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REMOVAL OF CARBAMAZEPINE BY ELECTROCOAGULATION: INVESTIGATION OF SOME KEY OPERATIONAL PARAMETERS

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Abstract

The performance of electrocoagulation (EC) process, a non-specific electrochemical technology, was investigated for the removal of carbamazepine (CBZ), an antiepileptic drug, from water. Experiments were carried out in synthetic wastewater in a batch cell. The respective influences of some key process parameters were studied, such as mixing conditions, initial pH, and current on aluminium electrodes. Experimental results showed that a CBZ removal efficiency of 62% was observed under slightly acidic initial conditions (pH 4) with a current density as high as 44 mA cm^{-2} (*I*=4.5 A) using Al electrode. This clearly indicates that CBZ removal proceeds through an electrochemical mechanism, while the adsorption of CBZ onto the aluminum hydroxide flocs was shown to be negligible. Furthermore, the increase of initial pH to alkaline values was shown to decrease the drug elimination efficiency. Conversely, as expected, an increase of current intensity improved the removal of CBZ. As a result, low initial pH 4 coupled with high current elevates the electrochemical elimination of CBZ: in this case, one metabolite could also be detected.

Key words: carbamazepine, electrocoagulation, micropollutants removal, wastewater treatment

1. Introduction

Water resources are contaminated when pollutants are directly or indirectly discharged into wastewater without adequate treatment to remove harmful compounds. This provides a serious threat to human health on one side, and to plants and organisms living in these bodies of water on the other side (Aziz et al., 2010; Caliman et al., 2002). Water contamination has been caused over decades by a number of natural and anthropogenic pollutions, such as the spillage of pesticides and herbicides in agriculture, hospital discharges, industrial discharges, for example, industries involving fuels, wood preserving operations and textile production. This leads to the presence of rather different types of pollutions, such as organic products which derive for example from agro-food waste, home and personal care products, textile dyes, pharmaceuticals, but may also correspond to heavy metals cations or oxianions, or to inorganic anions, in particular sulfide, fluoride, and nitrate.

Pharmaceuticals and their bioactive metabolites are continuously introduced in the

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aquatic environment, where they are detected at trace concentrations (i.e. found in the ng L^{-1} or $\mu g\ L^{-1}$ range, so that they are often referred to as "micropollutants"), and become pseudo-persistent (Caliman and Gavrilescu, 2009; Gavrilescu et al., 2015; Semrany et al., 2012; Sirés et al., 2012). First, most pharmaceuticals are not completely degraded after ingestion and they may be excreted directly or also produce secondary pollutants, i.e. metabolites and subsequently enter and harm the aquatic ecosystem. This results in the detection of pharmaceutically active compounds, such as lipid-regulating drugs, analgesics, antibiotics, antiseptics, antidiabetics, barbituarates, beta-agonists, psychiatrics, receptor antagonists, hormones, and chemotherapy and beta-blocking heart drugs in wastewaters, streams, and ground-water resources. Their occurrence in the environment is mainly due to:

1. the excretion of the fraction of pharmaceuticals that are not metabolized by human or animal bodies into wastewater, or their metabolites;

2. the discharge of unused or expired medications;

3. the discharge of hospital wastewater;

4. the residues from pharmaceutical manufacturing.

