mM, which are far below those used in the homogeneous EF treatment in this study (0.25 mM) and other optimal values reported in the literature by several authors (typically in the range of 0.3–1.0 mM) [44-48]. This would suggest that the heterogeneous catalysis is the predominant mechanism.

Overall, the incorporation of iron in the carbon powders ("pre" approach) rendered better results than in the prepared electrodes ("post" approach). For this reason, only this immobilization technique was selected for further investigations. In this sense, the generation of carboxylic acids as intermediates in the degradation of metronidazole during the heterogeneous EF assays with electrodes "pre" was measured. As indicated above, the $TOC_{balance}$ represents the total concentration of unreacted metronidazole and the carboxylic acids detected in the solution.

The material HC was the electrode which generated notably lower carboxylic acids, with a $TOC_{balance}$ after 150 min of 24 mg C L^{-1} (43 %), with a fraction of 65 % corresponding to unreacted metronidazole (Figure 5). For the cathode prepared with carbon CB, the $TOC_{balance}$ decay was similar (ca. 42 %) to that of carbon HC, although with a much higher contribution of carboxylic acids was (Figure 5, 90 %). This indicates that the process with cathode CB is closer to a complete mineralization. The process with cathode CQ showed the best performance, with a 52 % $TOC_{balance}$ decay after 150 min, accounting for 95 % of carboxylic acids (Figure 5). The prepared electrodes outperformed the CF in homogeneous EF (Figure 1).

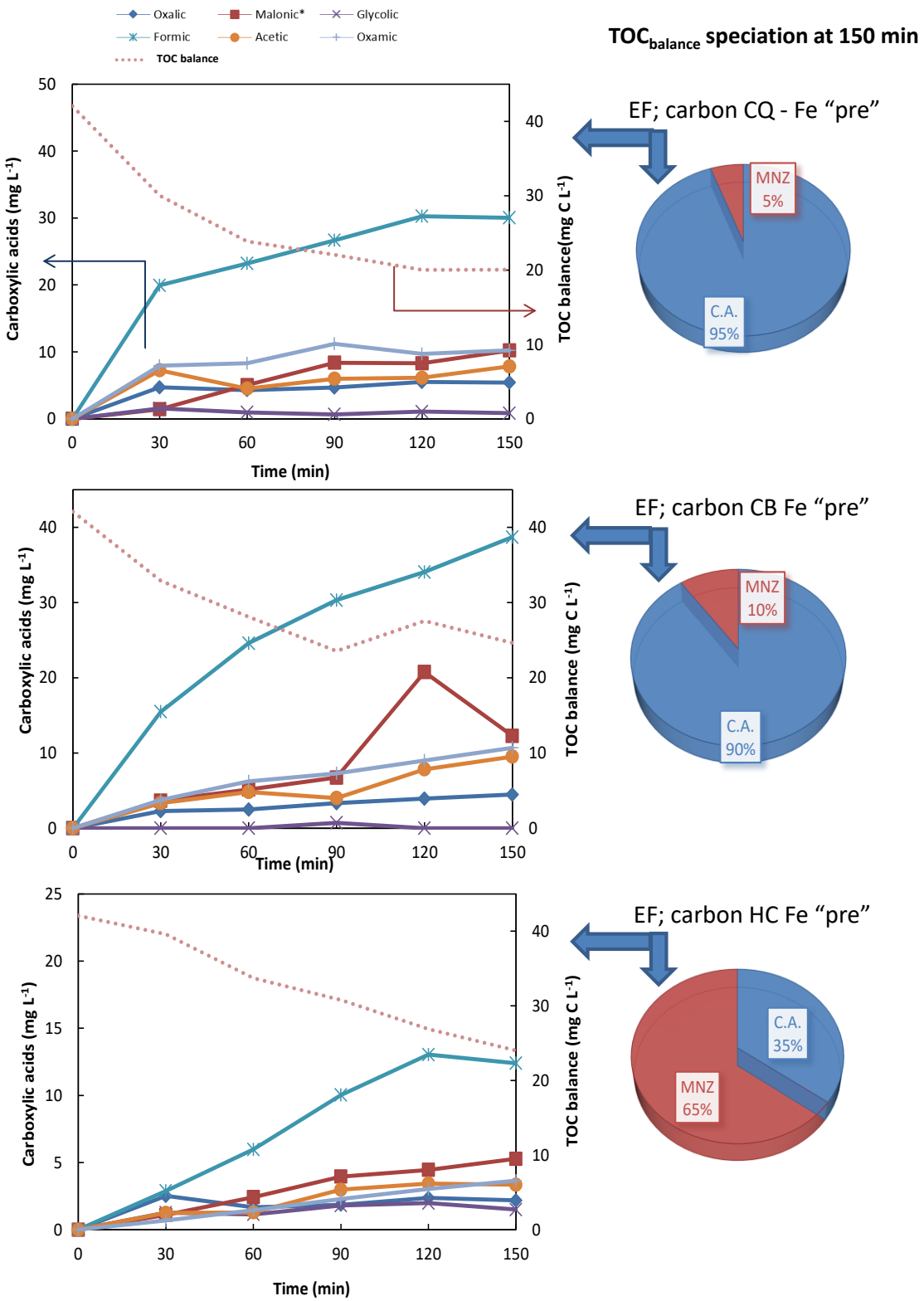


Figure 5. (left) Concentration of carboxylic acids and $TOC_{balance}$; (right) speciation of $TOC_{balance}$ (fraction of unreacted pollutant and carboxylic acids) at 150 min in heterogeneous EF with the cathode materials loaded with iron by the "pre" methodology. * Malonic and glyoxylic acids coeluted; calculations were done assigning the detected peak to malonic acid. Errors are below 3% in all measurements; error bars are not added to the plots for clarity.

Furthermore, the characterization of the electrodes of the "pre" series after the EF treatment confirmed that overall the studied carbons are quite stable. The porosity of the electrodes remained rather unchanged after the electrochemical treatment (Figure 6), with a slight decrease in surface areas and micropore volumes attributed to the amount of pollutant adsorbed in the pre-stabilization step. The stability of the used cathodes was also explored by cyclic voltammetry (Figure S2) and thermogravimetric analysis (Figure S3). The voltammograms of the cathodes before and after the electrochemical treatment were rather similar for carbon CQ (Figure S2), with slight modifications observed in carbons HC and CB. These could be due to the low conductivity of such high functionalized carbons (< 0.01 S/m for carbons HC and CB, compared to ca. 0.55 S/m for carbon CQ). On the other hand, the thermogravimetric profiles (Figure S3) showed a small mass loss between 200-400ºC, and is assigned to the desorption of the pollutant adsorbed in the pores of the cathodes. A second sharp peak featuring at 470 ºC arises from the decomposition of the PVDF binder in the electrodes. Overall the mass loss attributed to the pollutant retained in the pores accounted for less than 10 wt.% in all the cathodes, evidencing the lack of accumulation of the pollutants in the pores of the cathodes (that would imply a need for their regeneration).

