Antibiotics Removal from Aquatic Environments: Adsorption of Enrofloxacin, Trimethoprim, Sulfadiazine and Amoxicillin on Vegetal Powdered Activated Carbon

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This study addresses the growing concern about the high levels of antibiotics in water, outlining an alternative for their removal. The adsorption of four representative antibiotics from commonly used families (fluoroquinolones, β-lactams, trimethoprim and sulfonamides) was performed over vegetal powdered activated carbon. The evolution of the adsorption was studied during 60 min for different initial antibiotic concentrations, not only individually but also simultaneously to determine competitive adsorption. Moreover, this research studied the adsorption isotherms and kinetics of the process, as well as the pH influence, FTIR of the Activated Carbon before and after adsorption was carried out. Trimethoprim and sulfadiazine showed more affinity for the adsorbent than amoxicillin and enrofloxacin. This trend might be attributed to their structure, capable of stablishing stronger π-π interactions with the adsorbent, which showed high affinity for the active sites of the adsorbent via FTIR. In addition, the sorption isotherms of the substances tested followed a Langmuir type isotherm, except for amoxicillin which presented similar fittings to both Langmuir and Freundlich isotherms. The antibiotics followed pseudo-second order kinetics. Sulfadiazine and amoxicillin gave better performances in acidic conditions. By contrast, the sorption of trimethoprim was favored in basic environments. Variations of pH had a negligible effect on the removal of enrofloxacin.

Keywords: antibiotics removal, Powdered Activated Carbon (PAC), Drinking Water Treatment Plants (DWTPs), sulfonamides, fluoroquinolones, trimethoprim, ß-lactams

1. Introduction

In recent decades there has been a considerable increase in the use of antibiotics to fight a variety of diseases, leading to a rise of 65% of global consumption between 2000 and 2015 (Klein et al. 2018). As 90% of antimicrobials taken are subsequently excreted (Bartlett et al. 2013; European Centre for Disease Prevention and Control. Antimicrobial Consumption. 2018; EMA 2019), there is growing concern about the impact of this extensive use of antibiotics on surface waters. Concentrations of various pharmaceutical products on a worldwide scale of up to 450 µg/L in natural waters and up to 14000 µg/L in wastewaters have been reported (Fick et al. 2009; Jiang et al. 2011; aus der Beek et al. 2016; Danner et al. 2019). These levels can cause serious public health problems because of the generation of antimicrobial-resistant bacteria (ARB) associated with the consumption of polluted water (Ventola 2015). In addition, it is widely believed that high concentrations of antibiotics could lead to negative effects on aquatic environments such as fish reproduction changes (Mceneff et al. 2014).

Conventional treatments applied in Waste Water Treatment Plants (WWTPs) are not able to completely remove antibiotics from natural waters because they are not designed to remove low biodegradability organic pollutants (Watkinson et al. 2007; Moles et al. 2020a). This results in the presence of antibiotics in natural surface waters, which are the main source of drinking water. Various approaches have been tried to remove antibiotics not only in WWTPs, but also in Drinking Water Treatment Plants (DWTPs). The use of advanced oxidation processes (AOPs) is currently being researched for the removal of antibiotic compounds (Saitoh et al. 2017; Yang et al. 2019; Moles et al. 2020b). Meanwhile, conventional treatments such as adsorption are being applied to remove antibiotic compounds in DWTPs. Various materials, such as nanotubes and hydrogels, have been used as adsorbents (Wang et al. 2019; Yang et al. 2019; Ma et al. 2020). Nevertheless, adsorption onto activated carbon (AC) is one of the most common processes involved in this type of facility.

Vegetal activated carbon can be produced from a variety of sources, including corncob, rice hulls, corn straw or date stones (Ahmed and Darweesh 2017; Liu et al. 2017; Silva et al. 2018; Peñafiel et al. 2019). Among the various classification criteria apart from their origin, particle size is widely used to differentiate types of Activated Carbon (Lima et al. 2016). Those with a larger particle size are classified as granular activated carbon (GAC), while smaller sizes are known as powdered activated carbon (PAC). Both are commonly used in DWTPs.

The main advantage of PAC over GAC is that higher yields are achieved because of its higher contact surface. Its recovery, however, is the main disadvantage, as PAC adsorption usually involves a filtration or a coagulation-flocculation-decantation step. Both methods of recovery lead to higher costs (Chandrasekhar 2019).

As one of the objectives was to study the suitability of sorption over a variety of antimicrobial agents, four families of antibiotics commonly reported in surface waters were used: sulfonamides (Babić et al. 2006; Senta et al. 2013), trimethoprim (Al Aukidy et al. 2012; Golovko et al. 2014), β-lactams (Tuc Dinh et al. 2011; Rossmann et al. 2014) and fluoroquinolones (Tamtam et al. 2008; Wagil et al. 2014). These families are also considered to be a potential risk for the environment because they have been demonstrated to generate AMR and they are showing an incipient consumption in Europe (Carvalho y Santos 2016; EMA 2019). A representative antibiotic from each of the families was chosen: sulfadiazine (sulfonamide), trimethoprim (trimethoprim), amoxicillin (β-lactam) and enrofloxacin (fluoroquinolone).

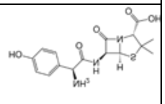
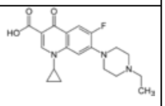
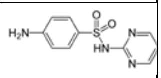
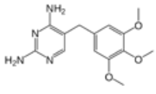
Some studies have focused on antibiotics commonly used in combination, such as trimethoprim/sulfadiazine or trimethoprim/sulfamethoxazole (Guillossou et al. 2019, 2020), or on groups of antibiotics belonging to the same family (Choi et al. 2008; Fu et al. 2017). However, this research work studies four antibiotics belonging to different families in order to analyze their adsorption performance over activated carbon. There is a lack of studies of simultaneous competitive adsorption of antibiotics, which has been also carried out in this study. This approach is considered to be closer to the real situation found in fresh water. Furthermore, the effect of the pH influence over the removal process of antibiotics from different families remains unclear, so this is also analyzed in this research. Moreover, the adsorption kinetics and isotherms of the selected antibiotics were also evaluated.

2. Materials and methods

2.1 Antibiotic characterization

The four antibiotics were supplied by Sigma-Aldrich. Their characteristics are shown in **Table 1** including the structure and physicochemical properties of the molecules.

