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The Electro-Fenton Process for Caffeine Removal from Water and Granular Activated Carbon Regeneration

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Abstract: The electro-Fenton process (EF) has faced major challenges, including mass transfer limitations. When the targeted pollutants are present in water at very low concentrations, the degradation kinetics are slower than desired, which leads to high energy consumption. To overcome this drawback, coupled adsorption on activated carbon (AC) and the EF process can be performed. Therefore, the compounds can be preconcentrated on AC before elimination by the EF process. As such, in this study, batch experiments were conducted using low-cost granular activated carbon (GAC) packed in a stainless-steel mesh for the adsorption of caffeine. Once saturated, GAC is used as a cathode during the EF process, where the adsorption capacity is regenerated. This approach allows the regeneration of the AC for multiple cycles and the degradation of the desorbed compounds. The EF process was studied to this end, for the purposes of the removal of caffeine as a model compound. The main goals of this work are (i) to study the removal of caffeine from water in three different matrices and (ii) to regenerate GAC by using the EF process. The results reported in this study show that it is possible to achieve caffeine degradation up to 95%, 100%, and 100%, and a mineralization up to 70%, 72%, and 76% in pure water, simulated wastewater, and wastewater effluent, respectively. In the regeneration process, total elimination of the desorbed caffeine was achieved, and a regeneration efficiency of 50% was obtained for the first cycle. The results confirm the ability of the EF process to achieve regeneration of AC loaded with caffeine.

Keywords: electro-Fenton; regeneration; granular activated carbon; caffeine; micropollutants

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1. Introduction

Adsorption on GAC is a widely used method for pollutant removal from water. Due to its highly porous structure and the presence of functionalized surface groups, GAC has a high adsorption capacity; in addition, it has a strong affinity toward a large range of components, such as organic substances and heavy metal ionseven at low concentrations [1,2]. Therefore, GAC is integrated into various water and wastewater treatment processes [3]. While it was originally produced from coal, GAC production processes currently follow a more sustainable production method by using different types of organic wastes and biomass as feedstocks, including agricultural wastes, food waste, coffee grounds, coconut shells, and many other organic carbon-rich materials [4,5]. After carbonization and chemical (or physical) activation, the specific surface area of AC can be over 1000 m^2/g [6]. Chemical activation using activation agents such as NaOH and KOH is preferred since it is performed quickly, requires moderate to low activation temperatures, and leads to a higher yield and development of porosity [6]. Nonetheless, chemical activation can be more costly than physical activation via steam due to the costs related to the activating agents [6].

Adsorption is a separation process in which the pollutants are transferred from the water to the AC surface. During this, the adsorption sites and micropores gradually

become filled; further, once the maximum adsorption capacity has been reached (called saturation), the AC can no longer retain additional pollutants from the water [7]. At this stage, sustainable management of saturated AC is needed. Currently, two main options are available for its management: (i) the disposal of the used material as waste, requiring a refill of the adsorption unit with a new adsorbent, and (ii) the regeneration of the material [6]. The replacement of GAC is costly and leads to the generation of a large amount of waste [7]. Furthermore, exhausted GAC is often landfilled, which includes a risk of releasing the adsorbed compounds from the GAC and subsequently polluting the environment again [6]. Powdered activated carbon (PAC), on the other hand, is frequently dosed in the activated sludge basin in order to achieve a combined adsorption/biodegradation process and is often incinerated together with the (dewatered) sludge due to the difficulty of separating it from the sludge [8,9].

The regeneration of GAC is a more sustainable technique since it enables the reuse of the adsorbent material, instead of disposal. Thermal regeneration is most commonly and widely applied at an industrial scale in most industrialized countries [7,10], mainly because it offers the recovery of saturated GAC and the removal of several adsorbates. However, this method presents many disadvantages, such as (i) the costs and energy consumption ($T > 1100$ K) [11]), (ii) the formation of surface oxygenated groups leading to a decrease in GAC adsorption capacity [10], and (iii) extensive GAC surface damage [10]. In addition, this method is usually performed ex situ, hence generating extra costs for transport.

Electrochemical advanced oxidation processes (eAOPs) are a promising alternative technology for the regeneration of spent GAC [6]. eAOPs rely on the electrodesorption of the adsorbates from GAC, followed by an in situ oxidation of the adsorbates in the eventuality they represent organic contaminants. This oxidation is performed by the generation of very powerful and nonselective hydroxyl radicals ($HO^{\bullet}$) [6,12]. $HO^{\bullet}$ is known to be the second most powerful oxidant after fluorine with a standard redox potential $E^{\circ}(HO^{\bullet}/H_2O) = 2.80$ V/SHE [12,13]. During the EF process, $HO^{\bullet}$ is produced by Fenton's reaction (Equation (1)). With a nonactive anode (high oxygen evolution overpotential), such as a boron-doped diamond (BDD) electrode, radicals can also be generated by water discharge at the anode surface $M(HO^{\bullet})$ (Equation (2)) [14,15]. The amount of generated $HO^{\bullet}$ at the anode surface will then depend on the applied current density [16]. Furthermore, H_2O_2 is continuously electrogenerated in situ at the cathode by a two-electron reduction in oxygen (Equation (3)), along with the regeneration of the Fe^{2+} catalyst added at the start of the process (Equation (4)). Due to the nontoxicity of its reagents and its efficiency in removing pollutants, the EF process is considered an eco-friendly process [14,17].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \quad (1)$$

