Environmental Technology & Innovation 26 (2022) 102365

Contents lists available at ScienceDirect

Environmental Technology & Innovation

journal homepage: www.elsevier.com/locate/eti

Degradation of ampicillin by combined process: Adsorption and Fenton reaction

Cassandra Bonfante de Carvalho *, Ivan Reis Rosa, Paola Del Vecchio, Ivone Vanessa Jurado Dávila, Keila Guerra Pacheco Nunes, Nilson Romeu Marcilio, Liliana Amaral Féris

Laboratory of Separation and Unit Operations, Chemical Engineering Department, Federal University of Rio Grande do Sul, Porto Alegre, Rio Grande do Sul 90035-007, Brazil

ARTICLE INFO

Article history:
Received 28 March 2021
Received in revised form 14 January 2022
Accepted 23 January 2022
Available online 31 January 2022

Keywords:
Ampicillin
Mineralization
Fenton
Adsorption
Regeneration
Activated carbon

ABSTRACT

When disposed incorrectly, antibiotics can cause complex effects on environmental matrices, such as bacterial resistance. In this context, the present work investigated the degradation and mineralization of the β-lactam antibiotic ampicillin (AMP) applying a combined treatment of Fenton reaction and adsorption onto granular activated carbon (GAC). Adsorption parameters of contact time (10–210 min) and GAC dosage (5–50 g L^{-1}) were evaluated, as well as adsorption kinetics. Both in Fenton reaction and combined process, the influence of H_2O_2 and Fe^{+2} concentrations were evaluated, using five combinations of H_2O_2/Fe^{+2}: 300/60 µM, 300/80 µM, 400/70 µM, 500/60 µM and 500/80 µM. Finally, because of the combined process, GAC regeneration was investigated in 3 cycles. Best adsorption conditions were determined as 150 minutes of contact time and GAC concentration of 20 g L^{-1}, reaching 57% of AMP removal and adsorbed amount of 0.58 mg g^{-1}. All Fenton experimental conditions led to a complete degradation of AMP within 1 min, suggesting the generation rate of hydroxyl radicals was faster in the first minutes of reaction. In the combined process, similar results for degradation were found. A higher mineralization (83%) and GAC regeneration (85%) was reached at $H_2O_2/Fe^{+2} = 500/80$ µM, indicating the influence of H_2O_2 and Fe^{+2} concentrations. GAC regeneration efficiency for the 3 cycles were, respectively, 84%, 71% and 49%. Thus, the results demonstrate the combined process of Fenton reaction and GAC adsorption is a feasible treatment reaching high mineralization.

1. Introduction

Different wastewater treatment technologies are investigated in order to remove pharmaceutical compounds from water (Verlicchi et al., 2015). Hospital wastewater treatment requires special attention due to its concentrated amounts of these contaminants, while disposal legislation is not standardized worldwide (Batt et al., 2017; Daouk et al., 2015; Mattrey et al., 2017). Although the consequences of incorrect disposal not being fully known, the effects of pharmaceutical compounds in the environment are already recognized as toxic (Orias and Perrodin, 2013; Verlicchi et al., 2012) once they affect aquatic life (Bu et al., 2016; Cardoso et al., 2014; Mezzelani et al., 2018) and human health (Azuma et al., 2018; Bottoni and Caroli, 2018). In the case of antibiotics, a serious consequence is bacterial resistance (Barraud et al., 2013;

* Corresponding author.
E-mail address: cassandra.bcarvalho@gmail.com (C.B. de Carvalho).

https://doi.org/10.1016/j.eti.2022.102365
2352-1864/

Bengtsson-Palme et al., 2019; Haller et al., 2018). On its turn, ampicillin (AMP), a broad-spectrum β-lactam antibiotic is one of the most consumed and detected drugs reported in literature (Souza and Féris, 2017).

Advanced wastewater treatments, based on removal of degradation of pollutants, have been studied and applied to manage complex and recalcitrant substances. In order to achieve higher efficiencies, it is possible to combine different techniques (Asaithambi et al., 2017; Li and Yeung, 2018; Wang et al., 2018; Zeng et al., 2013; Zhao et al., 2018).

Adsorption is a treatment based on the retention of pollutants on the surface of an adsorbent solid, removing it from the aqueous phase. Although the literature reports high removal percentages of antibiotics (de Franco et al., 2017; Gu et al., 2021; Habibi et al., 2018), the process depends on specific conditions, such as adsorbent properties, pH and temperature, that may limit its performance. Choosing which adsorbent solid to use is, therefore, an important step. Granular activated carbon (GAC) is a non-specific adsorbent that is capable of removing a wide variety of contaminants, including drugs (Chowdhury et al., 2020; Wei et al., 2018; Yu et al., 2016). To optimaze the adsorbent potential, solid regeneration is very interesting under the environmental and economic spectrum and should be considered in the process (McQuillan et al., 2018; Rosales et al., 2018; Zhang et al., 2017).

On the other hand, advanced oxidative processes (AOPs) act on the degradation and mineralization of pollutants, by generating of hydroxyl radicals, a strong oxidizing agent ($\varepsilon_{red} = +2{,}71$ V). One of the main AOPs is Fenton, the reaction of decomposing hydrogen peroxide in the presence of ferrous ions (Eq. (1)).

$$H_2O_2 + Fe^{+2} + H^+ \rightarrow \cdot OH + Fe^{+3} + H_2O \quad (1)$$

Fenton reaction is reported in literature with high degradation efficiencies for antibiotics, but results of high mineralization remains a challenge (Ledezma Estrada et al., 2012; Serna-Galvis et al., 2016; Vidal et al., 2019). Considering its oxidizing properties and relatively low cost, Fenton reaction can also be applied in the regeneration of a saturated adsorbent solid, by degrading the adsorbed molecules on the adsorption sites. Therefore, a combined AOP-adsorption process could promote better results than isolated techniques.

This way, the present work aims to investigate the combined process of adsorption on GAC followed by Fenton reaction, targeting the degradation and mineralization of ampicillin. The concentration of H_2O_2 e Fe^{+2} was evaluated for Fenton, while phase contact time and GAC dosage were evaluated in the adsorption process. Then, the best results of the isolated processes were combined, and the evaluation of GAC regeneration promoted by Fenton in the combined process was performed in three cycles.

2. Materials and methods

2.1. Reagents

Ampicillin (>96%, Sigma-Aldrich) stock solutions were prepared with distilled water and diluted to 20 mg L^{-1} for the experiments. Granular activated carbon (Êxodo Científica) was sieved in the particle size fractions between 1.4 and 2.36 mm. The surface area, average pore size and apparent density was estimated in, respectively, 444.215 m^2 g^{-1}, 19.214 Å and 0.60 g mL^{-1}. The point of zero charge was obtained from 11 point methodology elaborated by Regalbuto and Robles (2004), which consist of carbon in aqueous solutions under eleven different initial pH conditions (1.0–12.0). The point of zero charge is established as the pH at which the surface charge of the CA is neutral.

Hydrogen peroxide (35%, Dinâmica) and ferrous sulfate heptahydrate (99%, Anidrol) were applied as Fenton reagents. For pH adjustments, H_2SO_4 (98%, Anidrol) and NaOH (98%, Synth) 1 M solutions were used.

2.2. Adsorption

Experiments were performed in duplicate. Adsorption tests were performed in two steps:

(1) Evaluation of phase contact time (10, 15, 30, 50, 60, 75, 90, 120, 150, 180 and 210 min), under the conditions of natural pH, 20 mg L^{-1} AMP concentration and GAC dosage of 10 g L^{-1}.

(2) Evaluation of GAC dosage (10, 15, 20, 30 and 50 g L^{-1}), at natural pH and the phase contact time previously determined.

Adsorption tests, were carried out using 100 mL of AMP solution (20 mg L^{-1}), at room temperature (298 K), in 250 mL Schott flasks and stirred in an orbital shaker (Marconi, MA160BP) at 28 ± 2 rpm. Results are presented in terms of AMP percentage removal, according to Eq. (2).

$$\text{Removal } (\%) = (1 - \frac{C_f}{C_o}) \times 100 \quad (2)$$

where C_o and C_f are, respectively, the initial and final concentrations (mg L^{-1}) of ampicillin.