Table 1. Characteristics of the antibiotics selected: name, group, CAS number, molecular Weight, acid dissociation constant, octanol water partition coefficient and molecular structure

Antibiotics	**Group**	**CAS**	**MW (g/mol)**	**pKa**	**Log (K_{OW})**	**Molecular Structure**
Amoxicillin	β-lactam	26787-78-0	365.4	3.2 (carboxyl) 11.7 (amine)	0.87	
Enrofloxacin	Fluoroquinolone	93106-60-6	359.4	6.2	0.39	
Sulfadiazine	Sulfonamide	68-35-9	250.3	6.4	-0.09	
Trimethoprim	Trimethoprim	738-70-5	290.3	7.1	0.91	

Antibiotic concentration was quantified by UV-Vis adsorption molecular spectrometry, using a Helios ThermoSpectronic and a quartz cell with a 1.0 cm path. The characteristic wavelength for sulfadiazine was 254 nm, 202 nm for trimethoprim, 225 nm for amoxicillin and 271 nm for enrofloxacin (Carlesi Jara et al. 2007; Delgado et al. 2013; Chen et al. 2017; Zhao et al. 2019). Calibration curves were made using solutions of each antibiotic in deionized water in a range of 1-20 mg/L. The calibration curves for all the antibiotics showed a high linearity (r>0.99). Therefore, concentrations as low as 1 mg/L could be reliably measured under these conditions.

The determination of the concentration of antibiotics for the simultaneous adsorption essay was carried out via HPLC/MS/MS triple quadrupole. A Waters Acquity UPLC was used for the liquid chromatography with a Waters BEH C18 column, 1.7 µm particle size, (2.1x100) mm. A Waters Xevo TQ-S micro was used to carry out the mass spectrometry following the PT109 standard method.

2.2 Adsorbent characterization

VPlus vegetal powdered activated carbon (PAC) supplied by Chemivall was used as the adsorbent. According to the specifications given by the manufacturer, the particle size of 90% of the constituent particles was under 0.044 nm. Further specifications given are 10.3% humidity when packaging, 1.8% ashes on dry basis, as well as an iodine index of 950 mg/g.

Partial elemental analysis was also carried out, obtaining the carbon (95.8%), hydrogen (0.1%) and nitrogen (0.2%) contents. A SEM study complemented this information, the A SEM (JEOL JSM 64000) coupled to an Electron Back Scater difractor (INCA 300 X-sight, Oxford instrument) allowed to determine other relevant elements such as oxygen (2.9%), aluminum (0.4%), silicon (0.7%), and iron (0.2%). In addition, a BET isotherm was performed, using a Chemisorb 2700 (micrometrics Instruments), measuring the flux of N_2 at a temperature of 77K, yielding a superficial area of 745.4 m^2/g. The adsorbent was also characterized via FTIR spectroscopy before and after the adsorption of amoxicillin in a Bruker Vertex 70 spectrometer. The measurement of the samples was carried out in a KBr disk. The acquisition range of the characterization was 400-4000 cm^{-1}, the resolution was 4 cm^{-1} and the number of cumulative spectra was 32.

2.3 Experimental procedure of antibiotic adsorption

Batch mode adsorption experiments were carried out to study the effect of the initial antibiotic concentration during 60 min of contact time. The concentrations studied were within a range from 5 mg/L to 50 mg/L (5, 15, 25, 35 and 50 mg/L) prepared by dilution of each antibiotic individually in deionized water. For each initial concentration, eight flasks were prepared with 100 mL of the corresponding solution. The adsorption experiments were run for different times for each one of the aforementioned flasks: 5, 10, 15, 20, 30, 40, 50 and 60 min. The experiments were conducted in a Jar-test at 150 rpm in a continuous stirred-tank reactor at pH=6.5 applying a 0.1 g/L PAC dose. Simultaneous competitive adsorption experiment were carried out using 15 mg/L of initial concentration of each antibiotic mixed in a pH=6.5 ultrapure water solution in presence of 0.1 g/L of PAC. After the adsorption had taken place, the whole content of the flasks was filtered using a 0.45 μm nylon filter and the antibiotic concentration was analyzed by the methodology described in section 2.1.

In order to know the effects of acidic or basic environments on the adsorption process, solutions of 15 mg/L of each of the antibiotics were prepared in different pH conditions (pH 2-10). The pH was adjusted adding NaOH 0.1 mol/L or HCl 1 mol/L and measured by a Crison GLP 21 pH meter. The experimental conditions were: 0.1 g/L PAC solution volume of 200 mL and 60 min of contact time. Each experiment was conducted at least twice; standard deviation is not featured as it is negligible.

$$q = \frac{(C_0 - C_f)}{M} * V \qquad \textbf{(Eq. 1)}$$

$$Removal\ (\%) = \frac{C_0 - C_f}{C_0} * 100 \quad \textbf{(Eq. 2)}$$

The performance of PAC adsorption was evaluated by mean of the parameter q (mg of antibiotic adsorbed per gram of PAC), by means of the **Eq. 1**, where C_0 is the initial antibiotic concentration (mg/L), C_f is the antibiotic concentration at any time given (mg/L), M the adsorbent mass (g) and V the volume in which the adsorption experiment is carried out (L). Moreover, removal percentage was also used to determine the adsorbed performance, applying **Eq. 2**.

The effect of different pHs over the adsorbate was also studied via determination of the point of zero charge, pH_{pzc}. The point of zero charge is the pH value in which a surface presents a net charge equal to zero. A negative net charge is caused on the surface by pHs superior to pH_{pzc}, while inferior values cause a positive charge. As the electrostatic attraction or repulsion could influence the process, the determination is necessary. A pH_{pzc} of 7.3 was obtained following a sweep method described in the literature (Rivera-Utrilla et al. 2001). More precisely, the pH was adjusted to a value between 3 and 9 by addition HCl or NaOH solutions. The carbon sample was added to the solution and after 3h, and then pH was measured and plotted against the initial pH. Finally, the curve crossed the line $pH_{initial}=pH_{final}$ was taken as the point of zero charge, pH_{PZC}.

2.4 Adsorption kinetic and thermodynamic determination

Both isotherms and kinetics of the sorption process were studied using the data derived from the experiments of adsorption of the antibiotics at pH=6.5. There was no need for a separate experimental design for the study of the isotherms given the existence of experiments with different concentrations of a specific antibiotic. Moreover, the adsorption kinetics was determined by the study of the evolution of an initial concentration of the antibiotics.