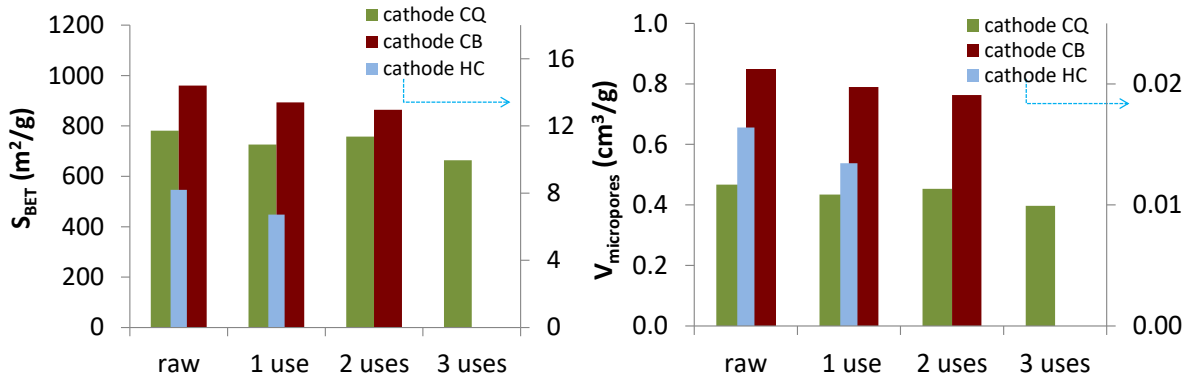


Figure 6. Characterization of the porosity of the cathodes loaded with iron using the "pre" methodology before and after various uses. Data of cathode HC is plotted in the second axis for clarity.

In sum, these results confirmed that the preparation of the iron-loaded electrodes by immobilization of the iron species in the carbon powders before the manufacture of the electrode is more advantageous. It produced a higher degradation extent and more advanced mineralization stage of metronidazole, pointing out the viability to use these low cost carbon materials as efficient cathodes for the heterogeneous EF treatment.

3.2.2. *Reusability*

After assessing the capacity of the iron-containing cathodes for the degradation of metronidazole by means of heterogeneous EF, we have studied their performance after several cycles. For the reusability tests we have selected the cathodes prepared with carbons CQ and CB, based on their best electrocatalytic performance discussed above. Data corresponding to the degradation of metronidazole in subsequent cycles is depicted in Figure 7. It can be observed that the cathode prepared with carbon CQ showed an outstanding stability, being the degradation of metronidazole during three consecutive cycles practically identical (ca. 97 % after 150 min). In the case of the cathode prepared with carbon CB, the degradation efficiency of the second and third cycles was slightly lower than the first one, but still attaining values above 83 %. The lixiviation studies of the cathodes upon subsequent cycles showed that despite a considerable amount of iron lixiviated after the first cycle for both carbons (Table 4), it seemed to stabilize in the subsequent cycles.

Table 4. Iron content on the cathodes CQ and CB in three subsequent uses.

Use	**Initial amount in electrode CQ (mg)**	**Initial amount in electrode CB (mg)**
1st	0.90	0.65
2nd	0.39	0.40
3rd	0.32	0.34

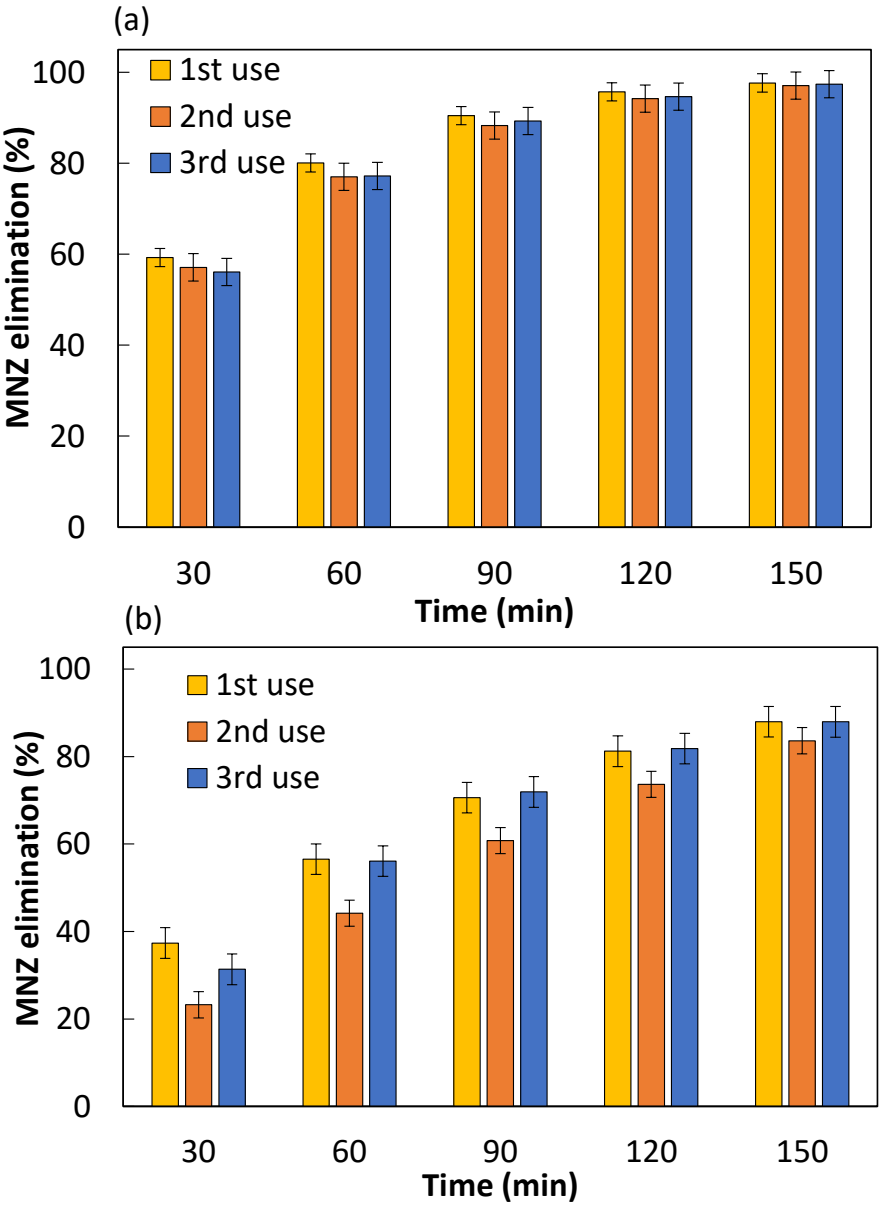


Figure 7. Evaluation of the cathodes reusability after three consecutive cycles for the heterogeneous EF treatment with cathodes CQ (a) and CB (b) prepared by the "pre" methodology.

As mentioned before, the amount of iron released to the solution is much lower than the optimal dose reported for homogeneous EF process, for which the main expected degradation mechanism is the heterogeneous catalysis. Furthermore, SEM images were performed to iron-

containing CQ cathodes before and after the first use demonstrated that there is still iron available in the electrode surface (Figures S4 and S5).