Adsorption kinetics were investigated with experimental data obtained in step 1. Pseudo-first-order (Eq. (3)) and pseudo-second-order (Eq. (4)) models were adjusted to data in terms of adsorbed amount (q_t). Nonlinear adjustments were performed in Microsoft Excel® software.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

$$q_t = \frac{qe^2 k_2 t}{1 + q_e k_2 t} \quad (4)$$

Table 1
Hydrogen peroxide and ferrous ions concentrations for Fenton reaction.

H_2O_2 (μM)	Fe^{+2} (μM)
300	60
300	80
400	70
500	60
500	80

2.3. Fenton reaction

Fenton tests were performed in Schott flasks with 500 mL of AMP (20 mg L^{-1}) solution. To avoid the precipitation of iron ions, the solution was acidified to pH 3. A predetermined amount of ferrous sulfate was weighted and added to the solution, under stirrring. An initial sample (10 mL) was taken and then reaction time was started right after the addition of hydrogen peroxide. After one hour of reaction and samples collected, the pH was adjusted to 11 to finished the reaction. All samples were filtered in 0.45 μm cellulose acetate membranes prior to HPLC analysis. Experiments were performed in duplicate.

The studied variables were ferrous ions and hydrogen peroxide concentrations, presented in Table 1. The evaluated concentrations were determined based on the studies of Rozas et al. (2010).

2.4. Combined process

The combined process consisted of an adsorption test in the best conditions achieved in the previous steps, followed by a Fenton reaction, performed in the specified conditions showed in Table 1. Reactions were carried out in Schott flasks containing 500 mL of AMP solution (20 mg L^{-1}) under stirring. Firstly, at the end of the adsorption experiment, both GAC and the aqueous solution were kept in the flask to pH adjustment to 3 and, then, the addition of Fenton reagents. After one hour, pH was adjusted to 11 to end Fenton reaction.

Both for Fenton reaction and combined process, analyzes were based on the decay of ampicillin concentration in solution, via HPLC analyzes and calculated by Eq. (2), as well as, on mineralization efficiency, as described in Eq. (5) and measured by total organic carbon. Samples were collected in 150, 151, 153, 155, 160, 165, 180 and 210 min to evaluate degradation, and in 150, 155, 165, 180 and 210 min to evaluate mineralization. This timing refers to the entire combined process, i.e., adsorption followed by Fenton reaction. All samples were filtered in 0,45 μm cellulose acetate membranes. Experiments were performed in duplicate. The cumulative volume taken in samples did not exceed 10% of the total volume.

$$\text{Mineralization efficiency (\%)} = (1 - \frac{TOC_f}{TOC_o}) \times 100 \quad (5)$$

where TOC_o and TOC_f are the initial and final TOC values, respectively.

2.5. Carbon activated regeneration through fenton reaction

After the combined process, GAC was filtered and dried at room temperature for about 20 h. To verify if Fenton process would also promote GAC regeneration, besides AMP degradation and mineralization, another adsorption process was carried after the combined process, in the same conditions of the previous adsorption test (100 mL of 20 mg L^{-1}AMP solution, 20 °C). Eq. (6) shows regeneration efficiency.

$$\text{Regeneration efficiency (\%)} = \frac{R_r}{R_o} \times 100 \quad (6)$$

where R_o and R_r are the AMP removal percentages before and after GAC regeneration.

2.6. Regeneration cycles with combined process

Aiming to estimate the feasibility of prolonged use of GAC, three cycles of regeneration were studied by applying the same concentrations of Fenton reagents as in the combined process of higher mineralization. The cycles consisted of repeated combined processes, performed with the same GAC and new AMP solution (20 mg L^{-1}).

After the combined process, GAC was filtered and dried at room temperature for 20 h. To avoid iron residues from previous Fenton reactions on the GAC surface, it was firstly filtered, followed by a pH adjustment to 11– so ferrous ions would precipitate in the hydroxide form – and then filtered again. TOC and regeneration efficiency were evaluated after each cycle.

Table 2
HPLC conditions to ampicillin quantification in solution.

Mobile phase composition	Flow ($mL\ min^{-1}$)	Injection volume (μL)	λ (nm)	Temperature (°C)
Ultrapure water (70%) Methanol (30%)	0.8	50	204	30

2.7. Analytical method

2.7.1. UV–Vis spectroscopy

In the adsorption tests, ampicillin concentration was determined at UV–Vis spectrophotometer (Thermo Scientific, model Genesis 10S UV-VS), at the wavelength 204 nm, using quartz cuvettes.

2.7.2. High performance liquid chromatography (HPLC)

At all Fenton reaction and combined processes, ampicillin was quantified by high performance liquid chromatography (HPLC) (Agilent model 1200 Infinity Series) using the method by Glauch et al. (2009), described at Table 2. A C18 column (Perkin Elmer) was the stationary phase, with dimensions 250 × 4.6 mm and 5 µm particle size. A calibration curve was previously constructed to relate the chromatogram areas (mAU) to the solute concentration (mg L^{-1}).

2.7.3. Total Organic Carbon (TOC)

Mineralization was evaluated by Total Organic Carbon analysis, which corresponds to the difference between the total carbon and the inorganic carbon present at the samples.

Analyzes were performed in a total carbon analyzer (Shimadzu, model TOC-VCSH). In the equipment, samples are oxidized by catalytic combustion and the carbon detection is done by non-dispersive infrared. Ultrapure synthetic air at 680 °C is used as carrier gas. TOC concentration is expressed in organic carbon milligrams per liter (mg C L^{-1}).

3. Results and discussion

3.1. Adsorption experiments

Adsorption experiments were performed in two steps: phase contact time and GAC dosage. The results were evaluated in terms of AMP percentage removal and adsorbed amount.

The GAC point of zero charge (pH_{PZC}) was 7.35, and close to this pH value, the aqueous solution pH kept constant, despite the initial pH of the solution. In a more alkaline medium (pH > 7.35), the GAC surface is negatively charged, as well as in an acidic condition (pH < 7.35) GAC is positively charged.

Adsorption tests were carried in natural pH, close to 5.5, in which the carbon surface has a positive charge. On the other hand, ampicillin is an amphoteric molecule that presents two dissociation constants ($pK_{a1} = 2.5$; $pK_{a2} = 7.1$); among this pH range, the molecule is neutral in the *zwitterion* form, in which the primary amine is protonated (positive) and the carboxyl is deprotonated (negative). This way, adsorption can occur by electrostatic attraction between the positively charged GAC and the carboxyl from ampicillin molecules (Peterson et al., 2010).

3.1.1. Phase contact time

Aiming to evaluate the influence of phase contact time in AMP adsorption onto GAC, removal percentage was calculated for each analyzed time instant, as shown in Fig. 1.

According to Fig. 1, it is possible to observe that, up to 150 min, AMP removal increases gradually, until reaching equilibrium at the carbon surface. Equilibrium is established when the dynamic mass transfer ceases by the equilibrium of adsorption–desorption reactions.

After performing a statistical test (ANOVA) between the points 150, 180 and 210 min, it was possible to infer that there is no significant difference at AMP removal after 150 min. This way, in the investigated conditions, a 43% removal was reached at 150 min, corresponding to the maximum adsorption capacity of 0.82 mg g^{-1}.

Del Vecchio et al. (2019) evaluated the effects of phase contact time in the adsorption of AMP (20 mg L^{-1}) onto commercial GAC, at similar conditions to the present study. The authors obtained 73% removal in 150 min, equivalent to a maximum adsorption capacity of 2.8 mg g^{-1}. The difference in the results can be explained by different porosities comparing the two GACs. The authors used a 32.2 Å pore size and 543.4 $m^2\ g^{-1}$ surface area GAC, higher values than the obtained for the GAC used in the present study.