$$BDD + H_2O \rightarrow BDD(HO)^{\bullet} + H^{+} + e^{-} \quad (2)$$

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

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \quad (4)$$

To perform the EF regeneration of GAC, the spent GAC is used as a cathode. The advantage of using GAC as a cathode resides in the cathodic polarization. This will protect the surface and the structure of the GAC, hence conserving the adsorption capacity of the material, even after several cycles of regeneration [18]. Moreover, GAC, being a carbonaceous material, contributes to the electrochemical generation of H_2O_2 during the EF process [18,19].

The EF process has previously been described as for the purposes of the regeneration of GAC when loaded with reactive blue dye [20] and toluene [21]. In this study, the EF process will, for the first time, be applied to regenerate GAC when loaded with the model pharmaceutical compound caffeine in three different water matrices. Caffeine can be found in many beverages, painkillers, and medicines, such as from analgesics to cold

medicines [22–24]. The presence of this compound in water is mainly due to its high solubility (21.6 g/L), and low octanol–water partition coefficient (log K_{ow} = 0.16) [22]. The concentrations of caffeine range from 20 to 300 µg/L in raw sewage; 0.1–20 µg/L in WWTP effluents; 3–1500 ng/L in rivers, lakes, and sea water; and 10–80 ng/L in groundwater [22]. Aquatic organisms are disturbed due to its toxicity and bioaccumulation [22,23]. Moreover, caffeine has a negative impact on the environment and human health [23]. Thus, it is important to develop efficient techniques capable of removing such persistent compounds and therefore preventing their entry into drinking water sources.

The first part of this study focuses on the removal of caffeine in deionized water (DW), simulated wastewater (SWW), and wastewater effluent (WWE), where the degradation and mineralization kinetics are investigated using two different cathode materials: stainless steel (SS) and carbon felt (CF). In the second part, the regeneration of GAC is carried out in the three water matrices listed above, with GAC saturated with caffeine being used as the cathode. The desorption of caffeine from GAC was monitored together with its degradation and mineralization.

2. Materials and Methods

2.1. Chemicals

Sulfuric acid (H_2SO_4, 96%), caffeine (purity, 99%), and HPLC grade acetonitrile were purchased from Sigma Aldrich (The Netherlands). Sodium sulfate (Na_2SO_4, ≥99%) was acquired from Boom Chemicals (Meppel, The Netherlands), and iron sulfate heptahydrate ($FeSO_4.7H_2O$, 99%) was acquired from Fisher Scientific (Landsmeer, The Netherlands). NORIT® GAC 612 WFD was used in all experiments.

2.2. Degradation of Caffeine in Water by Electro-Fenton

Batch experiments were performed in a cylindrical electrochemical cell. The degradation and mineralization of caffeine by the EF process in (i) DW, (ii) SWW, and (iii) WWE were studied. The active volume of the cell was 500 mL. The initial concentration of caffeine was 1 mM, which corresponds to the highest detected concentration during regeneration (Section 2.4). Na_2SO_4 (electrolyte) and Fe^{2+} (catalyst, in the form of $FeSO_4$) were added to the water at concentrations of 50 mM and 0.2 mM, respectively, after which the pH was adjusted to 3 using 37% H_2SO_4. The anode used in this study was a BDD-coated plate (2.5 cm × 5 cm × 0.1 cm). Both SS and CF (Mersen BeNeLux Schiedam, The Netherlands) were tested as cathode materials. The electrodes were placed centrally and face to face in the cell at a distance of 1.5 cm from each other. A constant current intensity of 200 mA was applied using a RIGOLE DP 711 potentiostat. The water was continuously mixed using a magnetic stir bar at 650 rpm. Air was bubbled through the cell with a flow rate of 2 NL/min throughout the EF tests.