The high conversion values upon the consecutive cycles despite the leaching of iron in the first cycle indicate that the amount of iron remaining in the electrodes is high enough to perform the heterogeneous EF treatment in the subsequent cycles. The degradation of metronidazole in the different cycles is higher than that obtained by the AO treatment for CB cathode (

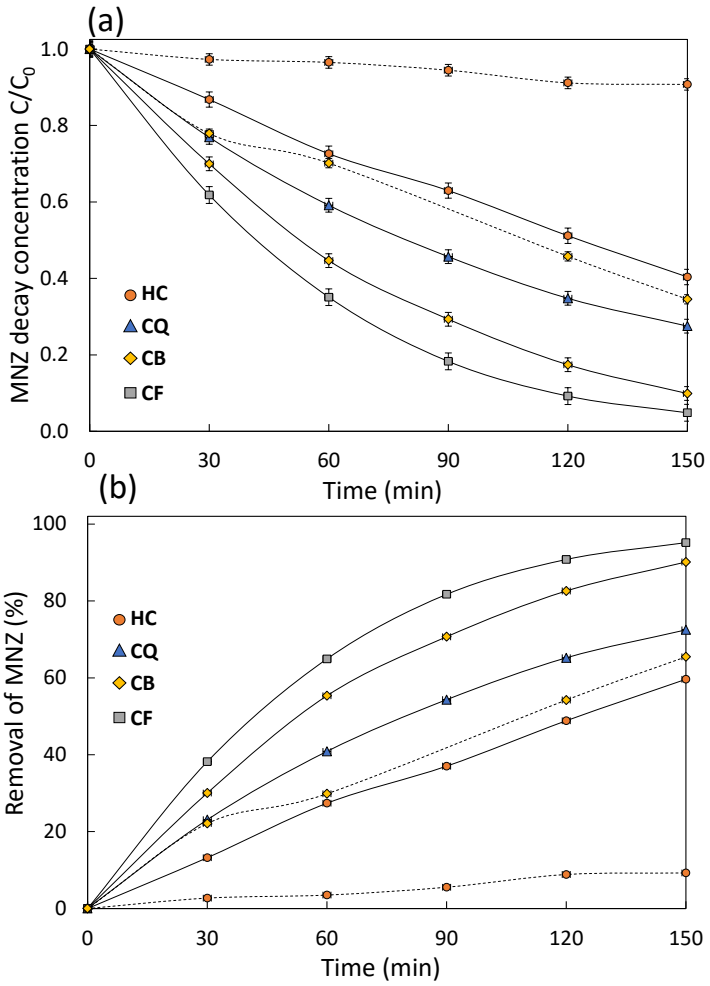


Figure 1.; see Table S1 for comparison) which confirms the occurrence of EF reaction even at the low amounts of iron in the cathodes after the first cycle (Table 4).

The characterization of cathodes after several uses also confirmed the stability of the prepared electrodes. As seen in Figure 6, the drop in the textural parameters of the cathodes followed a

small and smooth decrease with the number of uses (ca. 10% of drop for cathode CQ after 3 consecutive uses), demonstrating a low level of pore clogging with the reuses. As mentioned above, this is important since it delays the eventual regeneration of the electrodes. The thermogravimetric profiles after several uses (Figure S3) revealed a similar trend, as the mass loss between 200-400ºC (assigned to the pollutant adsorbed in the pores) did not increase with the number of uses.

3.2.3. *Degradation of sulfamethoxazole*

Given its good performance, the cathode prepared with carbon CQ was selected to explore the degradation of sulfamethoxazole upon both homogeneous and heterogeneous EF treatments. In the latter case the iron was incorporated following the "pre" methodology. Sulfamethoxazole is a widely used antibiotic that has been detected in several water sources and it is refractory to conventional treatments [49].

Figure 8 shows the degradation of sulfamethoxazole by applying homogeneous and heterogeneous EF to cathode CQ. The degradation efficiency is lower than that of metronidazole (Table S1). Furthermore, the extent of sulfamethoxazole degradation is higher upon heterogeneous EF, as similarly observed for metronidazole, highlighting the benefits of immobilizing the iron in the cathode compared to its presence in the bulk solution.

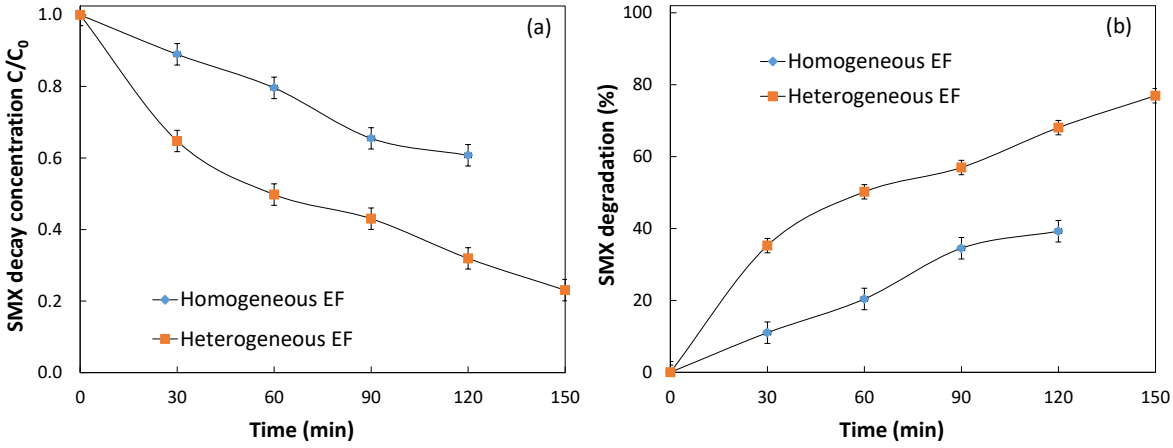


Figure 8. Degradation kinetics of sulfamethoxazole by homogenous and heterogeneous EF treatments using "pre" iron-loaded CQ-carbon as cathode: BDD as anode, 0.05 M Na_2SO_4 electrolyte, 100 mg L^{-1} of sulfamethoxazole, applied potential -0.75 V vs Ag/AgCl. Experimental data is shown as: (a) relative decay concentration of SMX, and (b) removal percentage.

The formation of several organic acids (i.e., oxamic, oxalic, acetic and formic acid) was also detected upon the electrocatalytic degradation of sulfamethoxazole (Figure 9). In the homogeneous EF, acetic and formic acid were formed and reached a maximum of concentration after 1 h of reaction. In contrast, in the case of the heterogeneous assay, all detected organic acids seem to accumulate in the solution after 150 min. This seems to indicate that since in the former treatment less sulfamethoxazole is degraded, the radicals would attack both the intermediates and the pollutant leading to the reduction in the concentration of carboxylic acids. The $TOC_{balance}$ (total concentration of unreacted sulfamethoxazole and carboxylic acids) after 120 min attained was twice larger for the homogeneous (31.8 mg C L^{-1}; 33 % decay) than for the heterogeneous assays (17.8 mg C L^{-1}, 62 % decay).

This value is better than the $TOC_{balance}$ for the degradation of metronidazole in the heterogeneous assay, indicating the highly refractory nature of metronidazole. Similar results have been reported by Munoz et al. [50], with higher mineralization degrees in pharmaceuticals

containing two aromatic rings (such as sulfamethoxazole) compared to metronidazole. Several pathways have been proposed in the literature for the degradation of SMX upon AOPs, most of them involving a complex route through a variety of cleavage, oxidation, hydroxylation, and demethylation reactions (Figure S1). The detection of acetic, oxalic, formic and oxamic acids in the solution after 150 min implies the breaking of the SMX molecule to a rather large extent (e.g., initially via the sulfonamide bond, and subsequent cleavage of the different primary cycle products) to form short carboxylic acids. This indicates the mineralization of a fraction of SMX molecules, even if the concentration of sulfamethoxazole in solution is still rather high. On the other hand, the presence of other complex intermediates not detected by our analytical methods (e.g., 3-amino-5-methylisoxazole, *p*-benzoquinone or *p*-amino benzene sulfonic acid) and widely reported in the literature cannot be completely discarded [51,52].