Carbamazepine (CBZ), commercialized as *Tegretol* (Zhang et al., 2008), is a pharmaceutical imminostilbene derivative, and a lipophilic, neutral tricyclic compound (Atkins et al., 2013; Bahlmann et al., 2014). It is mainly used as an anticonvulsant drug, and also as a specific analgesic for trigeminal neuralgia (Popa et al., 2014; Rao et al., 2010). Its efficacy and safety profiles have made it first choice for adults. It is administered chronically in high dosages of 100-2000 mg daily and, hence, its annual production is high (Kosjek et al., 2009). Approximately 72% of orally administered carbamazepine is absorbed, while 28% is unchanged and subsequently discharged through the faeces (Zhang et al., 2008). Environmental studies confirm the presence of CBZ as one of the most frequently detected pharmaceuticals in the effluents of sewage treatment plants, in river and sea water (Miao et al., 2005), in comparison to the other pharmaceutical micropollutants in Europe, America and Asia. For instance, the presence of CBZ has been reported at concentrations about 6.3 $\mu g\ L^{-1}$ in wastewater, 1.1 $\mu g\ L^{-1}$ in surface water, and 30 $\mu g\ L^{-1}$ in drinking water (Mohapatra et al., 2014) in Canada. It has also been detected about 2300 ng L^{-1} in Canada in a wastewater effluent and about 258 ng L^{-1} in the USA, but below 10 ng L^{-1} in Germany (Metcalfe et al., 2003). As a consequence, health-based guidance values have been established for CBZ upon fishery products consumption in both marine and freshwater, such as 2000 $\mu g/kg_{biota}$ or 130 $\mu g.L^{-1}$.

Due to the persistence and toxic effects of this molecule, various water remediation technologies have been investigated to remove CBZ from wastewater and drinking water, including conventional biological and physicochemical treatments, but also advanced oxidation and biological processes. Several studies showed that, the abatement yield of CBZ by the conventional activated sludge process is limited (typically below 10%) due to its high resistance to biodegradation, independent from hydraulic retention times (Hata et al., 2010).

Other studies have been investigated the removal efficiency of this molecule by white-rot fungi. A CBZ elimination yield of about 60% was obtained with fungal laccase, an enzyme from *Trametes versicolor* after 48h of treatment (Hata et al., 2010), while less than 10% CBZ elimination were achieved after treatment with membrane bioreactors using *Pseudomonas sp.* (Li et al., 2013). The efficiency of physicochemical treatments, such as coagulation and flocculation/flotation, was also investigated and these did not operate rather better than biological treatments, with typical yields of CBZ elimination from 20% to 35% (Carballa et al., 2005; Suarez et al., 2008). Conversely, many contributions from the literature showed that ozonation and advanced oxidation processes (AOPs) including Fenton, photo-Fenton and heterogeneous photocatalysis could be more efficient for the removal of this molecule from wastewater. For example, ozonation was found to remove up to 99% CBZ (Hua et al., 2006); UV/hydrogen peroxide in the presence of 25 $mg.L^{-1}$ of H_2O_2 promoted the elimination of 90% CBZ at 2.25 $J.cm^{-2}$ UV dose (Shu et al., 2013); Fenton and photo-Fenton process could possibly achieve a complete elimination of CBZ by Fenton oxidation (Mohapatra et al., 2013), and heterogeneous photocatalytic processes with more than 90% elimination (Doll and Frimmel, 2005; Martínez et al., 2011). However, AOPs are highly expensive for wastewater treatment (Betianu et al., 2008; Sirés et al., 2012). Other cheaper treatments such as electrodeposition, electrocoagulation, electroflotation, electrodisinfection, electrooxidation, and electroreduction are important alternatives for wastewater treatment, due to their high efficiency in pollution abatement, easy operation, and compact facilities (Al-Shannag et al., 2014; Behbahani et al., 2013).

The objective of this paper is to investigate the potential applicability of electrocoagulation process (EC), an electrochemical treatment, as a possible way to remove CBZ from water and wastewater. Up to now, electrochemical methods have been disregarded in the literature for the removal of CBZ. This paper will also analyze how CBZ removal is affected by mixing conditions, pH, and current intensity which is the major process parameter of EC.

2. Experimental

In this study, EC was applied to investigate CBZ removal from synthetic water in which the

initial concentration C_0 of CBZ is 12.5 mg L^{-1}. All solutions were prepared with carbamazepine of analytical purity (99%) supplied by *Sigma-Aldrich* (France). The composition of the synthetic water includes also KCl (6.33 g L^{-1}) as a supporting electrolyte. The initial conductivity of water is 2.8 mS cm^{-1} and pH is 8.2. Initial pH is then adjusted between 4 and 9 by the minute addition of either 0.1 M hydrochloric acid or sodium hydroxide solutions.