2.3. Adsorption of Caffeine on Granular Activated Carbon

The GAC was washed at least three times with deionized water in order to remove any impurities before use and then dried at 90 °C overnight. Adsorption isotherms of caffeine were developed via equilibrium tests at room temperature (22 °C ± 1) in 250 mL glass flasks placed on an orbital flask shaker (200 rpm). The equilibrium adsorption study was conducted by varying the concentration of caffeine between 5 mg/Land 100 mg/L, as well as in keeping the volume of the solution (200 mL) and GAC dose (30 mg) constant. The flasks were shaken for 10 days before sampling. Previous adsorption tests indicated that adsorption equilibrium was reached within 7–8 days. Once equilibrium was reached, the amount of adsorbed caffeine was calculated from the mass balance (Equation (5)). A control test was performed without GAC in order to assess the photodegradation and stability of the model compound. Caffeine solutions with known concentrations (1 g/L and 200 mg/L) were left under agitation for 10 days. The observed loss of caffeine was lower than 2%:

$$q_e = \frac{(C_0 - C_e) \times V}{\mathrm{m}} \quad (5)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of caffeine, respectively, V is the volume of the solution (L) and m is the mass of GAC (g) in the flasks. The common Langmuir (Equation (6)) and Freundlich (Equation (7)) isotherm models were used:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \times b} + \frac{C_e}{q_{max}} \quad (6)$$

where q_e is the amount of caffeine per gram of GAC at equilibrium (mg/g), q_{max} is the maximum adsorption capacity (mg/g), b is the constant related to the free energy of adsorption (L/g), and C_e is the concentration of caffeine in the solution at equilibrium (mg/L). Further:

$$q_e = K_f C_e^{1/n} \quad (7)$$

where K_f is the Freundlich constant, which represents adsorption capacity, and $1/n$ is an empirical constant indicating the adsorption intensity of the system.

Adsorption experiments for the regeneration study were performed in batch mode in Erlenmeyer flasks containing 200 mL of caffeine solution at a concentration of 2 (g/L) and 2 g of GAC. The GAC was packed in an SS mesh (500 µm) with the same shape and size as the anode to better control the surface area and thickness of the electrode. The SS bag allowed the use of GAC as a cathode during EF regeneration and avoided problems related to the physical separation of GAC from the solution after adsorption. The adsorption lasted until 4 days to reach saturation under continuous stirring (250 rpm).

2.4. Electro-Fenton Regeneration of GAC

The spent GAC (saturated with caffeine-Section 2.3) fulfils the role of the cathode during the EF process where it is regenerated. The EF process is performed in an undivided electrochemical cell with the same operating parameters and configuration as described in Section 2.2 and using the SS mesh containing caffeine-loaded GAC as the cathode. The regeneration time was 6 h, during which samples were collected in order to measure the concentration of desorbed caffeine and its mineralization.

Multiple regeneration cycles were performed on the same GAC sample in order to assess the adsorption capacity and regeneration efficiency (RE) evolution. The adsorption and regeneration experiments were alternately performed using the same experimental conditions at each cycle.

A blank test was performed to assess the amount of desorbed caffeine from the GAC without applying a current. The saturated GAC was stirred in 0.2 L of DW for 2 h. Afterwards, a caffeine concentration of ~0.12 mg/L was measured, which is most likely due to the transfer of small droplets of the caffeine solution from the adsorption medium (since the GAC is not dried or rinsed before its transfer to the regeneration reactor).

The RE of GAC is calculated as follows (Equation (8)):

$$\%RE = \frac{q_{r(n)}}{qi} \times 100 \quad (8)$$

where $q_{r(n)}$ (mg/g) is the adsorption capacity of GAC after n regenerations. Further, n is the cycle number and q_i (mg/g) is the adsorption capacity of pristine GAC.

2.5. Analytical Methods

The mineralization during the EF process was assessed with total organic carbon (TOC) analysis using a Shimadzu TOC analyzer (TOC-LCSH/CSN Standalone). The adsorption, desorption, and degradation of caffeine were assessed utilizing reverse-phase high-performance liquid chromatography (RP-HPLC). For this purpose, an Agilent

1260 Infinity II prime online LC system (Agilent Technologies, Waldbronn, Germany) equipped with a binary pump, an autosampler, a multicolumn thermostat, and diode-array detection (DAD) was used. The selected column for the separation was a Zorbax SB-C18 (2.1 mm × 30 mm × 1.8 µm; Agilent, Santa Clara, CA, USA) kept at a temperature of 80 °C. The instrument was run with a mobile phase composed of 0.1% formic acid in water (A) and 0.1% formic acid in acetonitrile (B). The elution method consisted of a gradient wherein the % B was increased from 5% to 95% for 1 min and then returned to the initial conditions. The analyses were carried out at a flow rate of 1.5 mL.min^{-1} and an injection volume of 1 µL. The DAD wavelength was set to 271 nm.