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \qquad \textbf{(Eq. 3)}$$

$$\frac{q_e}{K_F} = {C_e}^{1/n} \qquad \textbf{(Eq. 4)}$$

Various experimental models were considered, in order to determine which one is suitable to describe the behavior of antibiotics adsorption. The vast majority of the consulted bibliography (Ismadji et al. 2009; Ahmed y Theydan 2014; Yue et al. 2014; Peñafiel et al. 2019) make use of the Langmuir (**Eq. 3**) and Freundlich (**Eq.4**) non linear adsorption models. C_e corresponds to the solute concentration (mg/ L) in equilibrium conditions; q_e corresponds to the q value (mg of antibiotics adsorbed per gram of adsorbent), indicative of the adsorption performance in equilibrium conditions. In **Eq. 3** q_m is a constant related to maximum adsorption capacity (mg/g) and K_L is related to the adsorption energy (L/mg). In **Eq. 4** K_F is a constant that indicates the relative adsorption capacity (mg/g)·(L/mg)L/n), and n is a dimensionless quantity related to the intensity of adsorption. Both models were applied to the results, and were represented graphically over the experimental data using the *Solver* complement of *Microsoft Office Excel.*

$$R_L = \frac{1}{(1+C_0 * K_L)} \qquad \textbf{(Eq. 5)}$$

In addition, when the experimental data are fitted to a Langmuir isotherm model, the separation factor R_L can be determined (**Eq. 5**). R_L is an dimensional unit used to evaluate the performance of the adsorption process under Langmuir conditions, where K_L is the Langmuir constant related to the adsorption energy (L/mg), and C_0 is the concentration of the adsorbent (mg/L) (Ofomaja y Ho 2007). The value of the factor usually ranges between 0 and 1, being 0 an irreversible adsorption, while a value of 1 indicates linear adsorption. Thus, values of R_L between 0 and 1 characterize the adsorption process as favorable, and a factor higher than 1 means that desorption would take place instead of adsorption.

$$\ln(q_e - q_t) = lnq_e - k_1 t \qquad \textbf{(Eq. 6)}$$

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad \textbf{(Eq. 7)}$$

$$q = kt^{1/2} + l \qquad \textbf{(Eq. 8)}$$

Regarding the kinetics, the experimental data fulfills follows pseudo-first order (**Eq. 6**), pseudo-second order (**Eq. 7**) and Weber-Morris intraparticular diffusion (**Eq. 8**) and as reported in the bibliography (Ahmed y Theydan 2014; Yue et al. 2014; Ensano et al. 2019). In **Eq.6** k_1 is the rate constant of the pseudo-first-order model (L/min). In **Eq. 7** K_2 is the rate constant of the pseudo-second-order model (g/(mg·min)). In **Eq. 8** l is a parameter relating to the thickness of the boundary layer and k is the intraparticle diffusion rate constant.

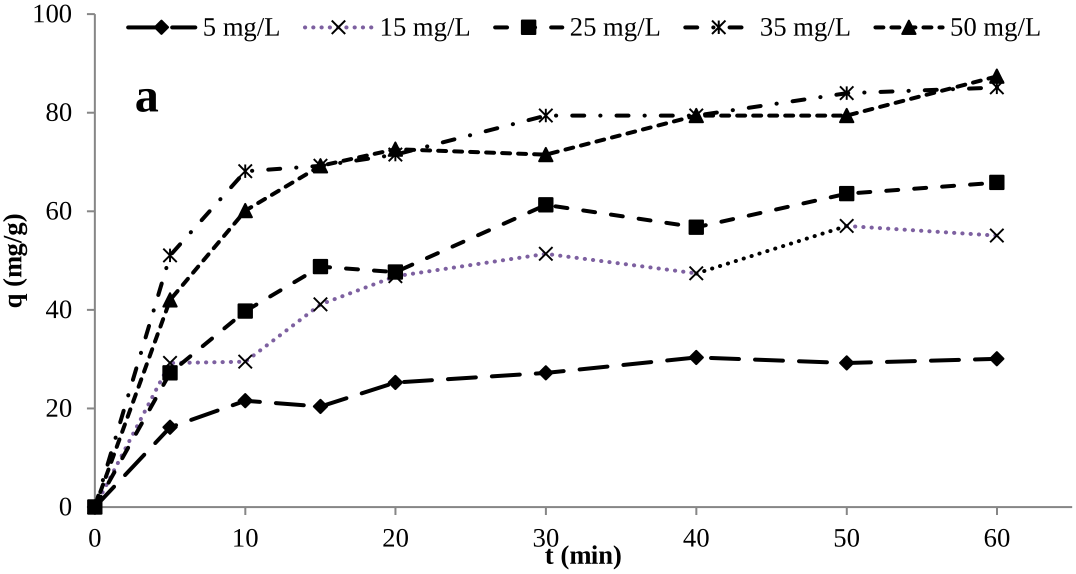
3. Results and discussion

3.1 Antibiotics adsorption experiment

The sorption patterns of the four antibiotics over PAC have been shown to be effective. The less concentrated solutions (5 mg/L) showed minor adsorption, while an increase in the initial concentrations of the antibiotics increased the adsorption, as seen in Fig. 1. This trend is consistent with the results reported in similar studies (Liu et al. 2017). The low yields for 5 mg/L are explained by the limited quantity of antibiotic present in the solution. Higher concentrations (15-

192 50 mg/L), by contrast, display higher yields. Although adsorption performance is directly related

193 to concentration, slight differences were found for high concentrations.