In addition, in the homogeneous treatment only ca. 9% of the $TOC_{balance}$ corresponds to carboxylic acids after 120 min of treatment (Figure 9), whereas in heterogeneous EF the value ranged from 22-15 % at 120 and 150 min of treatment. In any case, the fraction of carboxylic acids is remarkably lower when compared to the treatments of metronidazole (Figures 3 and 5). Thus, it is clear that the mineralization extent of sulfamethoxazole is in a much earlier stage.

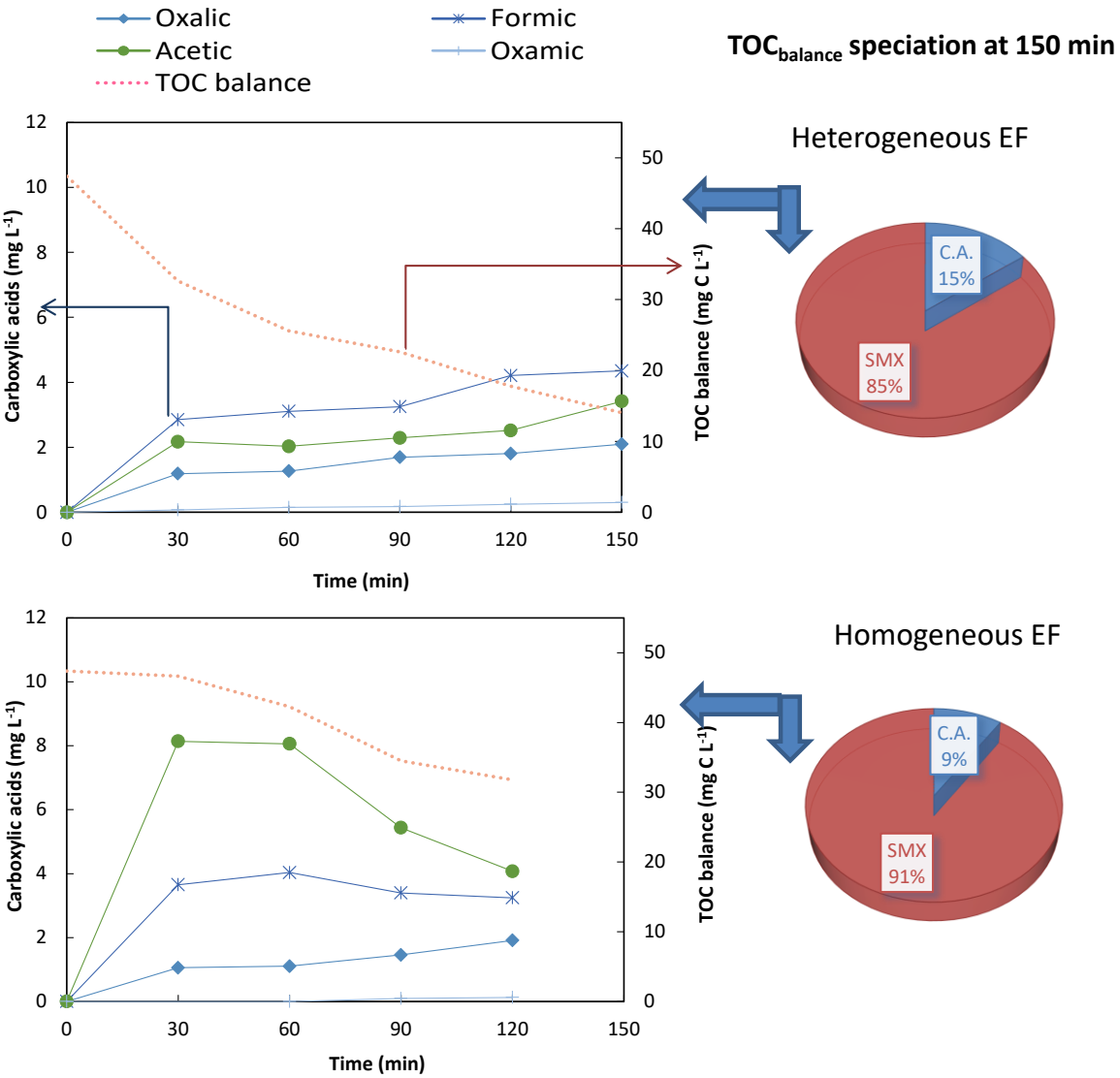


Figure 9. (left) Concentration of carboxylic acids and TOC $_{balance}$; (right) speciation of TOC $_{balance}$ (fraction of unreacted sulfamethoxazole and carboxylic acids) at 150 min in homogeneous and heterogeneous EF using cathode CQ. Errors are below 3% in all measurements; error bars are not added to the plots for clarity.

3.2.4. *Treatment of real wastewater*

Although fundamental research in synthetic water is essential to comprehend the mechanisms of the electrochemical remediation of water by means of EF, it is also of paramount importance to perform catalytic assays in real water matrixes. In a real-case scenario, water matrix is a parameter than cannot be controlled and it may have significantly impact in the selected treatment, due to the presence other species that might act as scavengers of the reactive radical

species responsible for the degradation of the target pollutant [53]. To account for this vision, the effectiveness of cathode based on carbon CQ for the heterogeneous EF treatment of metronidazole and sulfamethoxazole in a real wastewater matrix has been investigated.

Water obtained from the effluent of a municipal wastewater treatment plant in Spain was spiked with 30 mg L^{-1} of either metronidazole or sulfamethoxazole. Data in Figure 10 shows the evolution of the degradation extent; in the case of metronidazole, data was compared with that in synthetic water at the same initial concentration. As observed, the degradation of metronidazole after 150 min reached ca. 88 % in both synthetic water and real wastewater effluent, although the kinetics was faster in the latter case. This might be due to the presence of chloride ions in the real wastewater effluent, which would react with the hydroxyl radicals to produce active chlorine that accelerates the oxidation process [54]. The salinity and moderate COD values of the water matrix (Table 1) do not seem to have a significant impact in the performance of the EF reaction. For sulfamethoxazole, a lower degradation extent was observed (64 %) compared to metronidazole, as already reported in synthetic water. It should be noted that after the treatment of both antibiotics in the real wastewater, the amount of nitrates in the effluent increased, reaching values of 10.3 and 9.1 mg L^{-1} for metronidazole and sulfamethoxazole, respectively (initial value 8.2 mg L^{-1}, Table 1). This points out to the release of nitrates during the degradation of the antibiotics, which is in agreement with the degradation mechanisms proposed for both compounds in the literature [42,43,52,55].

All this confirms the potential of carbon CQ as cathode in the treatment of pollutants by heterogeneous EF treatments both in synthetic and complex water matrixes; the low cost of the carbon and its high availability highlight the interest in further research applying this type of carbon materials as cathodes in EAOPs, as they offer important economic advantages to conventionally used carbon felts, without sacrificing the catalytic performance.