For EC process, two rectangular aluminum electrodes were used as the anode and the cathode, of surface area S=102 cm^2 each, with an inter-electrode distance of 1 cm. EC consists of the controlled electrodissolution of the anodic material, as shown by Eq. (1).

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \qquad (1)$$

At the cathode, hydrogen gas is released through the electroreduction of water (Eq. 2).

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \qquad (2)$$
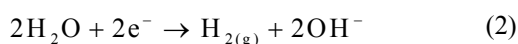
When pH is between 4 and 10, aluminium cations rapidly form insoluble oxyhydroxides and hydroxides, which readily precipitate and form flocs. This is usually summarized as given by Eq. (3).

$$Al^{3+}_{(aq)} + 3OH^- \rightarrow Al(OH)_{3(s)} \qquad (3)$$
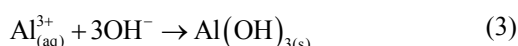
As a result, several mechanisms can promote pollution removal, among which:
1. the coagulation of colloidals or slightly soluble species;
2. the adsorption of pollutants onto the flocs;
3. the electrooxidation or electroreduction of the pollutants onto the electrodes.

To enhance these mechanisms, the EC cell consisted of a batch reactor of volume V=4.0 L, mechanically stirred using a standard Rushton turbine. Tests were carried out in an intensiostatic mode by means of a *BK-Precision* (USA) generator with a current (I) ranging between 1.5A and 4.5A. The electrolysis time of each run ranged between 30 and 120 minutes. The respective effects of mixing speed (from 100 to 400 rpm), current, and initial pH (pH$_i$) were investigated. Experiments were done at room temperature under atmospheric pressure.

Analytical tools can be summarized as follows. The conductivity and the pH of the solution were recorded online. The concentration of soluble CBZ at time t (C_t) was obtained using a sampling procedure, followed by HPLC analysis (*Waters 2410*, UV, France) under isocratic mode using a C18 column (*Waters SAS*, Symmetry, France). The mobile phase consisted of a solution of acetonitrile (*Sigma-Aldrich*, France) and ultra-pure water at 30:70 (v/v). The flow rate was 0.5 mL.min^{-1}, leading to a retention time of 20 min for CBZ when detected at a wavelength of 230 nm. Total organic carbon in

the liquid phase was measured using a total organic carbon analyzer (*TOC-V CSN, Shimadzu,* Japan). At the end of EC experiment, the flocs recovered by decantation or flotation were filtered, washed, and dried at 105°C overnight before being weighted. BET surface area of the flocs was then estimated using nitrogen adsorption (*Tristar II, Micromeritics Instr.*, USA). To detect the presence of adsorbed species on the dried solid, the solid phase was dissolved using a 0.1 N HCl solution and, then, subjected to chemical analysis using the total organic carbon analyzer and the HPLC described above. Fig. 1 summarizes the experimental setup coupled with analytical tools.

3. Results and discussion

3.1. Influence of mixing and initial pH using Al electrodes

Preliminary results were devoted to the analysis of the influence of mixing conditions. The rotation speed of the Rushton turbine was varied between 100 and 400 rpm and its potential influence on CBZ removal was investigated. Results showed that this parameter had a limited effect in the studied range on the CBZ removal.

This means that regardless of the mechanism of depollution (oxidoreduction at the electrodes or adsorption onto the flocs), there is no apparent limitation due to mass transfer in the EC process which is in accordance with other EC studies done on wastewater containing nitrate (Yehya et al., 2014) or for the removal of trivalent chromium (Golder, 2006).

This is of utmost importance because both oxidoreduction and adsorption may be controlled by mass transfer. For this work, a rotation speed of 100 rpm has been finally retained for the Rushton turbine: this presents not only the advantage to prevent swirl, but also reduces the power input for mixing purpose.