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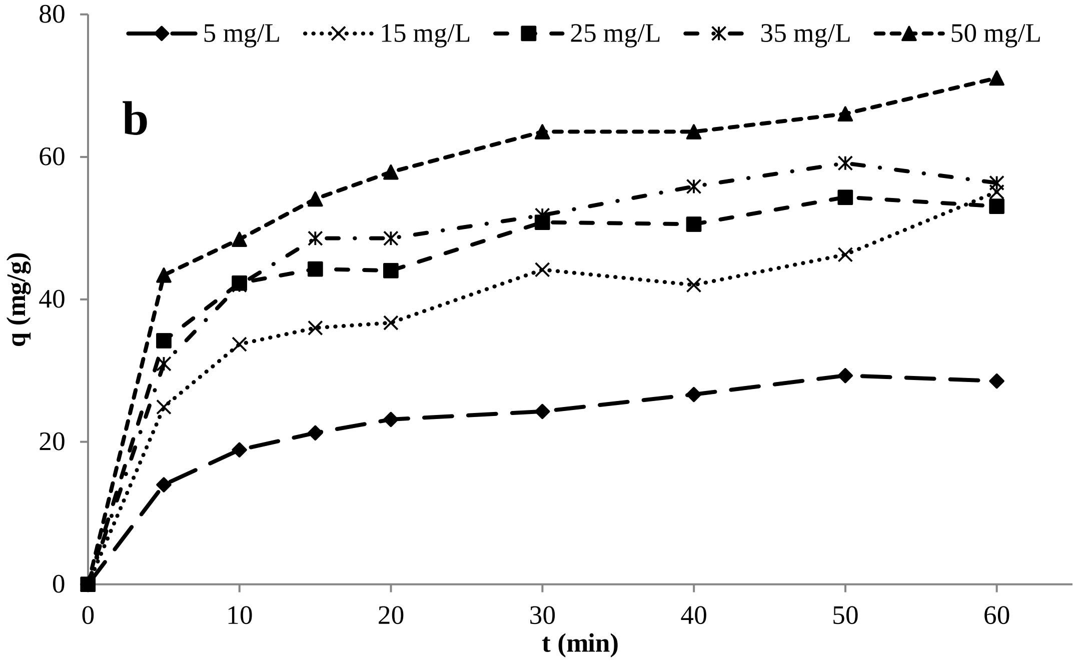

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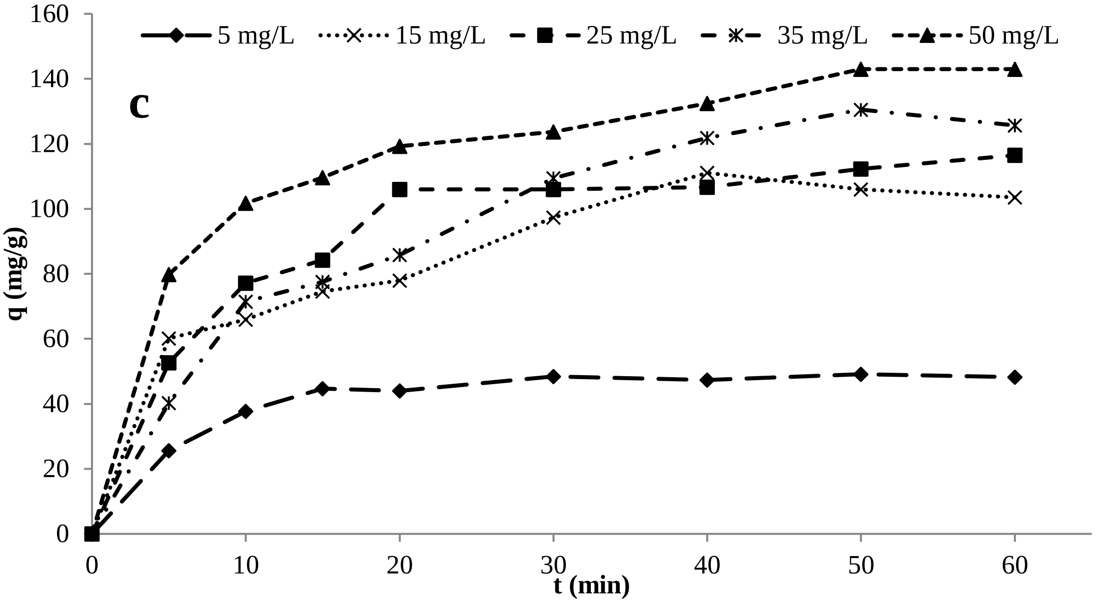


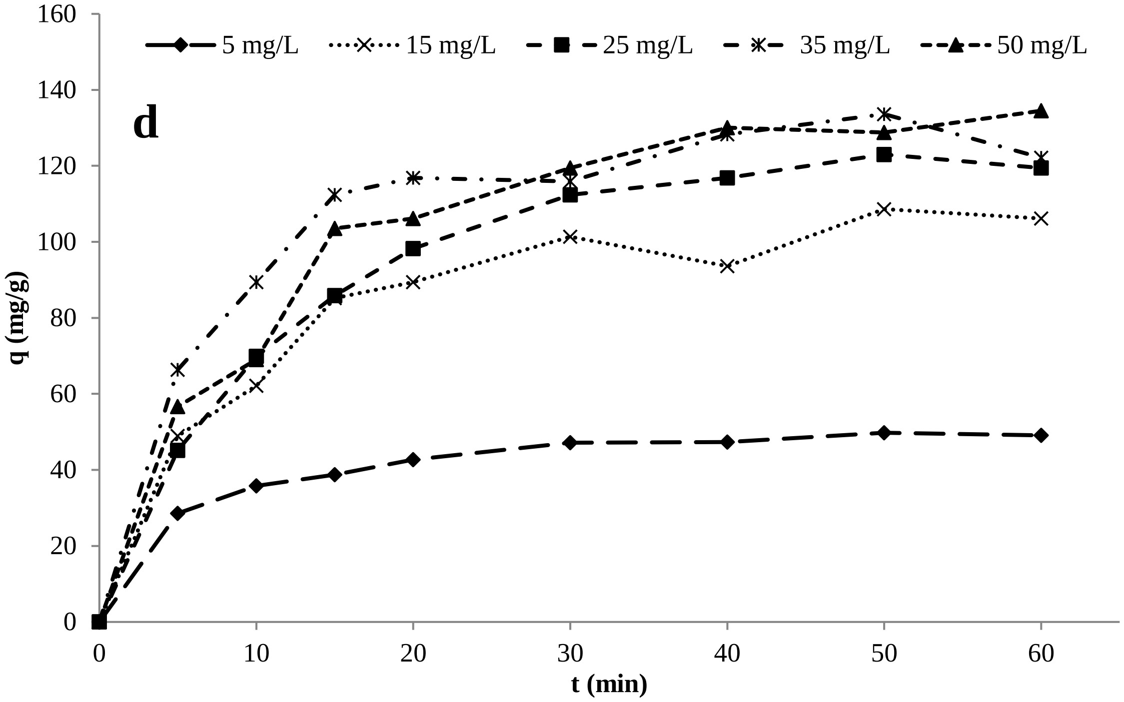


Fig 1 Amoxicillin (a), enrofloxacin (b), sulfadiazine (c) and trimethoprim (d) q (mg/g) evolution during 60 min of treatment (initial concentration: amoxicillin=5-50 mg/L, enrofloxacin=5-50 mg/L, sulfadiazine=5-50 mg/L, trimethoprim= 5-50 mg/L, PAC dose=100 mg/L, pH=6)