3. Results

3.1. Effect of the Water Matrix and Cathode Material on Degradation and Mineralization

The degradation and mineralization were assessed during the EF process. The results revealed that after 6 h of the EF process, similar removal efficiencies of 91% and 95% were obtained in DW for the SS and CF cathodes, respectively, while 100% removal was achieved in WWE using either SS or CF cathodes (Figure 1a). However, the degradation rates were faster when the CF cathode was used (Table 1). This can be explained by the ability of the CF material to produce H_2O_2 in bulk. In fact, during the EF process, the cathode material plays an important role, since the amount of HO$^{\bullet}$ that is formed by the Fenton reaction (Equation (1)) is dependent on the amount of H_2O_2 produced at the cathode surface (Equation (3)) [25]. In addition, CF has a high specific area for the regeneration of the Fe^{2+} catalyst during the EF process [26]. It was found that the SS's ability to produce H_2O_2 during the EF process is poor [25], which leads to the conclusion that during the experiments that were carried out with an SS cathode, degradation and mineralization occur at the anode surface via direct oxidation by the formed BDD(HO$^{\bullet}$) (Equation (2)). Furthermore, faster degradation kinetics were observed in the WWE than in the SWW and PW matrices. Approximately two times faster degradation was obtained in the WWE than in DW with a rate of 13.6 × 10^{-3} (min^{-1}) and 7.8 ×10^{-3} (min^{-1}), respectively. This may be explained by the presence of transition metal ions in the WWE, such as Cu^{2+}, in addition to the initially added Fe^{2+} catalyst. These metal ions exhibit catalytic behavior [6], further leading to a higher generation of HO$^{\bullet}$. Normally, the degradation rates in DW are higher than those in real effluent or other complex matrices [27]. The absence of organic compounds other than the targeted compounds in DW excludes oxidation competition. In this study, contrary to what is usually observed, similar removal efficiencies are achieved in the three matrices. This finding can be explained by the fact that all matrices used in this study were spiked with 1 mM caffeine. This concentration is much higher than those of the competing substances present in the WWE and SWW (ng/L to µg/L) [28]; thus, competitive oxidation is negligible. Nevertheless, competition may occur when caffeine is present at a lower concentration. A similar trend was observed by Minerva et al. [29] for the degradation of a mixture of diclofenac, ibuprofen, and naproxen via the EF process. Indeed, TOC removals of 92% and 90% were achieved in DW and WWE, respectively. However, when heterogeneous photocatalysis was applied in WWE for the removal of the anti-inflammatory drug mixture, lower TOC removal was observed. This result led to the conclusion that the effect of the water matrix depends on the type of treatment applied [29].