Unlike the effect of the stirring rate which can be easily overcome, pH is always the key parameter affecting the elimination of pollutants by EC both in terms of effectiveness and operating cost (Chafi et al., 2011). In a batch cell, pH varies with time and only the initial pH, pH$_i$, can be controlled. Accordingly, experimental data highlighted a strong influence of pH$_i$ on the abatement of CBZ over time during EC.
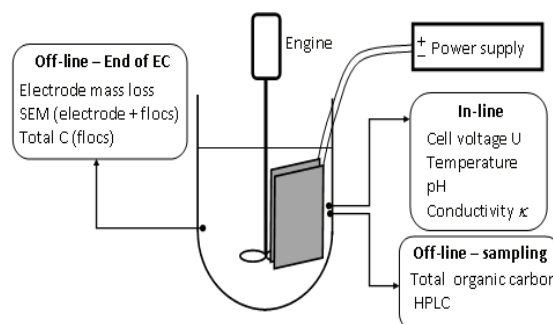

Fig. 1. Experimental setup

Concerning CBZ, it is known to have two pKa values of 13.9 and -0.49; this means that it is out of our pH range (4 to 9), and that it would be always chemically stable. However, the results obtained have shown a different behavior than expected. Fig. 2 highlighted a poor removal yield of CBZ when pH_i was 6 or 9, with values lower than 10% after 120 min of electrolysis, with a slightly higher yield when pH_i was 6. Conversely, CBZ was shown to be removed more efficiently when pH_i corresponded to acidic pH values, *i.e.* when pH_i was 4. Under these conditions the eliminated CBZ amount was up to 62%.
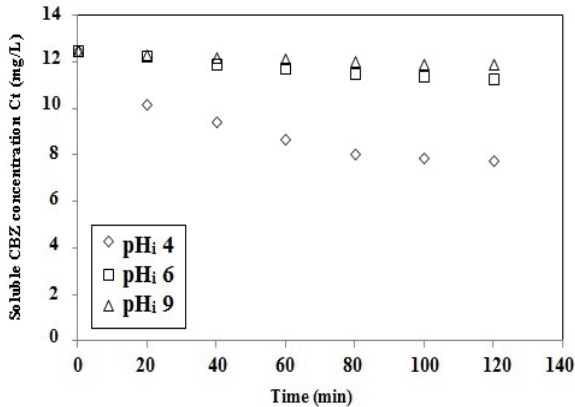

Fig. 2. Effect of initial pH during EC on the abatement of CBZ over time at *I*=3A

As pH increases during the EC process, the elimination rate of CBZ decreases, this means that CBZ removal mainly occurs when pH is between 4 and 6. This is clearly confirmed by Fig. 3: a sharp decrease of CBZ content is observed within the first five minutes, when pH varies rapidly from 4 to 6. Then, CBZ concentration passes through a plateau region when pH varies from 6 to 8.6, and then decreases again, but far slower when pH is equal or higher than 9.
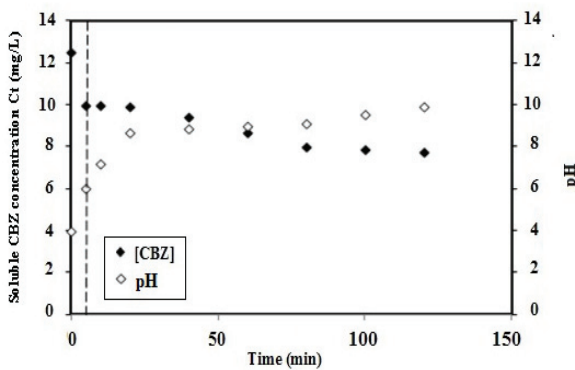

Fig. 3. Effect of the change of pH during EC on the abatement of CBZ at *I*=3A and pH_i 4, as a function of time