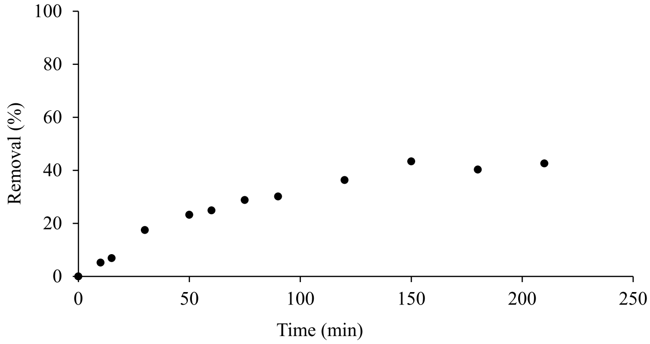

Fig. 1. Effect of contact time in ampicillin adsorption (Co = 20 mg L^{-1}, GAC = 10 g L^{-1} and natural pH).

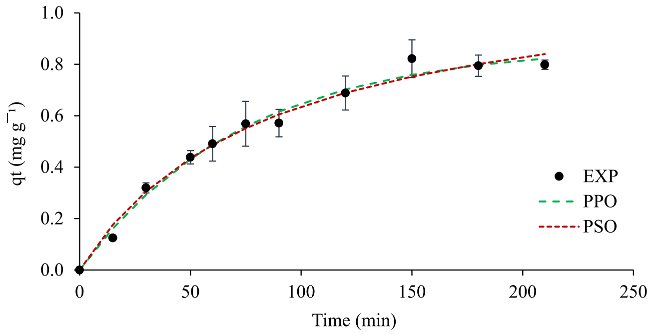

Fig. 2. Ampicillin adsorption in nonlinear pseudo-first order and pseudo-second order kinetics models adjustment (C_o = 20 mg L^{-1}, GAC = 10 g L^{-1} and natural pH).

Table 3
Parameters and determination coefficients of pseudo-first-order and pseudo-second-order models.

Pseudo-first order			Pseudo-second order		
q_1	0.8724	mg g^{-1}	q_2	1.1842	mg g^{-1}
k_1	0.0136	min^{-1}	k_2	0.0193	g (mg min)$^{-1}$
R^2	0.9881		R^2	0.9855	

3.1.2. Kinetics

In this work, two of the main kinetic models were selected to be adjusted to the experimental data: pseudo-first-order (PPO) and pseudo-second-order (PSO).

Fig. 2 presents the adsorbed amounts of ampicillin onto granular activated carbon along the phase contact time. Both kinetic models were adjusted to the experimental data through nonlinear adjustment.

Only analyzing the results found for the kinetic parameters, in Table 3, it is not possible to conclude which of the models best fits the experimental conditions used. Other factors must be considered in this analysis.

Both models were reported in literature for the adsorption of drugs onto activated carbon. In the studies of Flores-Cano et al. (2016), the adsorption of metronidazole, dimetridazole and diatrizoate onto activated carbons prepared from coffee waste and almond shells, was evaluated, and experimental results were best described through pseudo-first-order kinetics. As well, Varga et al. (2019) evaluated the adsorption of diclofenac, naproxen and carbamazepine in aqueous matrices onto commercial GAC and the authors found that the pseudo-first-order suited better the experimental data for all drugs. On the other hand, Manjunath and Kumar (2018) researched the adsorption of metronidazole on carbon from Prosopís julíflora and the pseudo-second-order kinetic model was found to well represent the removal.

3.1.3. Effect of GAC dosage

The influence of GAC dosage in the AMP adsorption process was evaluated varying the amount of GAC present in solution. According to Fig. 3, AMP removal increases along with the adsorbent solid dosage in the solution.

This behavior can be related to the increase in surface area and availability of active sites for the adsorption to occur, since the proportion of active sites increases in relation to the adsorbate concentration, which remains constant (Oladipo and Gazi, 2015). However, from a certain amount of adsorbent, due to the unavailability of active sites in it and the equilibrium establishment among AMP molecules on GAC surface and in solution, the physical limit of the process is

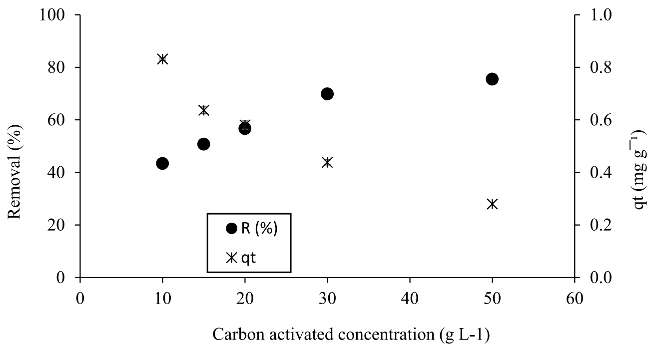

Fig. 3. Effect of carbon activated mass amount in ampicillin adsorption ($C_o = 20$ mg L^{-1}, t = 150 min and natural pH).

reached, in which the solid dosage does not influence the percentage removal anymore (Pouretedal and Sadegh, 2014). In the studied conditions, the maximum AMP removal (75.5%) corresponded to GAC dosage of 50 g L^{-1}.

Adsorption capacity, on the other hand, shows an opposite tendency, due to the decrease in total surface area available for adsorption. Fig. 3 also displays the obtained results in terms of adsorbed AMP related to the GAC dosage. As can be seen, at a GAC dosage of 50 g L^{-1} the adsorbed amount was 0.28 mg g^{-1}, which is considered relatively low, not being attractive to the process. That way, the choice of the most adequate solid dosage was is 20 g L^{-1}, reaching 57% AMP removal and adsorbed amount of 0.58 mg g^{-1}.

3.2. Fenton reaction

Fenton reaction experiments were performed in five different combinations of H_2O_2 and Fe^{+2}, described in Table 1, at pH 3 for 60 min. At all evaluated sets, the complete degradation of AMP was reached in a minute, while the mineralization did not exceed 10% at the end of the processes. The results are coherent, once AOPs allow a fast degradation of organic compounds through a low selectivity of hydroxyl radicals (Zhang et al., 2019). However, despite the fast degradation, mineralization is much slower in the determined conditions, due to the formation of reaction intermediates, as displayed in Fig. 4, an AMP degradation chromatogram.

As ampicillin retention time is around 8 min, the absence of the compound is shown at 1 min of reaction. This result points that the degradation of ampicillin is susceptible to generate recalcitrant organic intermediates which, on their turn, are not easily oxidized. Fig. 4 shows various signals which were attributed to AMP degradation intermediates such as the groups amino-hydroxyacetamide-carboxylic acid, amino-phenylacetic acid, and phenol.

Hydroxyl radicals' generation rate is directly connected to the oxidative power of the process. Thus, it can be inferred that the amount of hydroxyl radicals generated in the process was not sufficient to degrade all ampicillin by-products, therefore mineralization was lower.

To increase the hydroxyl generation rate, it is possible to combine other oxidizing agents to Fenton, such as radiation (ultraviolet, black light), ultrasound and catalysts (metallic ions or photocatalysts) (Ribeiro et al., 2015), as was done in the study by Rozas et al. (2010). The authors were able to increase mineralization percentage of ampicillin, as well as to decrease the reaction time by combining ultraviolet to Fenton under similar conditions in the present study, obtaining 50% and 20% mineralization for photo-Fenton and Fenton, respectively, after 60 min. In the present work, the investigation of adsorption combined to Fenton reaction was performed, targeting high mineralization percentages.

3.3. Combined process

The combined process consisted of an adsorption essay (AMP Co = 20 mg L^{-1}, 150 min, GAC dosage = 20 g L^{-1}) followed by a Fenton reaction (pH 3, 60 min, conditions of Table 1). Thus, the whole process lasted 210 min.