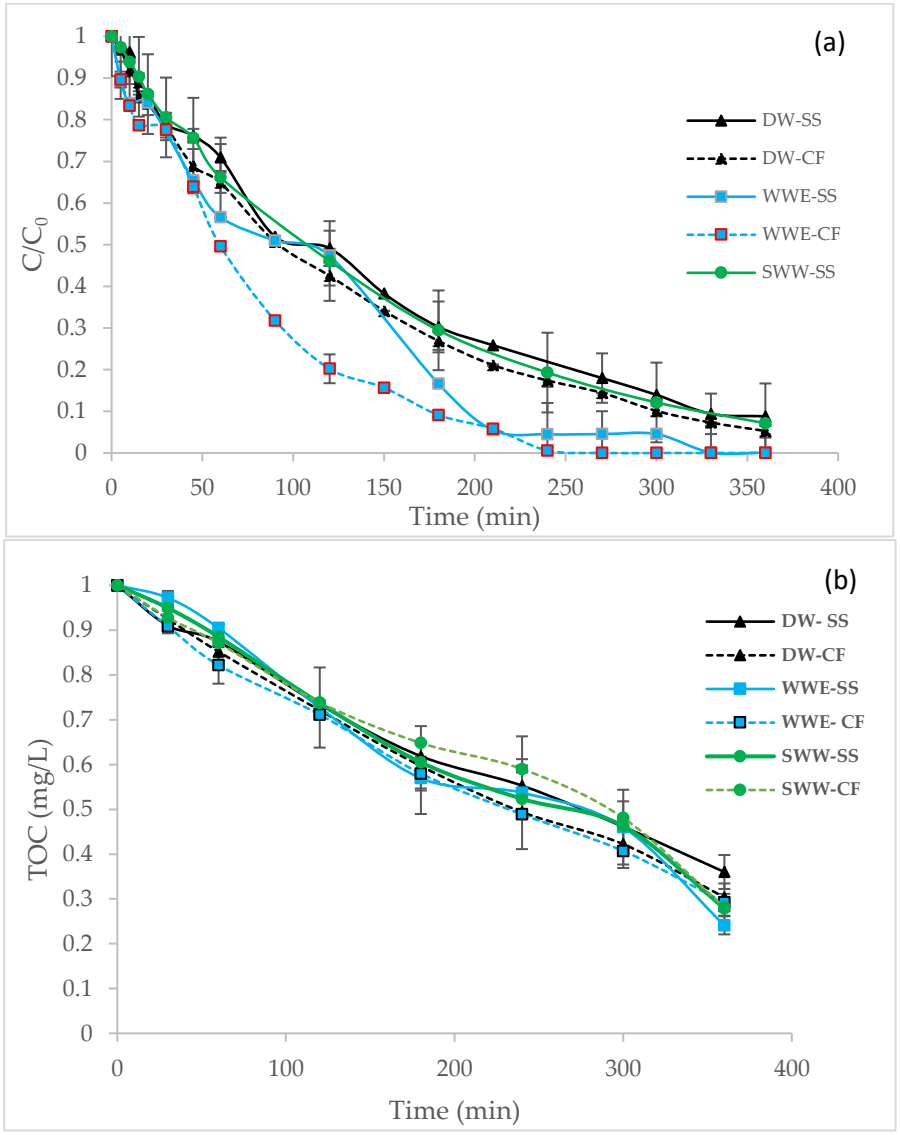


Figure 1. Evolution of the caffeine concentration (**a**) and total organic carbon (**b**) in the solution during the electro-Fenton treatment in deionized water (DW), wastewater effluent (WWE), and simulated wastewater (SWW) using stainless steel (SS) and carbon Felt (CF) cathodes. Used with a Boron-doped diamond (BDD) anode and an initial concentration of caffeine C_0 = 0.1 mM, I = 200 mA, V = 0.5 L, pH = 3, Na_2SO_4 = 50 mM, and Fe^{2+} = 0.20 mM.

Table 1. Degradation and mineralization kinetics parameters and efficiencies in, in deionized water (DW), wastewater effluent (WWE), and simulated wastewater (SWW) respectively using stainless steel (SS) and carbon felt (CF) cathodes. K_1 and K_0 are the first-order and zero order constants respectively.

		DW-SS	DW-CF	WWE-SS	WWE-CF	SWW-SS	SWW-CF
Degradation	K_1 (min^{-1})	6.7×10^{-3}	7.8×10^{-3}	10.1×10^{-3}	13.6×10^{-3}	7.1×10^{-3}	-
	R^2	0.996	0.995	0.990	0.990	0.998	-
	Removal %	91	95	100	100	93	-
Mineralization	K_0 (mg/L.min)	1.7×10^{-3}	1.9×10^{-3}	2.0×10^{-3}	1.9×10^{-3}	1.9×10^{-3}	1.7×10^{-3}
	R^2	0.990	0.995	0.975	0.990	0.988	0.990
	Mineralization %	64	70	72	76	71	-

In this study, regardless of the cathode material and matrix used, similar mineralization efficiencies in the range of 64% to 76% were obtained. Kinetics rates of 1.7×10^{-3} to 2.0×10^{-3} were observed in the different experiments (Figure 1b) following the order WWE-CF> WWE-SS>DW-CF>SWW-SS>DW-SS. The mineralization rates can be enhanced by increasing the current intensity or the concentration of oxygen in bulk. The current intensity can affect both the cathodic production of H_2O_2 and the generation of M($HO^{\bullet}$) at the BDD–water interface [24,30]. It was shown that an increase in the current intensity promotes the generation of $HO^{\bullet}$ through the reaction (Equations (1)–(4)) and consequently enhances the caffeine mineralization rate [24]. Nevertheless, a current intensity that is too high could also trigger side reactions that will inhibit the compound's removal ((Equations (9)–(13)). The electrogeneration of H_2O_2 is also dependent on the amount of dissolved oxygen and the mass transfer of the latter to the cathode surface [31,32]. Hence, the higher the concentration of O_2 in the water is, the better the electrogeneration of H_2O_2 [31].

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \quad (9)$$

$$2\ BDD(HO)^{\bullet} \rightarrow 2\ BDD + H_2O_2 \quad (10)$$

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO^{\bullet}{}_2 \quad (11)$$

$$HO^{\bullet}{}_2 + HO^{\bullet} \rightarrow H_2O + O_2 \quad (12)$$

This study, as well as studies by Ganzenko et al., show the ability of EF processes to remove caffeine from many water matrices. Ganzenko et al. used parameters and a system similar to those in the current study [24]. Although similar removal efficiencies were obtained, Ganzenko et al. obtained higher removal rates of caffeine [24] (Table 2). This difference can be due to the difference in initial concentration and treated volume, which were 10 times and twice as high, respectively, as in the current study. In fact, in addition to the amount of treated water, the initial concentration of the targeted compound affects the removal rates [27]. On the other hand, the removal rate obtained in the matrix containing 13 other compounds [33] was more than 10 times lower than in this study. These results indicate that competitive oxidation has occurred and that $HO^{\bullet}$ react with caffeine and all the other pharmaceuticals present in the matrix [33].

Table 2. Electro-Fenton removal of caffeine in pure water and complex matrices.