Similar changes of pH can be observed at different current values, as shown in Fig. 4 at *I*=4.5A. This figure also shows that final pH values are close, regardless of pH_i after 120 min, which means that final pH cannot be correlated to CBZ removal yield. Moreover, it was observed that, initial pH also

affected the amount of flocs formed at the end of EC. This varied from 7.3, 9.8 and 6.1 g in the conditions of Fig. 4 when the initial pH increased from 4, 6 and 9 after 120 min of electrolysis, respectively.
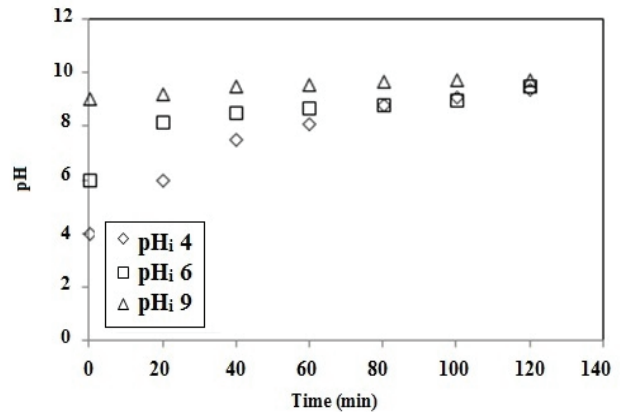

Fig. 4. Effect of initial pH on the change of pH over time during EC at *I*=4.5A

These results agree with the speciation of aluminium: soluble Al^{3+} cations dominate at low pH, soluble aluminate anions $Al(OH)_4^-$ prevail at a pH higher than 10 and the insoluble $Al(OH)_3$ hydroxides reign at intermediate pH. As a result, initial pH equal to 6 maximizes the mass of flocs because their formation is impaired only at the end of EC, while it is reduced at the beginning and the end when pH_i is 4 and during a large part of the electrolysis time when pH_i is 9. However, as for the final pH, no correlation could be found between the mass of flocs and CBZ removal yield.

This indicates that adsorption is unlikely to be the mechanism governing the CBZ elimination. On the contrary, HPLC highlighted the presence of a metabolite that was detected at the same wavelength as CBZ, but with a far smaller retention time (3 min). As there was no other organic compound in the synthetic water, this could only derive from CBZ. In addition, the increase in concentration of this new compound was always observed in parallel with a decrease of the CBZ concentration. As a result, its content was maximized at the end of electrolysis and was observed mainly when pH_i was 4.

A typical evolution of the metabolite production with time can be seen in Fig. 5 in which the areas of the detected peaks are compared because this compound has not been identified yet. This confirms the idea that an oxidoreduction mechanism at the electrode surface is responsible for CBZ removal.

3.2. Influence of current

The new set of experimental runs was dedicated to the study of the influence of the current intensity *I* on CBZ elimination using EC with Al electrodes. The results showed that an increase of current results in an acceleration of the CBZ removal at all pH_i values (Fig. 6) in particularly at pH_i 4 (Fig.

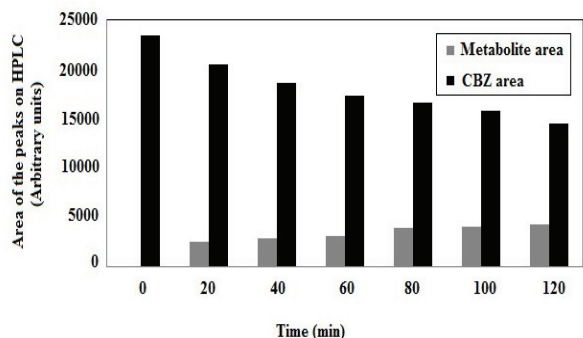6a). It was shown that the elimination was rapid at early times during EC and slowed down during the EC process.

Fig. 5. Bar graph showing the peak area of a CBZ metabolite and of CBZ detected by HPLC during EC at pH_i 4 and I=4.5A as a function of time

The reason is the elevation of pH and the consequent decrease in the probable oxidoreduction rate of CBZ. Current was also found to have an effect on the amount of Al^{3+} released and hence on the amount of flocs formed. Results obtained from the HPLC analysis showed the effect of the current intensity on the metabolite concentration that increased with the increase of current and with the decrease of CBZ concentration. It was also found that the pH change rate depended strongly on the current applied to the EC unit.

The highest current employed, led to the fastest rate of pH change during EC (Fig. 7) for all values of initial pH. The reason is the elevation of pH and the consequent decrease in the probable oxidoreduction rate of CBZ. Current was also found to have an effect on the amount of Al^{3+} released and hence on the amount of flocs formed.