3.3.1. H_2 O_2 e Fe^{+2} concentration effect in combined process

Likewise the results in the Fenton reaction, ampicillin degradation was complete within 1 min, under all conditions of the combined process. In this sense, the influence of the concentration of H_2O_2 and Fe^{+2} was evaluated on the mineralization efficiency during 60 minutes of Fenton reaction, as can be seen in Fig. 5. The time axis refers to the time required the complete process to occur (adsorption and Fenton).

Overall, mineralization efficiency enhances along with reactional time and reaches higher results the higher the Fenton reagents concentrations used. Also, in 5 minutes of Fenton reaction, 70% mineralization efficiency is reached, which means that there was about 20% reduction in organic load in relation to the beginning of the Fenton reaction, at which time the mineralization efficiency takes into account only adsorption. This demonstrates that the rate of production of hydroxyl radicals was fast in the first minutes of reaction and, after that time, it decreased due to the consumption of hydrogen

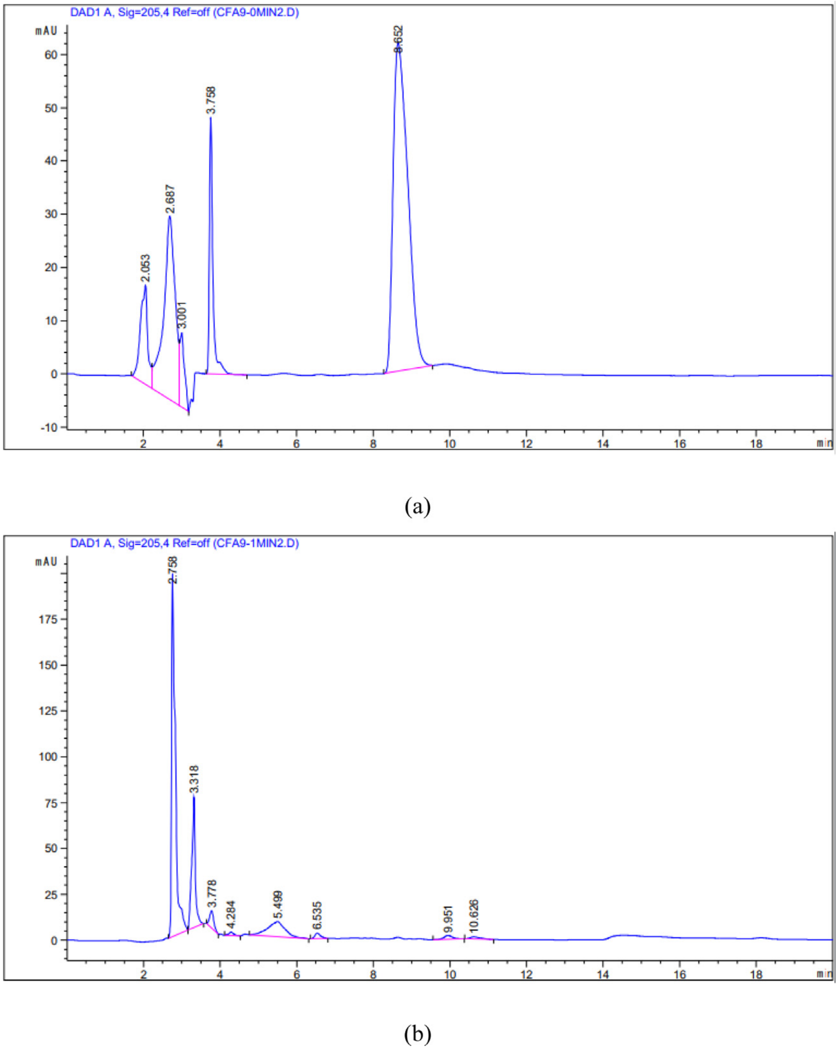

Fig. 4. (a) HPLC chromatogram of 20 mg L^{-1} ampicillin and (b) HPLC chromatogram of ampicillin degradation at 1 min of Fenton reaction (H_2O_2/Fe^{+2} = 500/80 μM).

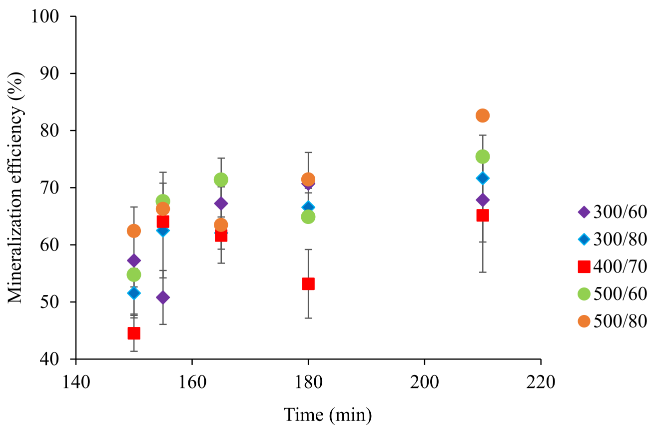

Fig. 5. Mineralization efficiency during Fenton reaction in combined process (adsorption: Co = 20 mg L^{-1}, 150 min, GAC dosage = 20 g L^{-1}; Fenton reaction: pH 3, 60 minutes).

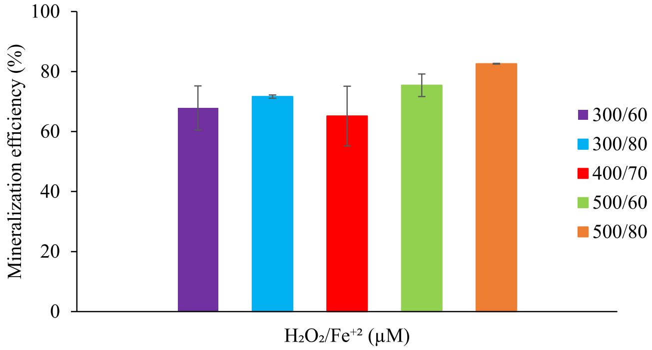

Fig. 6. Mineralization efficiency in combined process to degradation of ampicillin (Co = 20 mg L^{-1}, t = 210 min).

peroxide and iron ions. Such behavior of a fast kinetics at the first minutes followed by a decreasing rate is in agreement to previous works that studied the degradation of pharmaceutical compounds by Fenton processes (Aboudalle et al., 2018; Divyapriya et al., 2018; Gupta and Garg, 2018; Ioannou-Ttofa et al., 2019; Liu et al., 2018; Michael et al., 2019; Verma and Haritash, 2019).

3.3.1.1 Hydrogen peroxide concentration effect Hydrogen peroxide concentration plays a crucial role in the efficiency of the entire process. It has been observed that the pollutant degradation rate increases along with hydrogen peroxide concentration. However, excess amounts of the reagent can contribute to an increase in the COD of the effluent, in addition to reacting with hydroxyl radicals to form the hydroperoxyl radical, a species with lower oxidizing power compared to the hydroxyl radical (Babuponnusami and Muthukumar, 2014).

When H_2O_2 concentration increased from 300 μM to 500 μM, at the same Fe^{+2} concentration of 60 μM, the mineralization efficiency increased from 68% to 75%. Evaluating the same increase in H_2O_2 concentration, but with the Fe^{+2} concentration of 80 μM, mineralization efficiency increased from 72% to 83%.

Alalm et al. (2015) evaluated the degradation of amoxicillin, ampicillin, diclofenac and paracetamol by solar photo-Fenton. When evaluating the effect of hydrogen peroxide concentration, they observed a positive effect on the degradation percentage when increasing its concentration. As discussed earlier, the higher the concentration of hydrogen peroxide, the higher the concentration of hydroxyl radicals during the entire reaction time, which makes it possible to increase mineralization.

3.3.1.2 Iron ions concentration effect It is often reported in the literature that the degradation rate in Fenton reaction increases by increasing the concentration of ferrous ions, once it catalyzes the degradation of hydrogen peroxide and speeds the overall hydroxyl radical generation. However, a Fe^{+2} concentration above the ideal may result in turbidity and sludge formation (Mirzaei et al., 2017).