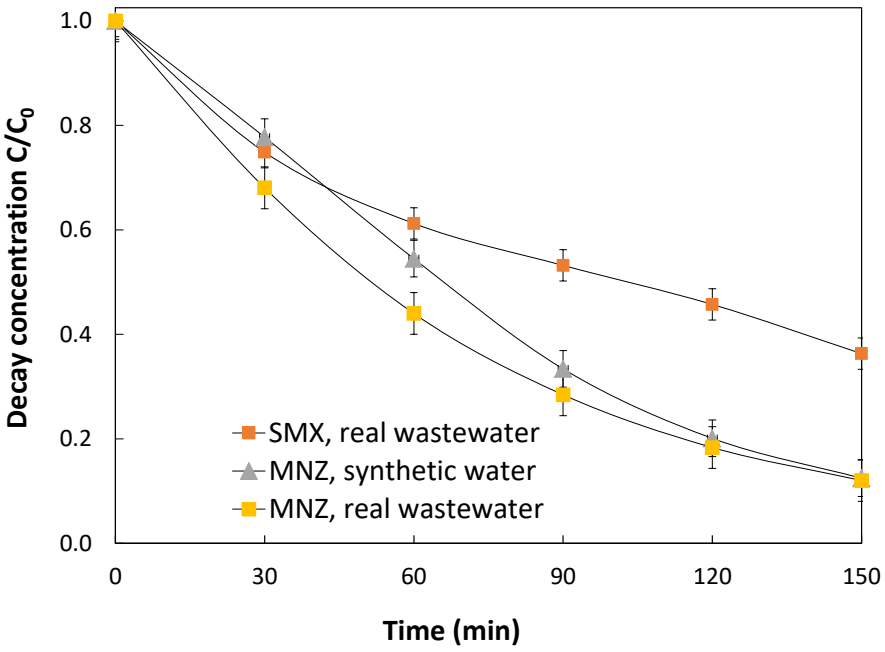


Figure 10. Decay concentration of metronidazole and sulfamethoxazole in real wastewater with heterogeneous EF using a CQ-cathode.

Conclusions

Three cost-effective carbon electrodes were successfully prepared using carbon materials from varied origins and tested as cathodes for AO and EF treatments in the degradation of recalcitrant pollutants. Regardless the nature of the carbon cathodes, the results obtained with the EF process for the degradation of metronidazole outperformed those of the AO. Similarly, heterogeneous EF treatments incorporating iron in the cathode showed better performance than the homogeneous catalytic process (iron in solution) for the degradation of metronidazole. The performance of the electrodes was particularly enhanced when the iron was incorporated to the carbon powders before the preparation of the electrode (pre-loaded series). Throughout all treatments carboxylic acids were detected, indicating that the pollutant was being mineralized. The cathodes showing better performances in heterogeneous EF (i.e. iron-containing electrodes

prepared from carbons CQ and CB) were tested for reusability, demonstrating excellent performance and stability after 3 consecutive cycles. The best results (in terms of pollutant conversion and mineralization) were obtained for the heterogeneous EF treatment of metronidazole with CQ electrode, attaining almost complete degradation within 150 min. The favored adsorption of metronidazole on the porosity of the carbon cathode seemed to be critical for assuring a good electrocatalytic performance. The same material showed a good performance in the electrocatalytic degradation of sulfamethoxazole by heterogeneous EF, and in a complex wastewater matrix for both target pollutants.

These results demonstrate the feasibility of using low-cost carbon materials as electrodes in electrochemical advanced oxidation processes for wastewater remediation. Owing to their sustainability, versatility of materials and low cost, the proposed carbon electrodes represent an interesting alternative to current competitor materials that could lead to boost the implementation of EAOPs in wastewater treatment. All this confirms the potential of carbon CQ as cathode in the treatment of pollutants by heterogeneous EF treatments both in synthetic and complex water matrixes.

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Author Contributions

Conceptualization, VPN, COA; Formal analysis, VPN, COA; Investigation, VPN, AGB; Supervision, MP, MAS, COA; writing-original draft, VPN, COA; Writing-review & editing, VPN, AGB, MP, MAS, COA.

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SUPPLEMENTARY INFORMATION

Table S1. Comparison of the degradation of antibiotics metronidazole and sulfamethoxazole in the studied carbon electrodes upon anodic oxidation (AO), homogenous and heterogeneous electro-Fenton (EF), after 150 min of treatment.

	Metronidazole				***Sulfamethoxazole***	
Carbon electrode	**AO**	**Homogeneous EF**	**Heterogeneous EF**		**Homogeneous EF**	**Heterogeneous EF Pre**
			Pre	**Post**		
CB	65%	90%	91%	72%	-	-
CQ	-	72%	98%	99%	39%[a]	77% (68%[a])
HC	9%	60%	70%	76%	-	-

[a] Data after 120 min of treatment.

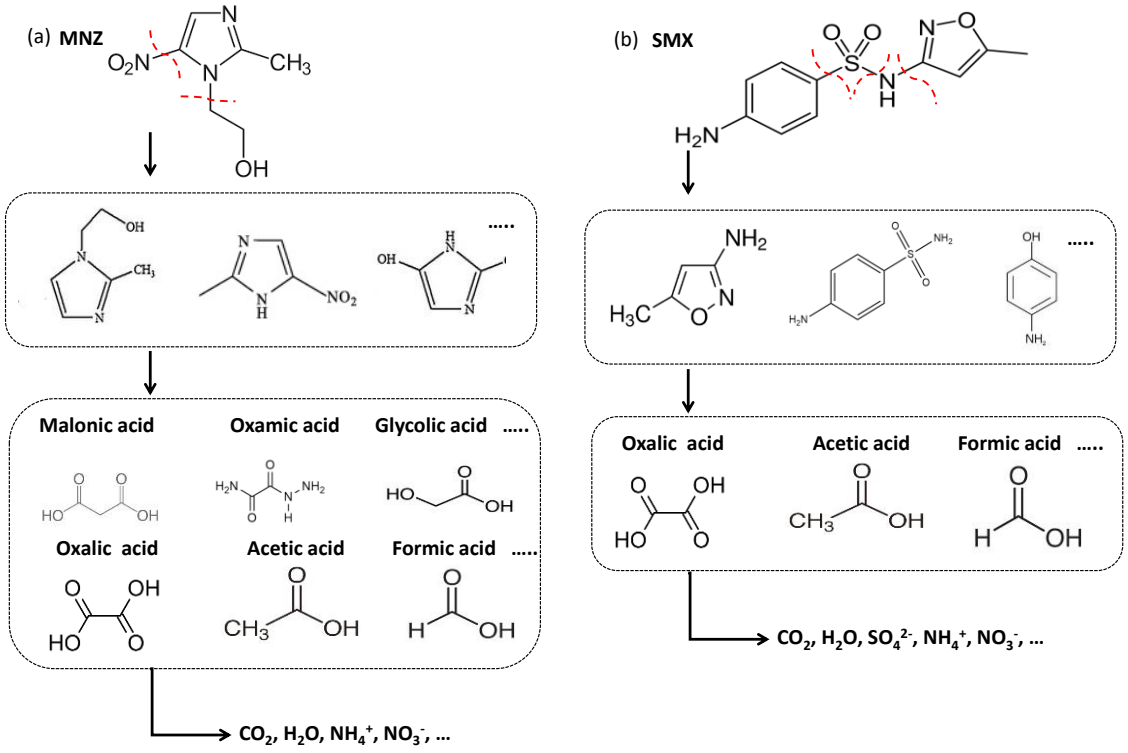


Fig. S1. Schematic representation of the most likely degradation routes of (a) MNZ and (b) SMX in EF treatments considering the detected intermediates. The proposed pathway is in agreement with other studies reported in the literature for both compounds.