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3.3. Speciation of the liquid and the solid phases

The analyses of the liquid sample at t=120 min during EC at I=4.5A and pH 4 on the HPLC found that almost 62% of CBZ has disappeared. The HPLC analysis showed that the disappearance of CBZ, was accompanied by the appearance of a new molecule that would possibly be a metabolite of CBZ having it appearing at the same wavelength of CBZ. If there was no adsorption on the solid phase or no gas release, 100% of the initial carbon should be found in the liquid samples when tested on the total organic carbon analyzer at nearly all times.
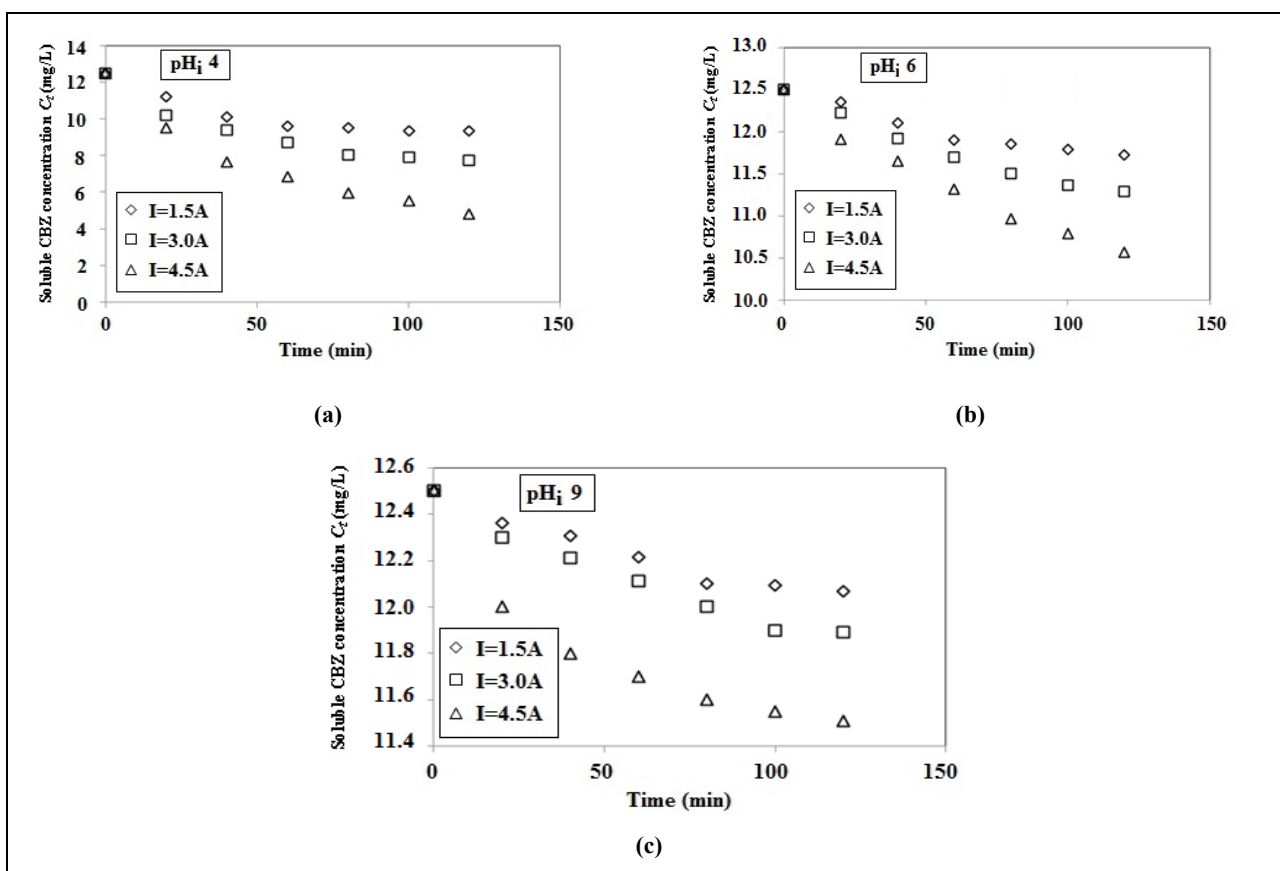