Electrodes Process Matrix	Experimental Parameters	C_0	Removal %	Removal Rate	Reference
BDD anode/ CF cathode EF PW	Fe^{2+} = 0.2 mM; Na_2SO_4 = 0.05 M V = 0.2 L pH = 3; I = 300 mA	0.1 mM	93	2.48×10^{-9} M^{-1} S^{-1}	[24]
BDD anode CF cathode EF Mixture of pharmaceuticals	Fe^{2+} = 0.2 mM; Na_2SO_4 = 0.05 M V = 0.2 L pH = 3; I = 400 mA	0.1 mM	-	1.47×10^{-10} M^{-1} S^{-1} *	[33]

* Value calculated based on the data in [33].

3.2. Adsorption of Caffeine on Granular Activated Carbon

The results for the adsorption of caffeine on GAC fit the Langmuir model, and the parameters are shown in Table 3. The Langmuir model indicates that the surface of GAC is energetically homogeneous. Hence, the coverage of the GAC surface is completed on a monolayer with no interaction between the caffeine molecules [34]. Furthermore, a study revealed that the adsorption of caffeine on activated carbon is mainly governed by

non-electrostatic interactions involving hydrogen bonding [34]. The maximum adsorption capacity obtained in this study is q_{max} = 227.27 mg/g. This value is comparable to the q_{max} obtained by Trellu et al. [35] for the adsorption of clofibric acid, which has a molecular weight close to caffeine, on AC fibers. This result affirms that the adsorption capacity of GAC for caffeine is in the high range of values reported in the literature, due to its high specific surface area and micro/mesopore volumes [35,36].

Table 3. Langmuir parameters were obtained from adsorption isotherms for the adsorption of caffeine on GAC at 20 ± 1 °C. These experiments were performed in triplicate.

Langmuir			**Freundlich**		
b (L/mg)	q_{max} (mg/g)	R^2	K_f	R^2	n
14.667	227.273	0.991	0.378	0.385	1.694

3.3. Caffeine Removal from GAC and Mineralization of Organics during EF Regeneration

After the adsorption step, the saturated GAC contained 220 mg of caffeine per 1 g of GAC (experimental q_{max}). This theoretically would correspond to a total concentration in the bulk of 880 mg/L (Equation (13)) and 434 mg/L (Equation (14)) of caffeine and TOC, respectively, if total desorption of the previously loaded caffeine is achieved:

$$[Caffeine] = \frac{m_{\mathrm{GAC}}}{V} \times q_{max(exp)} \quad (13)$$

where [*Caffeine*] is the concentration of caffeine in mg/L, mGAC is the mass of GAC in g, V is the volume of the bulk in L (0.5 L), and $q_{max(exp)}$ is the experimental maximum adsorption capacity of GAC. Further:

$$[TOC] = \%\, C \times [Caffeine] \quad (14)$$

where [*TOC*] is the total organic carbon concentration (mg/L) and % *C* is the carbon weight fraction in a caffeine molecule.

However, lower amounts were observed during the regeneration process. This was due to the incomplete regeneration of GAC in addition to the degradation and mineralization of the adsorbate by the in situ generated oxidants during the EF process occurring simultaneously with the desorption process [37]. An increase in TOC and caffeine concentrations was observed during the first hours of the treatment (Figure 2). This was due to the desorption of caffeine from GAC and the formation of degradation products. After that, a TOC decrease, and almost total elimination of caffeine were observed in both DW and SWW. This indicates that at the beginning of regeneration, the desorption process is more favorable due to the sorption equilibrium and the electrostatic repulsions of the adsorbate from the GAC surface. Afterward, the desorption kinetics decrease, and oxidation dominates. Furthermore, the caffeine concentrations observed during the first cycle were lower than those observed in the second cycle (Figure 2a). This could be explained by a change in the porosity of the GAC. After the first regeneration cycles, some micropores could have been changed into mesopores during the EF process, thus facilitating the desorption of caffeine from the adsorption sites [6]. Desorption is completed more easily from the mesopore surface than from a micropore surface due to the high mass transfer resistance in the latter [6,36]. Moreover, the regeneration efficiency is extremely dependent on desorption [37]; further, it is crucial to optimize the latter phenomenon as well as the degradation of the desorbed compounds. The removal of the desorbed compounds in bulk can affect the adsorptive equilibria between the solution and the adsorbate and shift it to promote desorption [34,35].