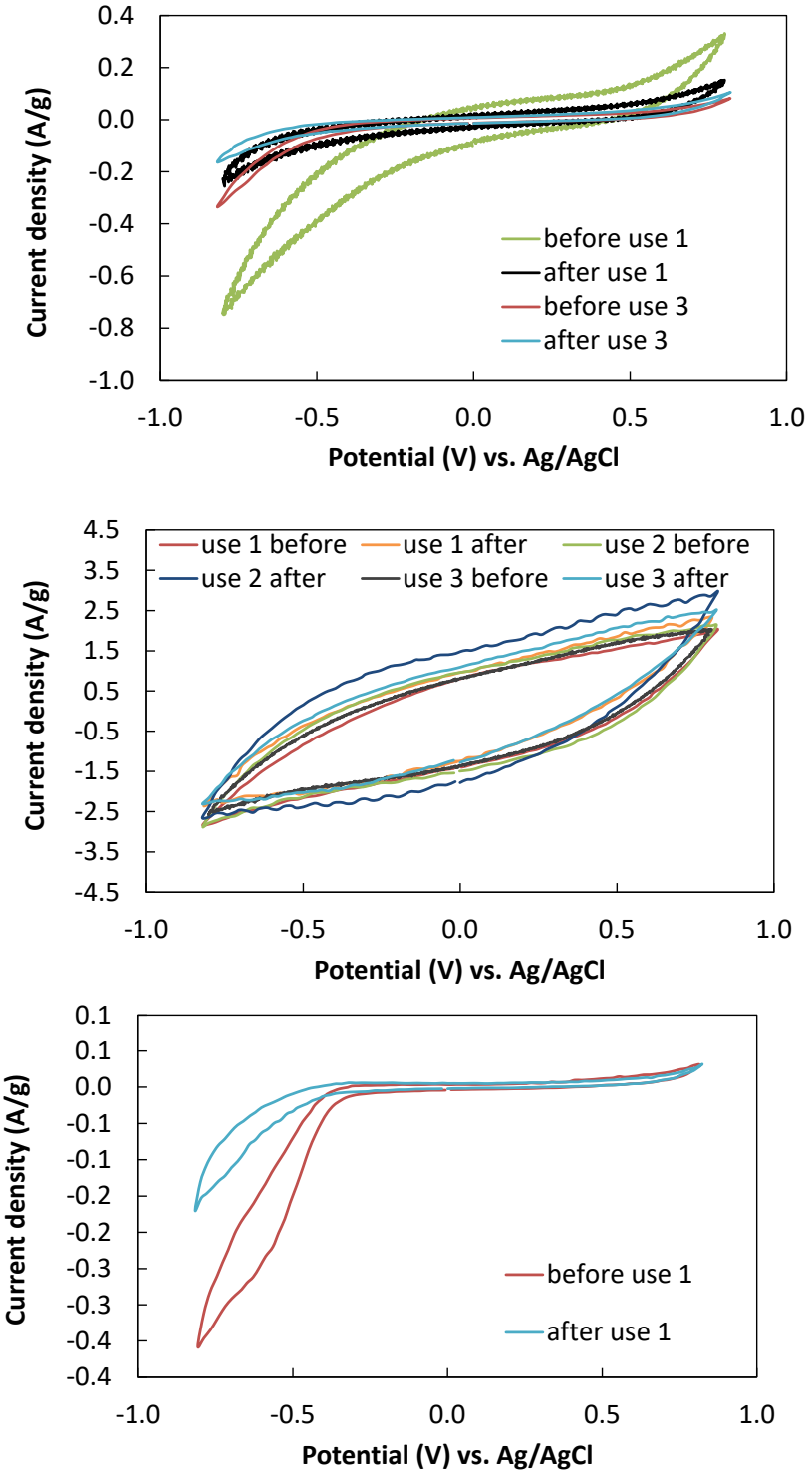


Fig. S2. Cyclic voltammetries of cathodes CB (top), CQ (middle) and HC (bottom) loaded with iron following the "pre" methodology, performed before and after the heterogeneous EF treatment. Third scans are represented for all the electrodes; 0.05 M Na_2SO_4 electrolyte, scan rate 20 mV/s.

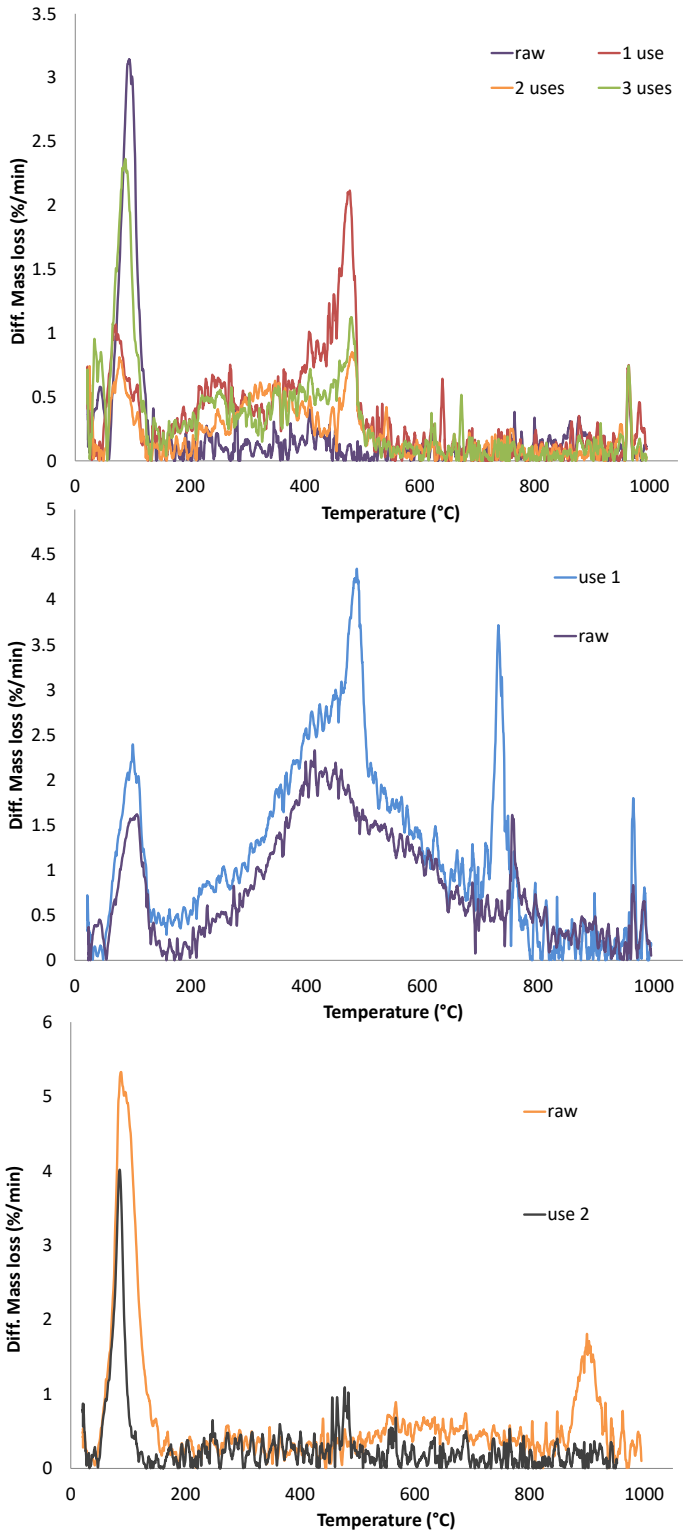
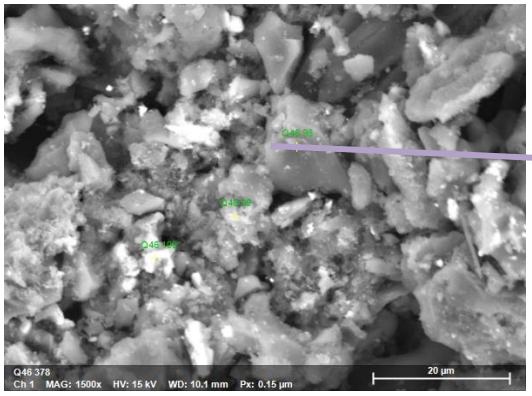
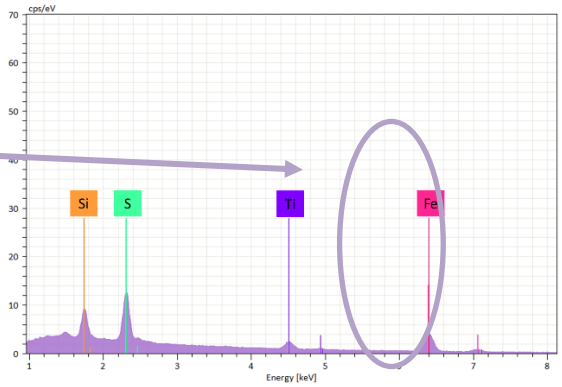
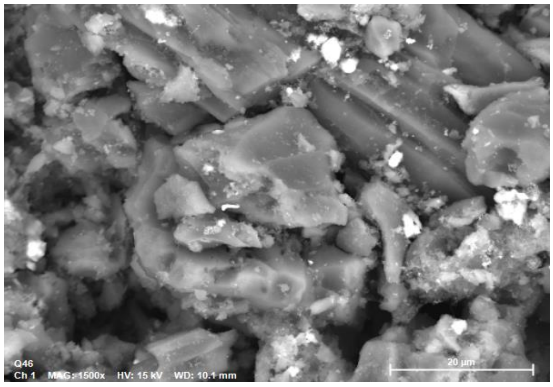