(a)

(b)

(c)

Fig. 6. Effect of current intensity on CBZ elimination: (a) at pH_i 4, (b) at pH_i 6, (c) at pH_i 9
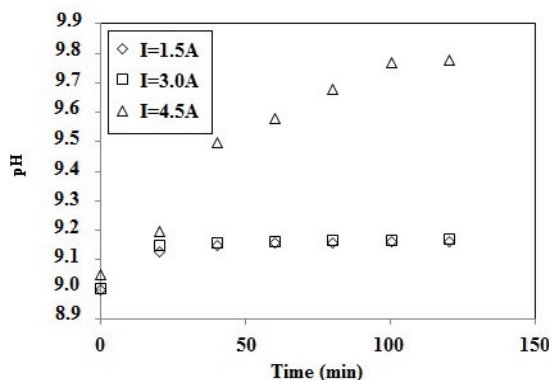
Fig. 7. Effect of current on the change of pH with pH_i 9

However, the amount of carbon found in the liquid samples when tested on the total organic carbon analyzer was about 79-82% of the initial amount of carbon found in CBZ particularly after t=20 min where the corresponding pH is around 7. So, this means that the rest (around 21%) was either been adsorbed on the solids throughout the experiment or released as CO_2. Analysis of the solid phase by nitrogen adsorption isotherm showed that it exhibited a high specific surface area as the BET method provided values that varied between 200 and 320 m^2g^{-1} floc as a function of current.

The dissolution of the flocs of EC with 0.1M HCl showed, by the analysis done on the total organic carbon analyzer, the presence of carbon entities on the solid phase that increase with the increase of current and the decrease of pH_i. The amount of these carbon entities comprises almost 20% of the total amount of carbon found as the form of CBZ at the beginning of EC.

The same samples were passed on the HPLC to test for the adsorbed species and revealed that the metabolite was found on the flocs with no minimal presence of CBZ. The inability of CBZ to adsorb on the flocs was confirmed at all the pH used in this study: the same solid phase was produced with the same composition, however, with no CBZ being added. Then, the solids were added to CBZ solutions of different concentrations. The solids were set in contact with CBZ for 24 hrs to attain equilibrium in order to test for adsorption. Analyzing the solutions on the total carbon analyzer showed no decrease of the CBZ concentration, hence no CBZ adsorption on the solid phase.

The total amount of carbon (on the solid phase and in the solution) depending on what is obtained from the total organic carbon is almost 98%, accounting for experimental error, from which we can conclude that there was no release of gaseous CO_2, or no formation of HCO_3^- or CO_3^{2-} anions in water.

Thus, we conclude that the elimination of CBZ by EC at I=4.5A and pH_i 4 is primarily an oxidoreduction mechanism comprising the change of 62% of initial CBZ concentration into a metabolite which in turn adsorbs onto the flocs at a relatively neutral pH comprising 20% of the initial carbon amount found in CBZ.

4. Conclusions

The electrochemical treatment of a biorefractory pharmaceutical molecule, CBZ, has been tested in this work using EC process. Collected data demonstrate that the CBZ is apt to electrochemical oxidoreduction reactions. CBZ was found to be eliminated mostly at pH 4 and at the highest current density of 44 mA cm^{-2} (4.5A) on Al electrodes.

The CBZ was shown to exhibit the highest elimination at pH between 4 and 6. The solid phase was found to capture a new molecule, a probable metabolite of CBZ comprising 20% of its initial carbon content. The increase of the concentration of the soluble and the adsorbed metabolite is in harmony with the decrease of CBZ. Compared to other biological and physicochemical treatments, EC was proven to be more effective in the treatment of CBZ from water than many other conventional techniques. Moreover, by optimizing the parameters of EC, this latter can be used rather than the expensive AOP treatments.

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