In the present study, Fe^{+2} concentration is proportionally related to the mineralization. By increasing Fe^{+2} concentration from 60 μM to 80 μM and hydrogen peroxide concentration set at 300 μM, mineralization efficiency increased from 68% to 72%. The same way, when peroxide concentration was 500 μM, mineralization efficiency increased from 75% to 83% when Fe^{+2} increased from 60 μM to 80 μM.

Verma and Haritash (2019) evaluated amoxicillin degradation by Fenton process and concluded, for the same evaluated time, the higher the ferrous ion concentration, the higher the antibiotic degradation. In turn, Gupta and Garg (2018) also observed a positive effect in Fenton reaction when increasing Fe^{+2} concentration, but until a certain point, on ciprofloxacin degradation and mineralization. The authors evaluated the stoichiometric proportions of $H_2O_2 : Fe^{+2}$ (H_2O_2 = 14,2 nM) equal to 1:5 and 1:10, that reached better results than the stoichiometric proportions of 1:20 e 1:50. The best result achieved was 70% of degradation and 55% of mineralization at the proportion 1:10 (H_2O_2 = 14,2 nM).

3.3.2 Mineralization efficiency of combined process

Compared to Fenton's experiments, the combined adsorption-Fenton process reached a higher mineralization efficiency, allowing to infer that the GAC acted as a catalyst and that the decrease in TOC was due to mineralization. From the obtained results, it is deduced that AMP oxidation happened both in solution and GAC surface. The generation of hydroxyl radicals could have been catalyzed not only by Fe^{+2} in solution, but also by the decomposition of hydrogen peroxide on the surface of activated carbon (Domínguez et al., 2013; Fang et al., 2014).

GAC regeneration results, discussed further in this article, corroborate to this understanding. Fig. 6 displays mineralization results after the combined process, at 210 min.

In general, hydrogen peroxide and ferrous ions positively influenced the obtained results. As seen in Fig. 6, mineralization results ranged from 65% to 83%, indicating the combined process proves to be effective in treating ampicillin-contaminated wastewater. Among the studied systems, the higher mineralization efficiency (83%) was reached at the ratio H_2O_2/Fe^{+2} = 500/80 μM.

Table 4
Mineralization efficiency for ampicillin and β-lactam antibiotics by Fenton process.

Antibiotic	Technique	Experimental conditions	Mineralization efficiency	Reference
Ampicillin	Adsorption + Fenton	$C_o = 20$ mg L^{-1} t = 210 min pH (adsorption) = 5.5 GAC = 10 g L^{-1} pH (Fenton) = 3.0 $Fe^{+2} = 80$ μM $H_2O_2 = 500$ μM	~83%	Present study
Ampicillin	Electro-Fenton	$C_o = 50$ mg L^{-1} t = 120 min 5 mA cm^{-2} $Fe^{+2} = 1$ mg L^{-1} $Na_2SO_4 = 0.05$ M pH = 2.8	42%	Vidal et al. (2019)
	Photo-Electro-Fenton	5 mA cm^{-2} $Fe^{+2} = 1$ mg L^{-1} $Na_2SO_4 = 0.05$ M pH = 2.8 luz UV 365 nm	63%	
Ampicillin	Fenton	$C_o = 20$ mg L^{-1} t = 60 min pH = 3.7 $Fe^{+2} = 87$ mol L^{-1} $H_2O_2 = 373$ μM	~20%	Rozas et al. (2010)
	Photo-Fenton	pH = 3.5 $Fe^{+2} = 87$ mol L^{-1} $H_2O_2 = 454$ μM UV 360 nm	~50%	
Amoxicillin	Photo-Fenton	$C_o = 50$ mg L^{-1} t = 480 min $Fe^{+2} = 0.05$ mM $H_2O_2 = 120$ mg L^{-1} pH = 2.5 Solar simulation at 290 nm	73%	Trovó et al. (2011)
Cefalexin	Electro-Fenton	$C_o = 50$ mg L^{-1} t = 480 min 6.66 mA cm^{-2} $Fe^{+2} = 1$ mM pH = 3.0	62%	Ledezma Estrada et al. (2012)
Oxacillin	Photo-Fenton	$C_o = 47, 23$ μmol L^{-1} t = 27 min $H_2O_2 = 1000$ μmol L^{-1} $Fe^{+2} = 90$ μmol L^{-1} pH = 5.6 150 W	~35%	Serna-Galvis et al. (2016)

Table 4 shows the comparison among the present work and other researches about ampicillin degradation and some β-lactam antibiotics degradation by Fenton processes. As can be noted, this work presents a great mineralization efficiency in comparison to literature.

3.4 GAC regeneration

Granular activated carbon regeneration by Fenton reaction was evaluated in the end of the combined process, where GAC was filtered and dried at room temperature. Then, a new adsorption assay was performed. Fig. 7 shows the regeneration efficiency for different conditions in Fenton reaction.

Residual AMP concentration in solution, after adsorption, ranged between 8 to 10 L^{-1}. It was hoped the Fenton process would promote AMP oxidation not only in solution, but also at the carbon surface (Cabrera-Codony et al., 2015; Rosales et al., 2018). Thus, in consequence, the expected results were high mineralization and GAC regeneration efficiencies. As can be seen in Fig. 7, the regeneration efficiency under all conditions was in the range of 78% and 85%, a result that is in line with the expectation.

Cabrera-Codony et al. (2015) evaluated the regeneration of siloxane-exhausted GAC through the advanced oxidative processes O_3, H_2O_2 and H_2O_2 with an iron-impregnated GAC, the latter a Fenton process. The authors observed a much higher regeneration efficiency in the Fenton process (92%) than the other processes (40% and 45% for O_3 and H_2O_2). Also,

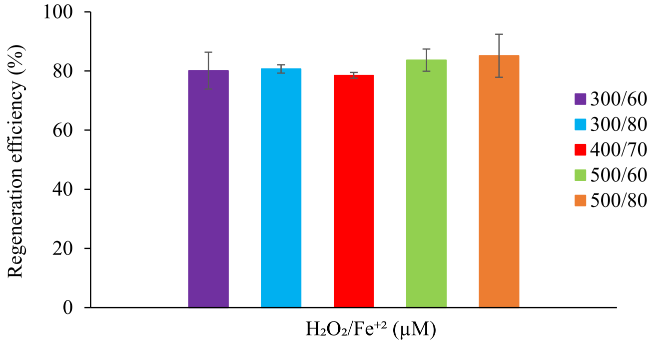

Fig. 7. Regeneration efficiency of activated carbon with combined process (Co = 20 mg L^{-1}, t = 210 min).

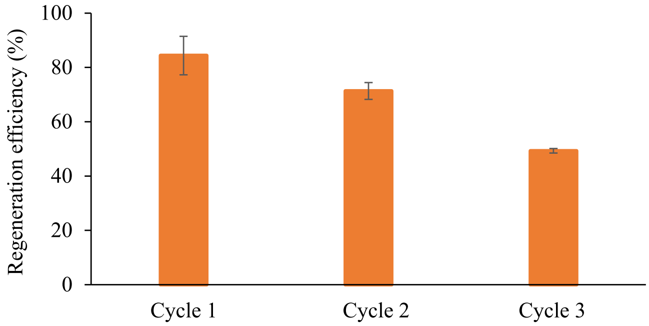

Fig. 8. Regeneration efficiency of activated carbon in three regeneration cycles with combined process (Co = 20 mg L^{-1}, t = 210 min, H_2O_2/Fe^{+2} = 500/80 µM).

Trellu et al. (2018) evaluated the regeneration potential of electro-Fenton for the phenol saturated GAC fiber, achieving 78% efficiency. The authors applied the adsorbent successfully for 10 adsorption/regeneration cycles, efficiencies varying between 65% and 78%. These results demonstrate the capacity and applicability of Fenton processes in regenerating adsorbent solids. Insight of evaluating a long-term application for the combined process, three cycles were evaluated.

3.5 Regeneration cycles with combined process

The evaluation of three regeneration cycles was performed with four combined processes (I, II, III and IV) using, the same GAC and fresh 20 mg L^{-1} AMP solution for each combined process. Fig. 8 presents the regeneration efficiencies for every cycle.