Fig. S3. Thermogravimetric profiles of cathodes CQ (top), HC (middle) and CB (bottom) loaded with iron following the "pre" methodology, performed before and after the heterogeneous EF treatment upon several consecutive uses.


Q46 378
Ch 1 MAG: 1500x HV: 15 kV WD: 10.1 mm Px: 0.15 µm
20 µm


cps/eV
Si
S
Ti
Fe
Energy [keV]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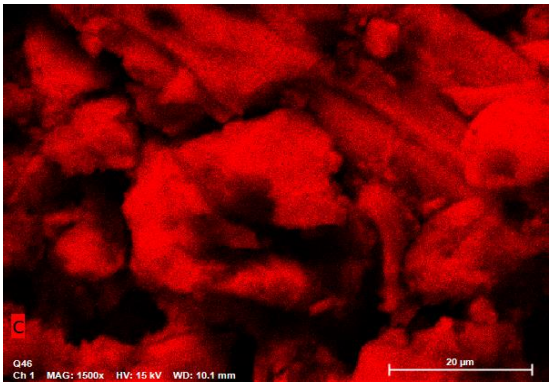
20 µm


C
Q46
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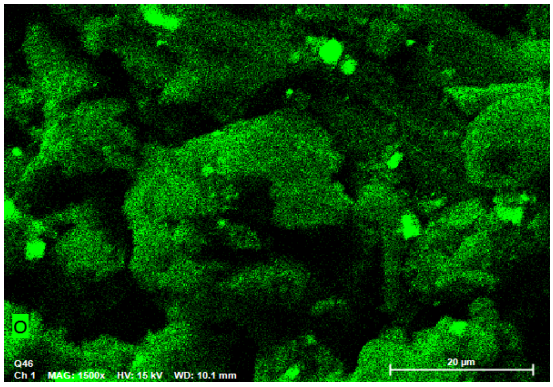
20 µm


O
Q46
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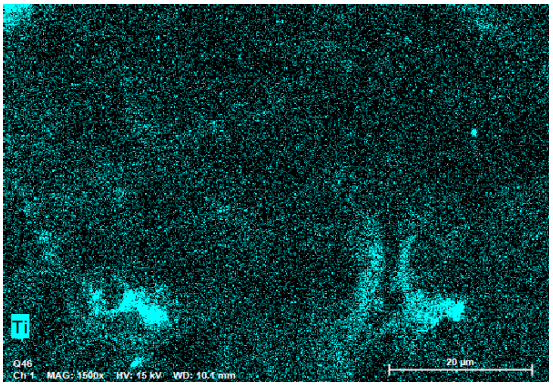
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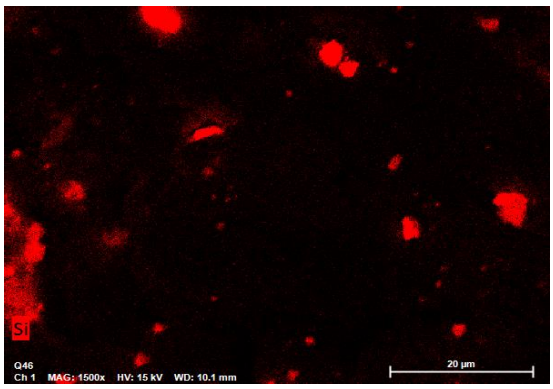
20 µm