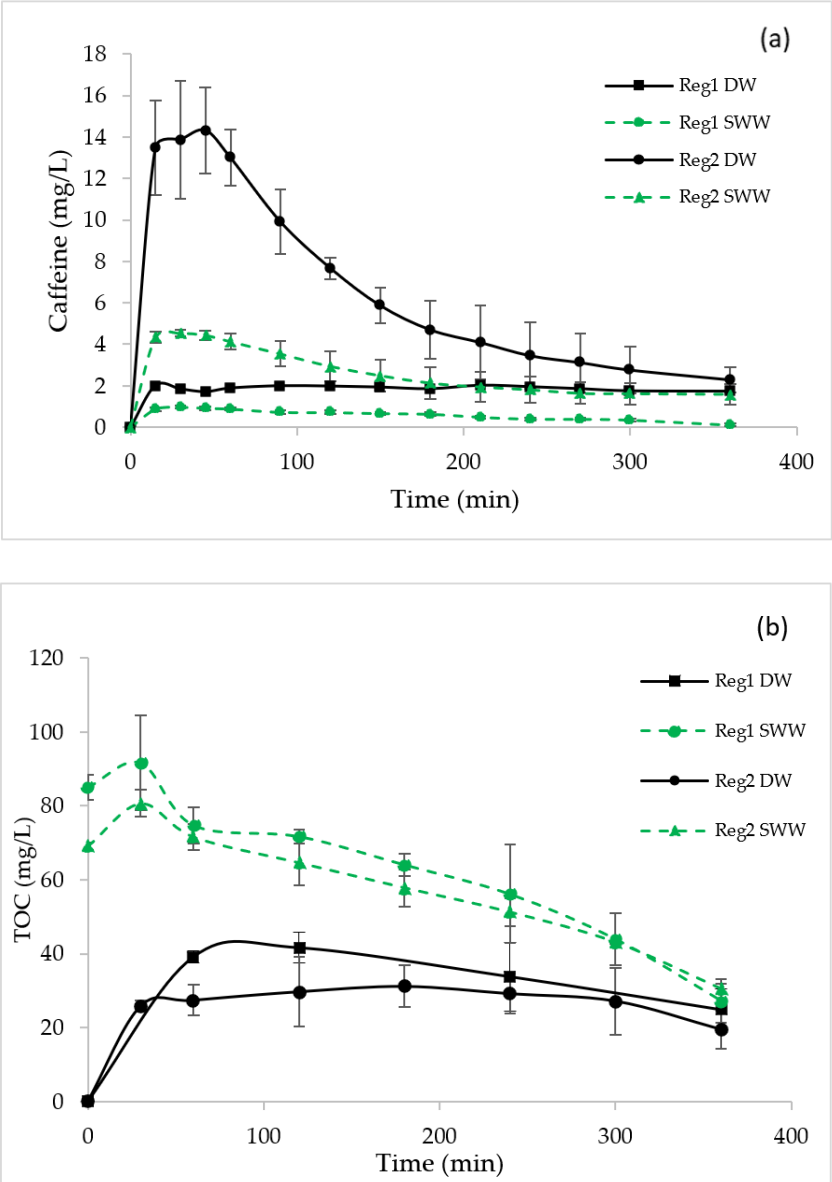


Figure 2. Evolution of the caffeine concentration (**a**) and total organic carbon (**b**) in the solution during the first cycle (Reg 1) and second cycle (Reg 2) of regeneration in deionized water (DW) and simulated wastewater (SWW). This was achieved using the saturated GAC in stainless steel mesh bag as cathode, with a boron-doped diamond (BDD) anode, at pH = 3, I = 200 mA, V = 0.5 L, Na_2SO_4 = 50 mM, and Fe^{2+} = 0.20 mM.

3.4. Regeneration Cycles

A similar TOC evolution is observed in all the experiments in Figure 3a, while the adsorption capacity and RE decrease is shown in Figure 3b. The first regeneration led to a 50% RE, suggesting that the GAC was partially regenerated. The efficiency dropped to 25% in the second cycle (Figure 3), which may be due to the remaining caffeine on the GAC surface [2]. During the third cycle the RE remained stable (25%), and, finally, in the fourth cycle a decrease was observed. The incomplete regeneration of GAC could be due to the blockage of the carbon adsorption sites by other compounds, such as the formed degradation molecules. Furthermore, better regeneration rates could be obtained with a longer regeneration time, higher current intensity, or higher pH [37]. In fact, by increasing the pH, the solubility of organic compounds increases, which promotes desorption from

GAC to water [37]. This aligns with the results observed by Couto, where caffeine removal from water by adsorption on AC was lower at high pH [34].