Fig 1 shows the adsorption performance results for the four antibiotics. The results suggest that, starting from 50 mg/L and applying 60 min of adsorption, both sulfadiazine and trimethoprim have the highest q values: 143 mg/g and 135 mg/g respectively. Amoxicillin and enrofloxacin both display similar q values at lower concentrations, while amoxicillin shows a higher adsorption capacity at higher concentrations. Starting from 50 mg/L and applying 60 min of adsorption enrofloxacin reaches an adsorption performance of 71 mg/g while amoxicillin adsorption featured 87 mg/g. The suitable contact time of adsorption for each antibiotic was also determined by the observation of changes in the slope in **Fig 1**. As this time is also dependent on the initial concentration of the antibiotic, the suitable contact time is determined for the maximum initial concentration (50 mg/L). The suitable amoxicillin contact time was 20 minutes, while for the rest of the target antibiotics it was 30 minutes.

The adsorption of antibiotics on activated carbon is determined by a variety of factors, such as (i) the ability of the adsorbed molecule to establish π- π interactions between its aromatic rings and the surface of the adsorbate, (ii) the formation of hydrogen bonds with electronegative atoms present in the molecule and (iii) electrostatic interactions (Peng et al. 2016; Moura et al. 2018). Other authors have also regarded hydrophobia as being influential in the process (Peñafiel et al. 2019). The structures of both sulfadiazine and trimethoprim feature two aromatic rings, while enrofloxacin and amoxicillin feature one aromatic ring and show a weaker adsorption over PAC. Therefore, π- π interactions are regarded as the main influential factor in the performance of the sorption process for the studied molecules.

In order to confirm the importance of each interaction type between the adsorbed molecules and PAC, a FTIR was performed. Two samples of the adsorbent were tested, before and after adsorbing amoxicillin during 60 minutes. As it is shown in **Table S1**, the new bands found in the amoxicillin-adsorbed PAC are located in the range between 1600 and 2000 cm^{-1}, being these assigned to aromatic C-C bonds and aromatic ring overtones, which indicate the adsorption of the rings over PAC. C=O bonds, present in the amoxicillin molecular structure, also appear in these range. No bands appear between 3000 and 3500 cm^{-1}, the characteristic range of O-H bonds. This support the previous hypothesis of π- π interactions being the main factor determining the success of the adsorption process, as no evidence of hydrogen bonds is found.

Simultaneous adsorption results are shown in **Fig 2**. The results suggest that the removal rates of antibiotics simultaneous adsorption tend to be inferior than when an individual adsorption is performed. This trend could be due to a competitive affinity for the active sites of PAC, as literature suggests (Ahmed and Hameed 2019). Regarding selected antibiotics, amoxicillin presents a similar removal rate in the simultaneous and individual adsorption. This behavior could be attributed to the presence of aromatic C-C, which have been reported to have high-affinity to the adsorbent, and concretely to the PAC used in this study, this affinity was proved via FTIR (**Table S1**). Finally, it should be noticed that the initial concentration of the selected antibiotics was three orders or magnitude superior to the usual concentration reported in natural waters and wastewaters. This fact implies that the adsorbent tends to be colmated earlier and the antibiotics would predictably reach superior removal rates if the adsorption is applied to real wastewater.

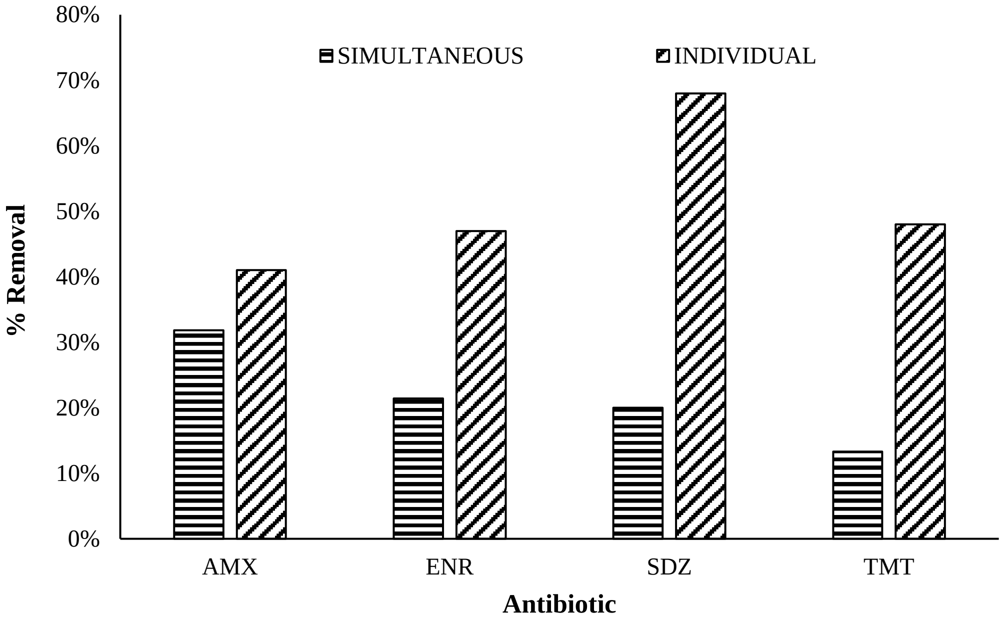


Fig. 2. Simultaneous antibiotic adsorption versus individual antibiotic adsorption for amoxicillin, enrofloxacin, sulfadiazine and trimethoprim (C_0=15 mg/L of each antibiotic, PAC dose= 100 mg/L, contact time= 30 min, ultrapure water)

3.2 Study of pH influence

Fig 3 shows the results of the study of the pH influence on the adsorption performance of the selected antibiotics. The results suggest that the sorption potential of sulfadiazine dramatically decreases with an increase in the pH, particularly in basic environments. A similar but less steep trend was observed when the adsorption was performed with amoxicillin, which presented optimal conditions for adsorption at pH=4. The yield of the process with enrofloxacin was barely affected by variations of the acidity, as no significant changes were registered in the range of pH=2-8, and a small decrease of the adsorption potential was observed for pH=10. However, trimethoprim showed a distinct behavior from the rest of the antibiotics as the increase in pH caused a higher adsorption yield. It should be noted that at pH=7 (typical pH of drinking waters) similar removal percentages of sulfadiazine and trimethoprim were achieved, while the percentage removal of enrofloxacin and amoxicillin remained almost constant.