Si
Q46
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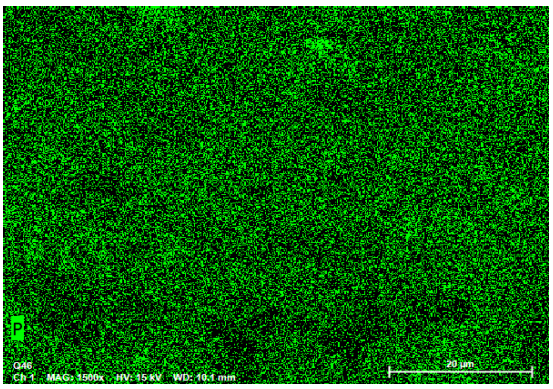
20 µm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Q46
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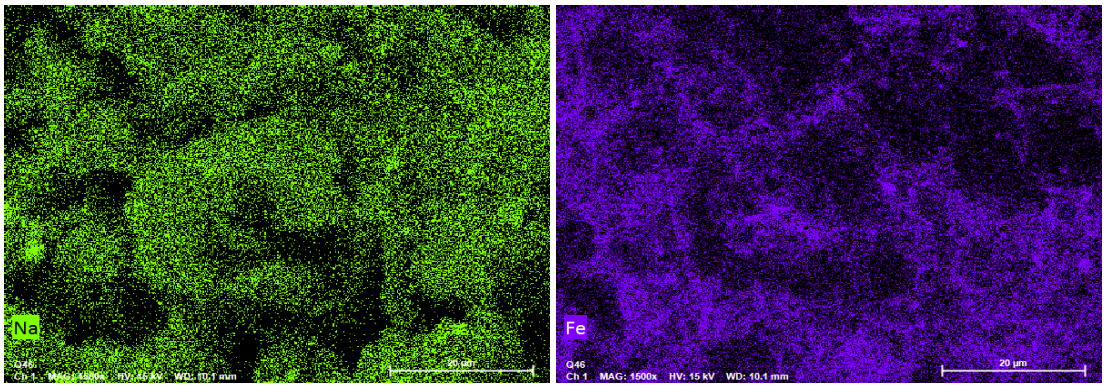
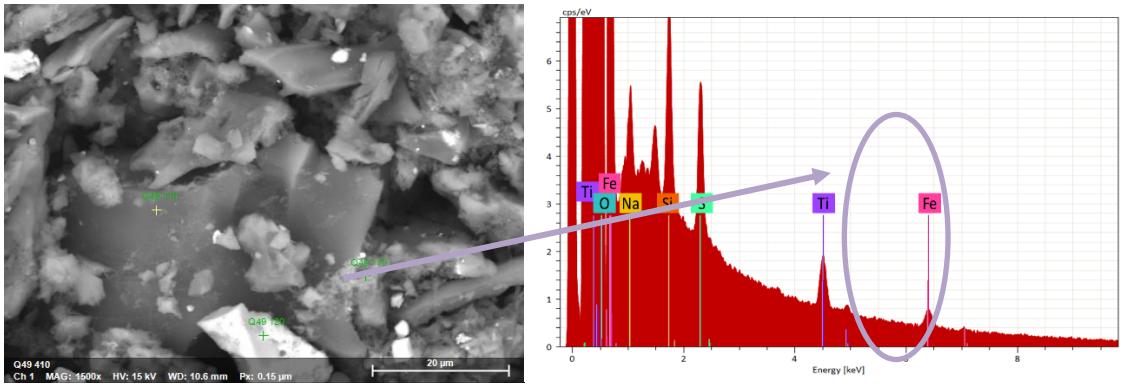
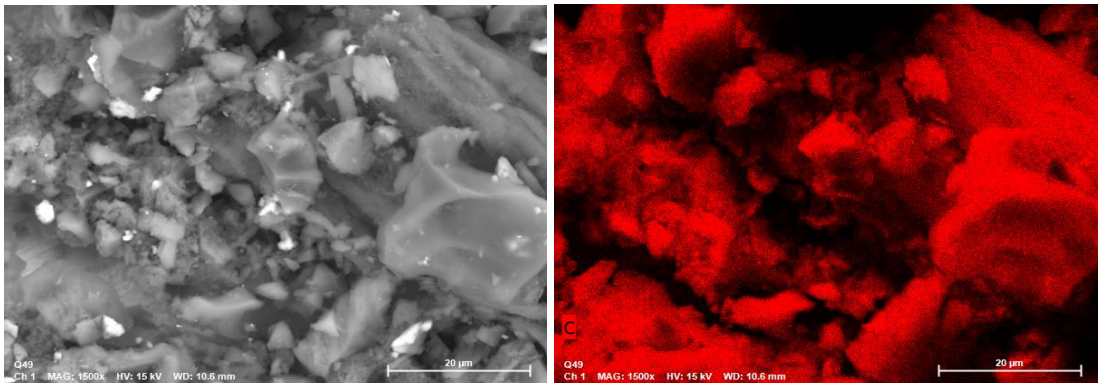


Fig. S4. SEM images of an iron-containing CQ cathode before its use.





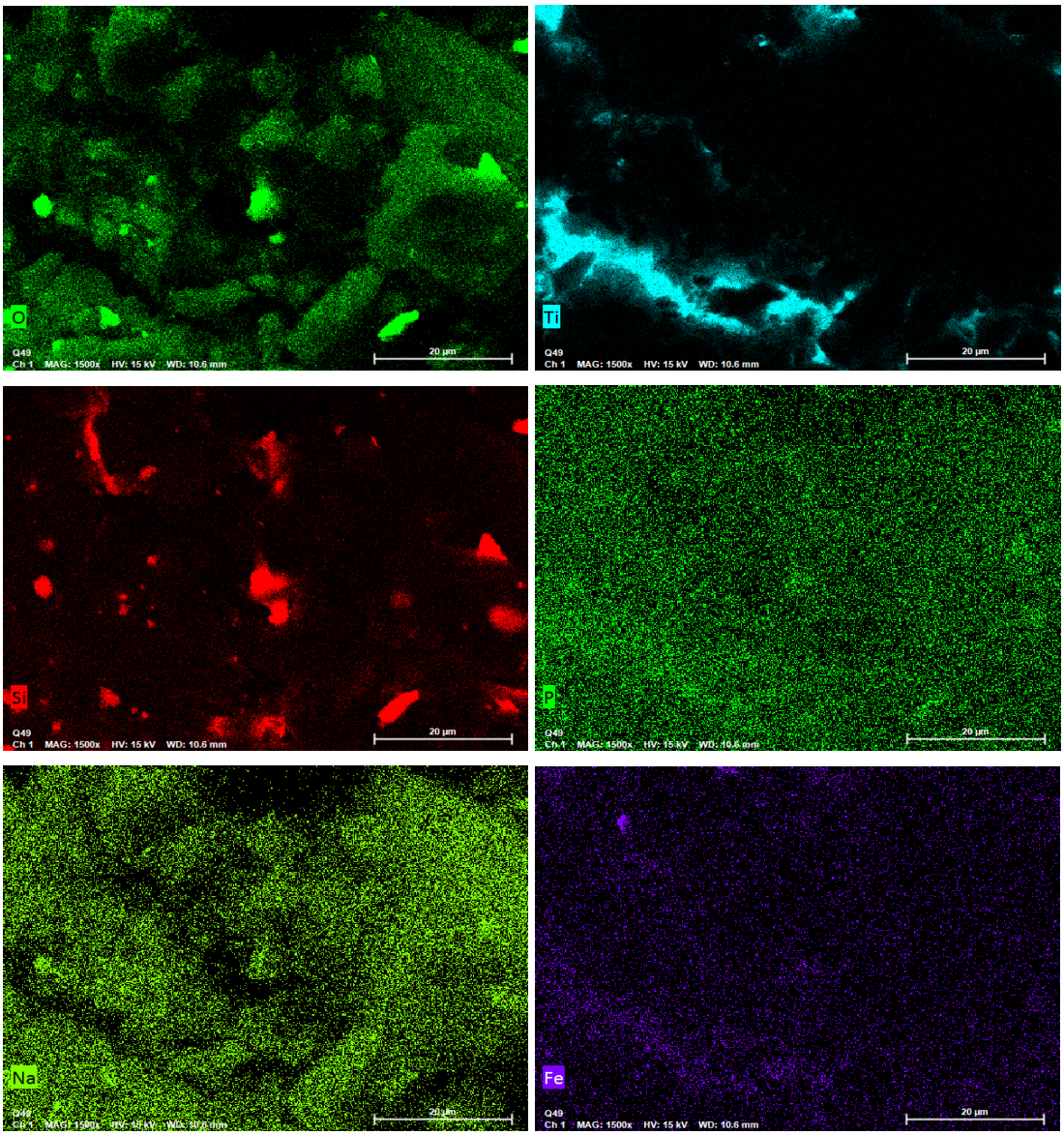


Fig. S5. SEM images of an iron-containing CQ cathode after 1 use in the heterogeneous EF treatment of metronidazole.