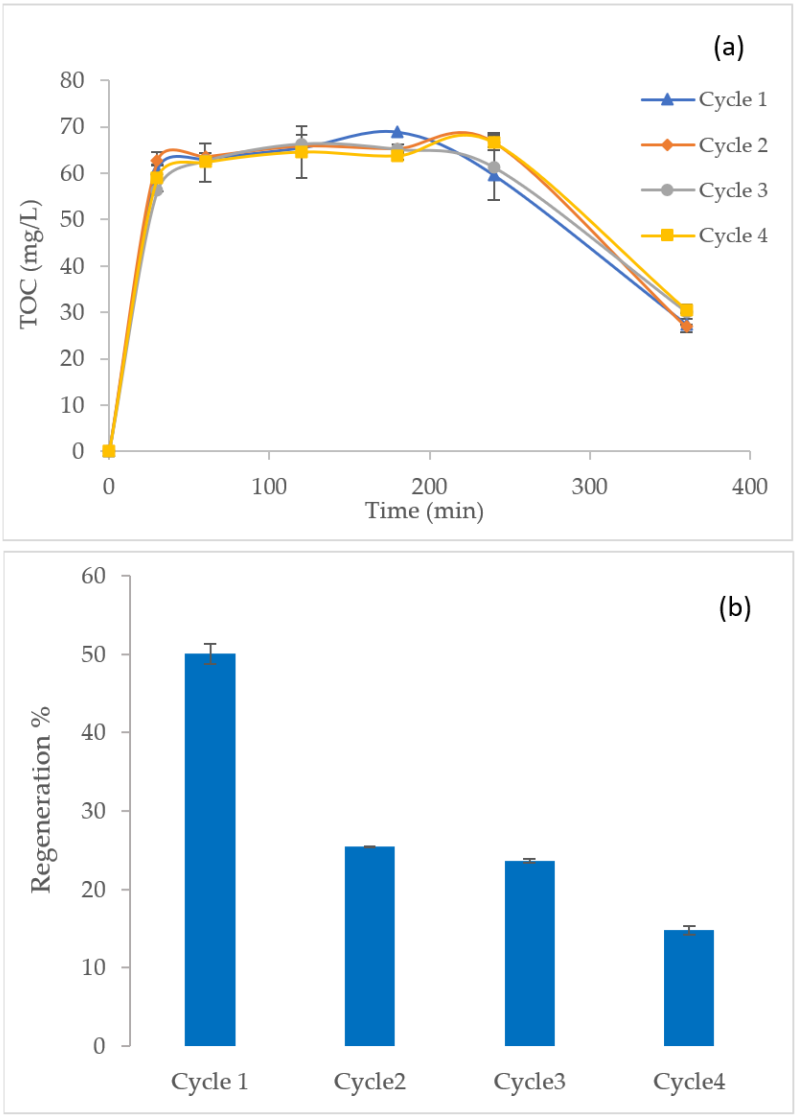


Figure 3. Evolution of (**a**) total organic carbon (TOC) during the regeneration (**b**) regeneration efficiency in pure water (PW) using caffeine saturated GAC in stainless steel mesh bag as cathode, with boron doped diamond (BDD) anode, at pH = 3, I= 200 mA, and V = 0.5 L, Na_2SO_4 = 50 mM, and Fe^{2+} = 0.20 mM.

4. Conclusions

This study showed that caffeine can be removed effectively from water through the EF process. Total caffeine removal and an average mineralization of 73% were achieved in three different water matrices (DW, SWW, and WWE). The highest degradation and mineralization rates of 100% and 73% were obtained with the CF cathode in WWE, respectively.

This work also demonstrated that the electrochemical regeneration of caffeine-loaded GAC via the EF process is feasible. When saturated GAC was used as a cathode, a regeneration efficiency of 50% was obtained after 6 h of EF treatment. A decrease in efficiency during the second cycle was observed, and this behavior was assumed to be due to the short regeneration time or a change in the surface structure of the GAC. Further study of the mechanism of regeneration and the optimization of this process is necessary in order to achieve higher efficiency and durability after several cycles. The combined process of adsorption on AC and the EF process is a technology of interest as it makes it possible to

regenerate the adsorbent material, as well as the degradation and mineralization of the initially adsorbed compounds. Here, 83% degradation and 64% caffeine mineralization were achieved during regeneration. Therefore, the technology described above can overcome the mass transfer limitation of eAOPs, when applied to very dilute compounds by preconcentrating the pollutants on the GAC. In addition, the efficient removal of the desorbed and formed compounds during the EF process brings another advantage compared to the conventional treatment, where the pollutants are only desorbed, which is the case in thermal treatment under nonoxidizing conditions. The results of the current study indicate that the EF process combined with adsorption on AC is a promising tertiary treatment alternative for the removal of micropollutants.

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Abbreviations

GAC	Granular activated carbon
AC	Activated carbon
CF	Carbon felt
PAC	Powder activated carbon
eAOPs	Electrochemical advanced oxidation processes
$HO^{\bullet}$	Hydroxyl radicals
EF	Electro-Fenton
BDD	Boron-doped diamond
RE	Regeneration efficiency
DW	Deionized water
SWW	Simulated wastewater
WWE	Wastewater effluent
SS	Stainless steel
RP-HPLC	Reverse-phase high-performance liquid chromatography

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