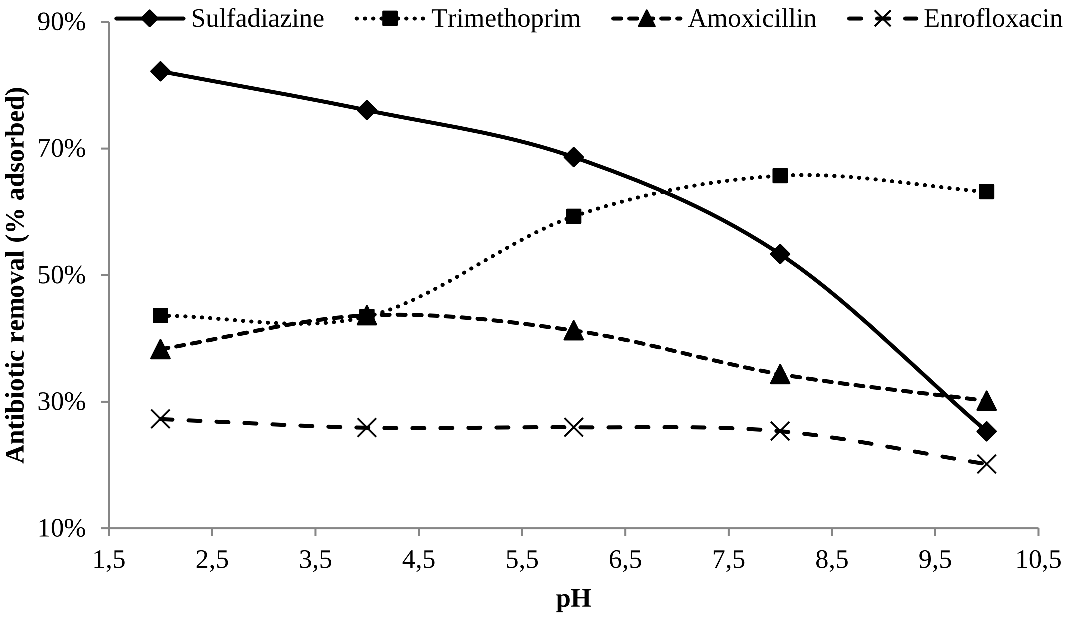


Fig 3 Comparison of variation of the percentages adsorbed of initial antibiotic concentrations for amoxicillin, enrofloxacin, sulfadiazine and trimethoprim after 60 minutes (initial concentration: amoxicillin= 15 mg/L, enrofloxacin = 15 mg/L, sulfadiazine = 15 mg/L, trimethoprim= 15 mg/L, PAC dose=100 mg/L, pH=2-10).

The behavior of the adsorption of the antibiotics at different pHs is determined by the electrostatic interactions between the adsorbate and the molecules. For pH<pH$_{pzc}$, the surface of the activated carbon is positively charged, while for pH>pH$_{pzc,}$ the absorbate presents a negative charge at its surface. The pH of the environment also influences the possible appearance of charges in the studied molecules, thus both repulsive and attractive interactions could be caused. A molecule with a similar pKa value to pH_{pzc} would result in worse adsorption performances at pH values furthest from the point of zero charge, due to a lesser electrostatic repulsion for values of pH near pH_{pzc} (Rivera-Utrilla et al. 2001; Peñafiel et al. 2019). This is the case of trimethoprim (pKa =7.1), in which this effect has an important influence, especially in acidic pHs.

However, the influence of the point of zero charge can be countered by several phenomena. Sulfadiazine and enrofloxacin include oxygen and fluoride atoms in their structures, which can establish hydrogen bonds with the adsorbate surface. This is believed to cause higher removals of both antibiotics in acidic conditions, as sorption is enhanced in spite of electrostatic repulsion. By contrast, counter effects in amoxicillin may be due to the ionization of the carboxyl group (pKa=3.2). The presence of a negatively charged group in the molecule, along with a positively charged activated carbon surface, increases the possibility of electrostatic attractions when $pH<pH_{pzc}$. The similar values in the acidic environments could be explained by this effect.

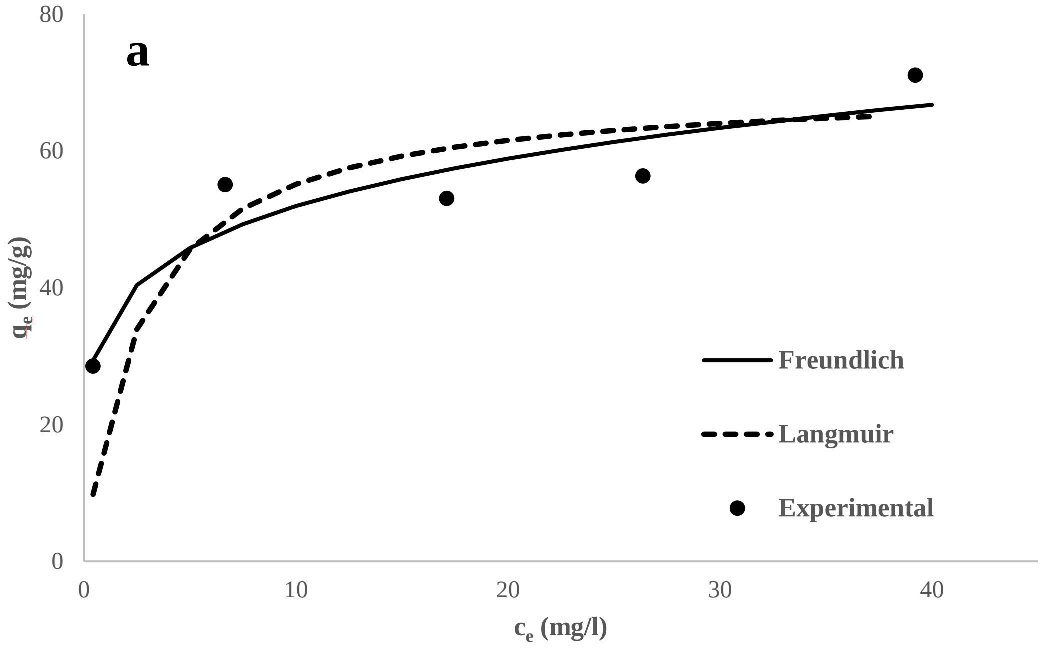
3.3 Thermodynamic determination of adsorption