According to Fig. 8, regeneration efficiency decreases with the number of cycles performed. This behavior is a consequence of lower AMP removal percentages at each combined process. This result is shown in Fig. 9, for the combined processes performed in duplicate.

The same tendency was observed for mineralization efficiency: in the first combined process (I), the obtained result was about 80%, while for the process IV, mineralization efficiency was around 20%. The decreased adsorption capacity and mineralization efficiency is likely caused by textural and chemical properties of the GAC surface. It is challenging to determine the specific effect of chemical changes on catalytic performance as they can affect the number of active sites, adsorption capacity, and surface functional groups. In principle, the efficiency of the process will be determined by multiple factors such as the mass transfer via diffusion of different species into the porous structure of GAC, the organic contaminants reactivity and oxidation by-products (Chen et al., 2017).

Surface oxygen complexes, basic, acidic or neutral are formed on activated carbons when they are treated with oxidant agents. The fixation of acidic groups, such as carbonyls, phenolic hydroxyls, lactones and quinones, on the surface of activated carbons, makes them more hydrophilic. The porous structure of activated carbons can also change in the process, improving or worsening the applicability as adsorbents or catalysts (Pradhan and Sandle, 1999).

Fang et al. (2014) researched the mechanism of catalytic decomposition of hydrogen peroxide by activated carbon. The generation of hydroxyl radicals was inhibited by acidic functional groups and promoted by basic groups. The correlation between total acidity and HO• generation was not significant, however, the OH groups were negatively correlated to HO•, due to the reactivity between the species.

Chen et al. (2017) evaluated the performance of Fenton and hydrogen peroxide in the regeneration of GAC used for a tertiary treatment of dyeing wastewater. The saturated carbons used in the study recovered around 50% of their

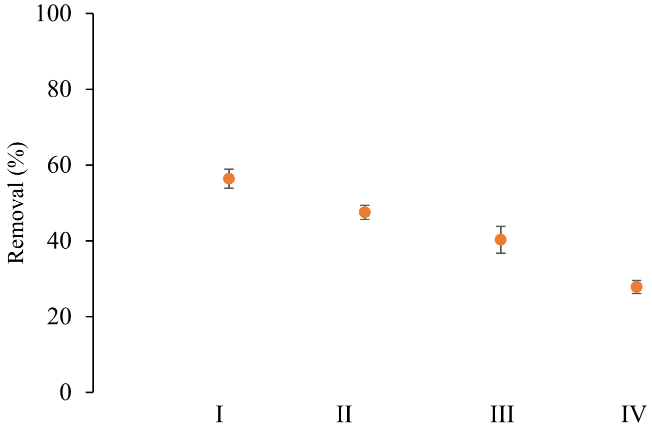

Fig. 9. Ampicillin removal in the adsorption steps in three regeneration cycles with combined process (Co = 20 mg L^{-1}, t = 210 min, H_2O_2/Fe^{+2} = 500/80 μM).

adsorption capacities and specific surface areas in both Fenton and hydrogen peroxide treatment. However, chemical oxidation introduced large amounts of acidic oxygen groups on the carbon surface, which can cause a decrease in catalytic and adsorptive performances. This way, it is necessary to study GAC surface modifications in consequence of Fenton to develop a more optimized process for many cycles.

4 Conclusion

The results demonstrate the combined process of adsorption onto granular activated carbon and Fenton reaction is efficient in the degradation and mineralization of ampicillin. Adsorption reached 57% (0.58 mg g^{-1}) after 150 minutes of contact time and 20 g L^{-1} of GAC. In the Fenton reaction, ampicillin degradation was observed at 1 min of reaction. The same degradation behavior occurred in the combined process, which was evaluated by mineralization. The combination that showed the highest AMP mineralization efficiency, around 83%, was H_2O_2/Fe^{+2} = 500/80 μM. The effect of hydrogen peroxide and iron ions concentrations was positive, since the mineralization was greater the greater the concentration of those. Because of the combined process, a regeneration efficiency of 85% was achieved at the ratio H_2O_2/Fe^{+2} = 500/80 μM. The regeneration efficiency decreased along the three regeneration cycles: 84%, 71%, and 49%, respectively. Overall, the developed process is an efficient way to treat ampicillin-contaminated waters with high mineralization results and fast degradation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors thank the CNPq for the scholarship.

References

Aboudalle, A., Fourcade, F., Assadi, A.A., Domergue, L., Djelal, H., Lendormi, T., Taha, S., Amrane, A., 2018. Reactive oxygen and iron species monitoring to investigate the electro-Fenton performances. Impact of the electrochemical process on the biodegradability of metronidazole and its by-products. Chemosphere 199, 486–494. http://dx.doi.org/10.1016/j.chemosphere.2018.02.075.

Alalm, M.G., Tawfik, A., Ookawara, S., 2015. Degradation of four pharmaceuticals by solar photo-Fenton process: Kinetics and costs estimation. J. Environ. Chem. Eng. 3, 46–51. http://dx.doi.org/10.1016/j.jece.2014.12.009.

Asaithambi, P., Sajjadi, B., Aziz, A.R.A., 2017. Integrated ozone–photo–Fenton process for the removal of pollutant from industrial wastewater. Chin. J. Chem. Eng. 25, 516–522. http://dx.doi.org/10.1016/j.cjche.2016.10.005.

Azuma, T., Otomo, K., Kunitou, M., Shimizu, M., Hosomaru, K., Mikata, S., Ishida, M., Hisamatsu, K., Yunoki, A., Mino, Y., Hayashi, T., 2018. Environmental fate of pharmaceutical compounds and antimicrobial-resistant bacteria in hospital effluents, and contributions to pollutant loads in the surface waters in Japan. Sci. Total Environ. http://dx.doi.org/10.1016/j.scitotenv.2018.11.433, #pagerange#.

Babuponnusami, A., Muthukumar, K., 2014. A review on Fenton and improvements to the Fenton process for wastewater treatment. J. Environ. Chem. Eng. 2, 557–572. http://dx.doi.org/10.1016/j.jece.2013.10.011.

Barraud, O., Casellas, M., Dagot, C., Ploy, M.C., 2013. An antibiotic-resistant class 3 integron in an enterobacter cloacae isolate from hospital effluent. Clin. Microbiol. Infect. 19, E306–E308. http://dx.doi.org/10.1111/1469-0691.12186.

Batt, A.L., Furlong, E.T., Mash, H.E., Glassmeyer, S.T., Kolpin, D.W., 2017. The importance of quality control in validating concentrations of contaminants of emerging concern in source and treated drinking water samples. Sci. Total Environ. 579, 1618–1628. http://dx.doi.org/10.1016/j.scitotenv.2016.02.127.

Bengtsson-Palme, J., Milakovic, M., Švecová, H., Ganjto, M., Jonsson, V., Grabic, R., Udikovic-Kolic, N., 2019. Industrial wastewater treatment plant enriches antibiotic resistance genes and alters the structure of microbial communities. Water Res. 162, 437–445. http://dx.doi.org/10.1016/j.watres.2019.06.073.

Bottoni, P., Caroli, S., 2018. Presence of residues and metabolites of pharmaceuticals in environmental compartments, food commodities and workplaces: A review spanning the three-year period 2014–2016. Microchem. J. 136, 2–24. http://dx.doi.org/10.1016/j.microc.2017.06.016.

Bu, Q., Shi, X., Yu, G., Huang, J., Wang, B., 2016. Assessing the persistence of pharmaceuticals in the aquatic environment: Challenges and needs. Emerg. Contam. 2, 145–147. http://dx.doi.org/10.1016/j.emcon.2016.05.003.

Cabrera-Codony, A., Gonzalez-Olmos, R., Martín, M.J., 2015. Regeneration of siloxane-exhausted activated carbon by advanced oxidation processes. J. Hazard. Mater. 285, 501–508. http://dx.doi.org/10.1016/j.jhazmat.2014.11.053.