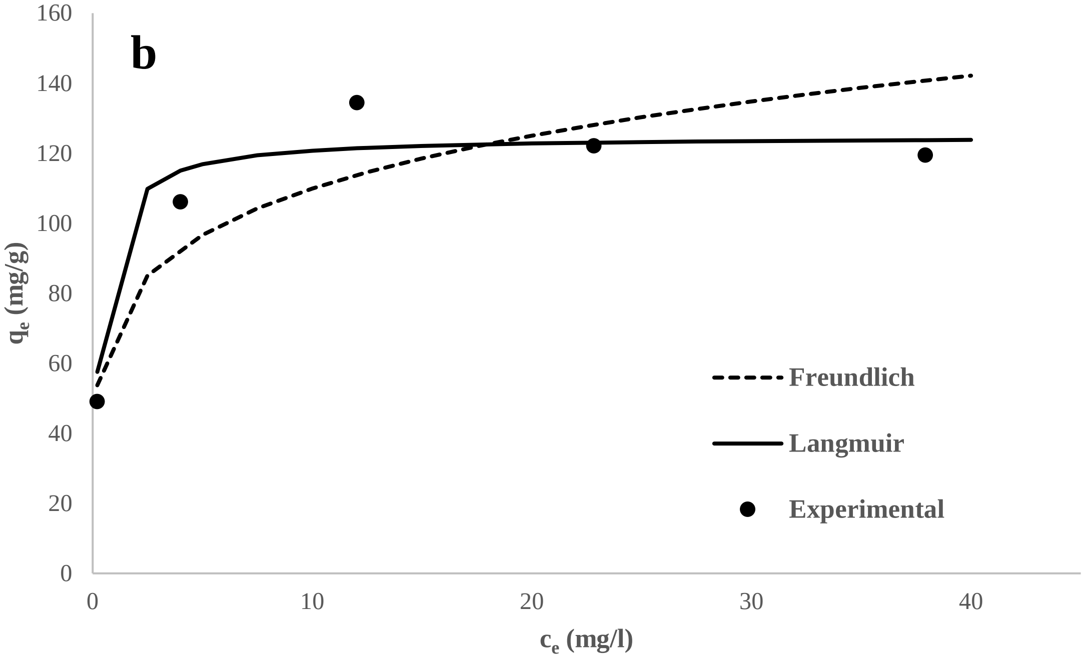
The experimental data were fitted to Langmuir and Freundlich isotherms. The fitting parameters are shown in **Table 2**. The results suggest that the sorption process of sulfadiazine, trimethoprim and enrofloxacin can be explained better with the Langmuir experimental model, given the regression coefficient values. Therefore, it is assumed that the sorption of these antibiotics is chemisorption, which implies the formation of a monolayer and adsorption sites uniformly distributed on the adsorbent. Furthermore, it is selective to antibiotics, and by-products are likely to be generated as a result of the formation of new chemical bonds.

The affinity for the Langmuir experimental model has been found in previous studies performed with trimethoprim (Ngo et al. 2010; Liu et al. 2012), sulfadiazine (Liu et al. 2017) and enrofloxacin (Chowdhury et al. 2019; Mogolodi Dimpe y Nomngongo 2019). In the case of amoxicillin, however, the results suggest that both Langmuir and Freundlich isotherms could explain the sorption in the conditions studied. Similar studies using amoxicillin showed a better fitting to the Freundlich experimental model (de Franco et al. 2017; Limousy et al. 2017). As the four antibiotics could be explained by the Langmuir isotherm model, RL can be studied. The obtained factor values show that the adsorption of the antibiotics over the powdered Activated Carbon is favored. The antibiotic with most affinity for PAC is trimethoprim as its R_l factor value (0.715) is the nearest to 0, and sulfadiazine has the lesser affinity of the four tested antibiotics (0.932). **Fig 4** represents the experimental data for the four antibiotics as well as the fitting to both isotherms.

Table 2 Numeric parameters of the fitting to Freundlich and Langmuir experimental models for amoxicillin, enrofloxacin, sulfadiazine and trimethoprim

Freundlich	**Amoxicillin**	**Enrofloxacin**	**Sulfadiazine**	**Trimethoprim**
N	3.87	5.72	7.68	6.85
K_f (L/mg)	35.05	34.91	85.54	79.11
Langmuir	**Amoxicillin**	**Enrofloxacin**	**Sulfadiazine**	**Trimethoprim**
q_m (mg/g)	80.41	61.12	137.22	125.88
K_L (L/mg)	0.86	1.91	0.73	3.98
R_L	0.921	0.840	0.932	0.715