Cardoso, O., Porcher, J.M., Sanchez, W., 2014. Factory-discharged pharmaceuticals could be a relevant source of aquatic environment contamination: Review of evidence and need for knowledge. Chemosphere 115, 20–30. http://dx.doi.org/10.1016/j.chemosphere.2014.02.004.

Chen, Q., Liu, H., Yang, Z., Tan, D., 2017. Regeneration performance of spent granular activated carbon for tertiary treatment of dyeing wastewater by Fenton reagent and hydrogen peroxide. J. Mater. Cycles Waste Manage. 19, 256–264. http://dx.doi.org/10.1007/s10163-015-0410-y.

Chowdhury, A., Kumari, S., Khan, A.A., Chandra, M.R., Hussain, S., 2020. Activated carbon loaded with Ni-Co-S nanoparticle for superior adsorption capacity of antibiotics and dye from wastewater: Kinetics and isotherms. Colloids Surf. A 125868. http://dx.doi.org/10.1016/j.colsurfa.2020.125868.

Daouk, S., Chèvre, N., Vernaz, N., Bonnabry, P., Dayer, P., Daali, Y., Fleury-Souverain, S., 2015. Prioritization methodology for the monitoring of active pharmaceutical ingredients in hospital effluents. J. Environ. Manage. 160, 324–332. http://dx.doi.org/10.1016/j.jenvman.2015.06.037.

de Franco, M.A.E., de Carvalho, C.B., Bonetto, M.M., Soares, R. de P., Féris, L.A., 2017. Removal of amoxicillin from water by adsorption onto activated carbon in batch process and fixed bed column: Kinetics, isotherms, experimental design and breakthrough curves modelling. J. Clean. Prod. 161, 947–956. http://dx.doi.org/10.1016/j.jclepro.2017.05.197.

Del Vecchio, P., Haro, N.K., Souza, F.S., Marcílio, N.R., Féris, L.A., 2019. Ampicillin removal by adsorption onto activated carbon: Kinetics, equilibrium and thermodynamics. Water Sci. Technol. 79, 2013–2021. http://dx.doi.org/10.2166/wst.2019.205.

Divyapriya, G., Nambi, I., Senthilnathan, J., 2018. Ferrocene functionalized graphene based electrode for the electro-Fenton oxidation of ciprofloxacin. Chemosphere 209, 113–123. http://dx.doi.org/10.1016/j.chemosphere.2018.05.148.

Domínguez, C.M., Ocón, P., Quintanilla, A., Casas, J.A., Rodriguez, J.J., 2013. Highly efficient application of activated carbon as catalyst for wet peroxide oxidation. Appl. Catal. B Environ. 140–141, 663–670. http://dx.doi.org/10.1016/j.apcatb.2013.04.068.

Fang, G.D., Liu, C., Gao, J., Zhou, D.M., 2014. New insights into the mechanism of the catalytic decomposition of hydrogen peroxide by activated carbon: Implications for degradation of diethyl phthalate. Ind. Eng. Chem. Res. 53, 19925–19933. http://dx.doi.org/10.1021/ie504184r.

Flores-Cano, J.V., Sánchez-Polo, M., Messoud, J., Velo-Gala, I., Ocampo-Pérez, R., Rivera-Utrilla, J., 2016. Overall adsorption rate of metronidazole, dimetridazole and diatrizoate on activated carbons prepared from coffee residues and almond shells. J. Environ. Manag. 169, 116–125. http://dx.doi.org/10.1016/j.jenvman.2015.12.001.

Glauch, A., Tuqan, A., Assi, H.A., 2009. Antibiotic removal from water: elimination of amoxicillin and ampicillin by microscale and nanoscale iron particles. Environ. Poll. http://dx.doi.org/10.1016/j.envpol.2008.12.024.

Gu, W., Huang, X., Tian, Y., Cao, M., Zhou, L., Zhou, Yi, Lu, J., Lei, J., Zhou, Yanbo, Wang, L., Liu, Y., Zhang, J., 2021. High-efficiency adsorption of tetracycline by cooperation of carbon and iron in a magnetic Fe/porous carbon hybrid with effective Fenton regeneration. Appl. Surf. Sci. 538, 147813. http://dx.doi.org/10.1016/j.apsusc.2020.147813.

Gupta, A., Garg, A., 2018. Degradation of cipro fl oxacin using Fenton's oxidation: Effect of operating parameters, identification of oxidized by-products and toxicity assessment. Chemosphere 193, 1181–1188. http://dx.doi.org/10.1016/j.chemosphere.2017.11.046.

Habibi, A., Belaroui, L.S., Bengueddach, A., López Galindo, A., Sainz Díaz, C.I., Peña, A., 2018. Adsorption of metronidazole and spiramycin by an Algerian palygorskite. Effect of modification with tin. Microporous Mesop. Mater. 268, 293–302. http://dx.doi.org/10.1016/j.micromeso.2018.04.020.

Haller, L., Chen, H., Ng, C., Le, T.H., Koh, T.H., Barkham, T., Sobsey, M., Gin, K.Y.H., 2018. Occurrence and characteristics of extended-spectrum β-lactamase- and carbapenemase- producing bacteria from hospital effluents in Singapore. Sci. Total Environ. 615, 1119–1125. http://dx.doi.org/10.1016/j.scitotenv.2017.09.217.

Ioannou-Ttofa, L., Raj, S., Prakash, H., Fatta-Kassinos, D., 2019. Solar photo-Fenton oxidation for the removal of ampicillin, total cultivable and resistant E. Coli and ecotoxicity from secondary-treated wastewater effluents. Chem. Eng. J. 355, 91–102. http://dx.doi.org/10.1016/j.cej.2018.08.057.

Ledezma Estrada, A., Li, Y.Y., Wang, A., 2012. Biodegradability enhancement of wastewater containing cefalexin by means of the electro-Fenton oxidation process. J. Hazard. Mater. 227–228, 41–48. http://dx.doi.org/10.1016/j.jhazmat.2012.04.079.

Li, Y., Yeung, K.L., 2018. Polymeric catalytic membrane for ozone treatment of DEET in water. Catal. Today http://dx.doi.org/10.1016/j.cattod.2018.06.005.

Liu, X., Zhou, Y., Zhang, J., Luo, L., Yang, Y., Huang, H., Peng, H., Tang, L., Mu, Y., 2018. Insight into electro-Fenton and photo-Fenton for the degradation of antibiotics: Mechanism study and research gaps. Chem. Eng. J. 347, 379–397. http://dx.doi.org/10.1016/j.cej.2018.04.142.

Manjunath, S.V., Kumar, M., 2018. Evaluation of single-component and multi-component adsorption of metronidazole, phosphate and nitrate on activated carbon from Prosopís julíflor. Chem. Eng. J. 346, 525–534. http://dx.doi.org/10.1016/j.cej.2018.04.013.

Mattrey, F.T., Makarov, A.A., Regalado, E.L., Bernardoni, F., Figus, M., Hicks, M.B., Zheng, J., Wang, L., Schafer, W., Antonucci, V., Hamilton, S.E., Zawatzky, K., Welch, C.J., 2017. Current challenges and future prospects in chromatographic method development for pharmaceutical research. TRAC Trends Anal. Chem. 95, 36–46. http://dx.doi.org/10.1016/j.trac.2017.07.021.

McQuillan, R.V., Stevens, G.W., Mumford, K.A., 2018. The electrochemical regeneration of granular activated carbons: A review. J. Hazard. Mater. 355, 34–49. http://dx.doi.org/10.1016/j.jhazmat.2018.04.079.

Mezzelani, M., Gorbi, S., Regoli, F., 2018. Pharmaceuticals in the aquatic environments: Evidence of emerged threat and future challenges for marine organisms. Mar. Environ. Res. 140, 41–60. http://dx.doi.org/10.1016/j.marenvres.2018.05.001.

Michael, S.G., Michael-Kordatou, I., Beretsou, V.G., Jäger, T., Michael, C., Schwartz, T., Fatta-Kassinos, D., 2019. Solar photo-Fenton oxidation followed by adsorption on activated carbon for the minimisation of antibiotic resistance determinants and toxicity present in urban wastewater. Appl. Catal. B Environ. 244, 871–880. http://dx.doi.org/10.1016/j.apcatb.2018.12.030.

Mirzaei, A., Chen, Z., Haghighat, F., Yerushalmi, L., 2017. Removal of pharmaceuticals from water by homo/heterogonous Fenton-type processes – A review. Chemosphere 174, 665–688. http://dx.doi.org/10.1016/j.chemosphere.2017.02.019.

Oladipo, A.A., Gazi, M., 2015. Nickel removal from aqueous solutions by alginate-based composite beads: Central composite design and artificial neural network modeling. J. Water Process Eng. 8, e81–e91. http://dx.doi.org/10.1016/j.jwpe.2014.12.002.

Orias, F., Perrodin, Y., 2013. Characterisation of the ecotoxicity of hospital effluents: A review. Sci. Total Environ. 454–455, 250–276. http://dx.doi.org/10.1016/j.scitotenv.2013.02.064.

Peterson, J.W., Burkhart, R.S., Shaw, D.C., Schuiling, A.B., Haserodt, M.J., Seymour, M.D., 2010. Experimental determination of ampicillin adsorption to nanometer-size Al2O3 in water. Chemosphere 80, 1268–1273. http://dx.doi.org/10.1016/j.chemosphere.2010.06.055.

Pouretedal, H.R., Sadegh, N., 2014. Effective removal of Amoxicillin, Cephalexin, Tetracycline and Penicillin G from aqueous solutions using activated carbon nanoparticles prepared from vine wood. J. Water Process Eng. 1, 64–73. http://dx.doi.org/10.1016/j.jwpe.2014.03.006.
Pradhan, B.K., Sandle, N.K., 1999. Effect of different oxidizing agent treatments on the surface properties of activated carbons. Carbon 37, 1323–1332.
Regalbuto, J.R., Robles, J.O., 2004. The Engineering of Pt/Carbon Catalyst Preparation. Univ. Illinois, Chicago, p. 13.
Ribeiro, A.R., Nunes, O.C., Pereira, M.F.R., Silva, A.M.T., 2015. An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched directive 2013/39/EU. Environ. Int. 75, 33–51. http://dx.doi.org/10.1016/j.envint.2014.10.027.
Rosales, E., Anasie, D., Pazos, M., Lazar, I., Sanromán, M.A., 2018. Kaolinite adsorption-regeneration system for dyestuff treatment by Fenton based processes. Sci. Total Environ. 622–623, 556–562. http://dx.doi.org/10.1016/j.scitotenv.2017.11.301.
Rozas, O., Contreras, D., Mondaca, M.A., Pérez-Moya, M., Mansilla, H.D., 2010. Experimental design of Fenton and photo-Fenton reactions for the treatment of ampicillin solutions. J. Hazard. Mater. 177, 1025–1030. http://dx.doi.org/10.1016/j.jhazmat.2010.01.023.
Serna-Galvis, E.A., Silva-Agredo, J., Giraldo, A.L., Flórez, O.A., Torres-Palma, R.A., 2016. Comparison of route, mechanism and extent of treatment for the degradation of a β-lactam antibiotic by TiO2 photocatalysis, sonochemistry, electrochemistry and the photo-Fenton system. Chem. Eng. J. 284, 953–962. http://dx.doi.org/10.1016/j.cej.2015.08.154.
Souza, F.S., Féris, L.A., 2017. Consumption-based approach for pharmaceutical compounds in a large hospital. Environ. Technol. 38, 2217–2223. http://dx.doi.org/10.1080/09593330.2016.1255262.
Trellu, C., Oturan, N., Keita, F.K., Fourdrin, C., Péchaud, Y., Oturan, M.A., 2018. Regeneration of activated carbon fiber by electro-Fenton process. Environ. Sci. Technol. http://dx.doi.org/10.1021/acs.est.8b01554.
Trovó, A.G., Pupo Nogueira, R.F., Agüera, A., Fernandez-Alba, A.R., Malato, S., 2011. Degradation of the antibiotic amoxicillin by photo-Fenton process - Chemical and toxicological assessment. Water Res. 45, 1394–1402. http://dx.doi.org/10.1016/j.watres.2010.10.029.
Varga, M., ELAbadsa, M., Tatár, E., Mihucz, V.G., 2019. Removal of selected pharmaceuticals from aqueous matrices with activated carbon under batch conditions. Microchem. J. 148, 661–672. http://dx.doi.org/10.1016/j.microc.2019.05.038.
Verlicchi, P., Al Aukidy, M., Galletti, A., Petrovic, M., Barceló, D., 2012. Hospital effluent: Investigation of the concentrations and distribution of pharmaceuticals and environmental risk assessment. Sci. Total Environ. 430, 109–118. http://dx.doi.org/10.1016/j.scitotenv.2012.04.055.
Verlicchi, P., Al Aukidy, M., Zambello, E., 2015. What have we learned from worldwide experiences on the management and treatment of hospital effluent? - An overview and a discussion on perspectives. Sci. Total Environ. 514, 467–491. http://dx.doi.org/10.1016/j.scitotenv.2015.02.020.
Verma, M., Haritash, A.K., 2019. Degradation of amoxicillin by Fenton and Fenton-integrated hybrid oxidation processes. J. Environ. Chem. Eng. 7, 102886. http://dx.doi.org/10.1016/j.jece.2019.102886.
Vidal, J., Huiliñir, C., Santander, R., Silva-Agredo, J., Torres-Palma, R.A., Salazar, R., 2019. Degradation of ampicillin antibiotic by electrochemical processes: evaluation of antimicrobial activity of treated water. Environ. Sci. Pollut. Res. 26, 4404–4414. http://dx.doi.org/10.1007/s11356-018-2234-5.
Wang, T., Wang, Z., Wang, P., Tang, Y., 2018. An integration of photo-Fenton and membrane process for water treatment by a PVDF@CuFe2O4 catalytic membrane. J. Membr. Sci. 572, 419–427. http://dx.doi.org/10.1016/j.memsci.2018.11.031.
Wei, X., Wu, Zhansheng, Wu, Zhilin, Ye, B.C., 2018. Adsorption behaviors of atrazine and Cr(III) onto different activated carbons in single and co-solute systems. Powder Technol. 329, 207–216. http://dx.doi.org/10.1016/j.powtec.2018.01.060.
Yu, F., Li, Y., Han, S., Ma, J., 2016. Adsorptive removal of antibiotics from aqueous solution using carbon materials. Chemosphere 153, 365–385. http://dx.doi.org/10.1016/j.chemosphere.2016.03.083.
Zeng, Z., Zou, H., Li, X., Arowo, M., Sun, B., Chen, J., Chu, G., Shao, L., 2013. Degradation of phenol by ozone in the presence of Fenton reagent in a rotating packed bed. Chem. Eng. J. J. 229, 404–411. http://dx.doi.org/10.1016/j.cej.2013.06.018.
Zhang, C., Dai, C., Zhang, H., Peng, S., Wei, X., Hu, Y., 2017. Regeneration of mesoporous silica aerogel for hydrocarbon adsorption and recovery. Mar. Pollut. Bull. 122, 129–138. http://dx.doi.org/10.1016/j.marpolbul.2017.06.036.
Zhang, M. hui, Dong, H., Zhao, L., Wang, D. xi, Meng, D., 2019. A review on Fenton process for organic wastewater treatment based on optimization perspective. Sci. Total Environ. 670, 110–121. http://dx.doi.org/10.1016/j.scitotenv.2019.03.180.
Zhao, Z., Liu, Z., Wang, H., Dong, W., Wang, W., 2018. Sequential application of Fenton and ozone-based oxidation process for the abatement of Ni-EDTA containing nickel plating effluents. Chemosphere 202, 238–245. http://dx.doi.org/10.1016/j.chemosphere.2018.03.090.