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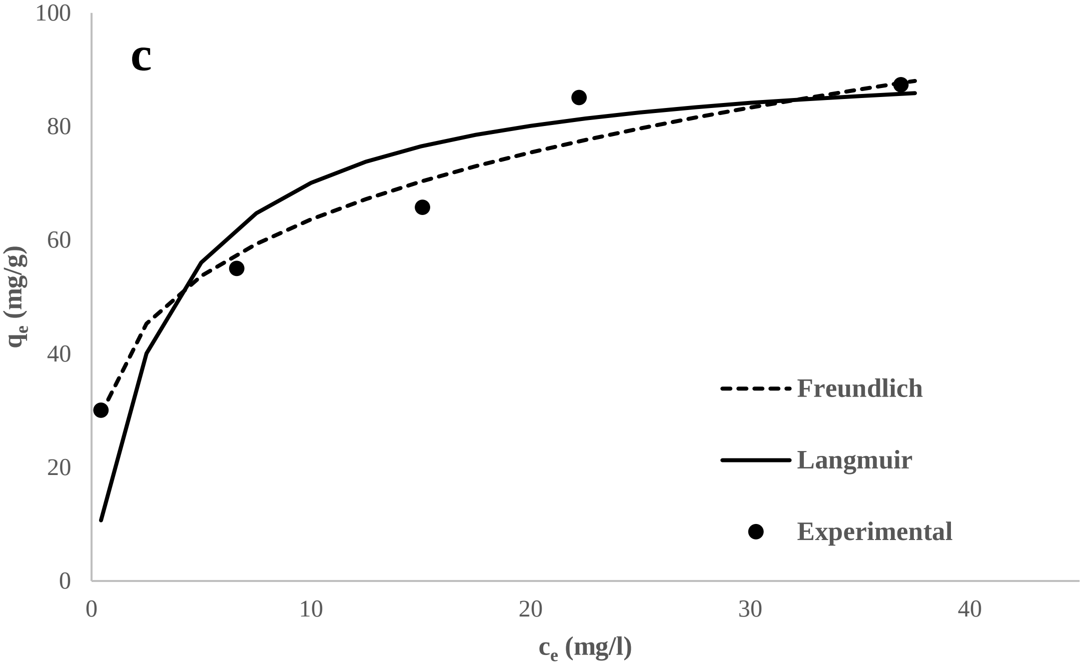
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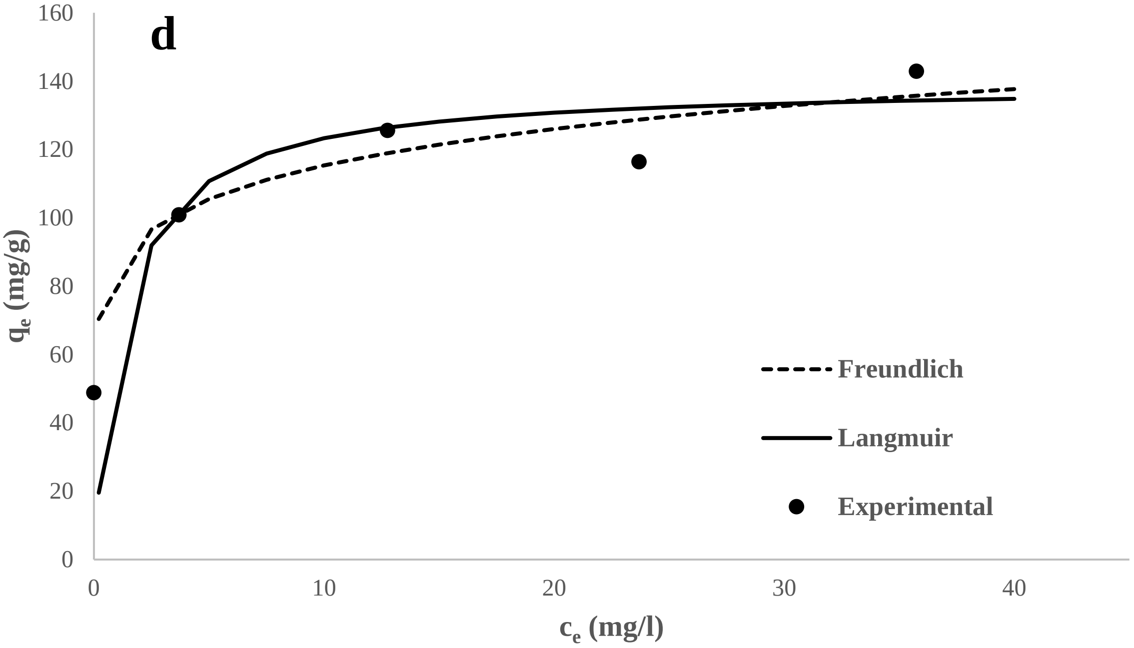

Fig 4 Experimental data and theoretical Langmuir and Freundlich isotherms for (a) amoxicillin, (b) enrofloxacin, (c) sulfadiazine and (d) trimethoprim: q (mg/g) evolution during 60 min of treatment (initial concentration: amoxicillin= 5-50 mg/L, enrofloxacin= 5-50 mg/L, sulfadiazine= 5-50 mg/L, trimethoprim= 5-50 mg/L, PAC dose=100 mg/L, pH=6).

3.4 Kinetic determination of adsorption

The q (mg/g) of every experiment was fitted to the pseudo-second order, Morrison-Weber intra-particle diffusion and pseudo-first order models. Regardless of the tested antibiotic or the initial concentration, the kinetics of the adsorption process presented an overall better fitting to the pseudo-second order equation, ruling out intraparticle diffusion as a limiting step. **Table 3** gathers the adsorption kinetics parameters for the fitting of both equations to the data of the antibiotics for an initial concentration of 50 mg/L.

Table 3 Kinetic fitting parameters for amoxicillin, enrofloxacin, sulfadiazine and trimethoprim (amoxicillin = 50 mg/L, enrofloxacin = 50 mg/L, sulfadiazine = 50 mg/L, trimethoprim = 50 mg/L, PAC dose =100 mg/L, pH = 6)

Pseudo second order	**Amoxicillin**	**Enrofloxacin**	**Sulfadiazine**	**Trimethoprim**
q_e (mg/g)	92.20	74.59	155.83	143.92
k_2 (g/mg min)	1.80 x 10^{-3}	2.55 x 10^{-3}	1.09 x 10^{-3}	6.99 x 10^{-4}
R	0.996	0.998	0.998	0.998
Intra-particle difussion	**Amoxicillin**	**Enrofloxacin**	**Sulfadiazine**	**Trimethoprim**
k (mg/g $min^{1/2}$)	6.65	4.73	10.85	13.45
I (mg/g)	36.64	34.62	64.36	28.51
R	0.923	0.980	0.973	0.943
Pseudo first order	**Amoxicillin**	**Enrofloxacin**	**Sulfadiazine**	**Trimethoprim**
q_e (mg/g)	56.76	43.55	92.80	127.17
-K_1 (L/min)	5.21 x 10^{-2}	5.21 x 10^{-2}	5.75 x 10^{-2}	9.52 x 10^{-2}
R	0.924	0.932	0.957	0.998

The suggested kinetics are consistent with the reported bibliography for enrofloxacin (Chowdhury et al. 2019), trimethoprim (Ngo et al. 2010), amoxicillin (Moussavi et al. 2013; Limousy et al. 2017) and sulfadiazine (Liu et al. 2017). This trend is reported in previous literature (Xu et al. 2016). **Fig 5** shows the linearization of the pseudo second order model for the four antibiotics with an initial concentration of 50 mg/L. It is observed that the antibiotics with a higher retention power, trimethoprim and sulfadiazine, have a bigger q_e and show a less steep slope

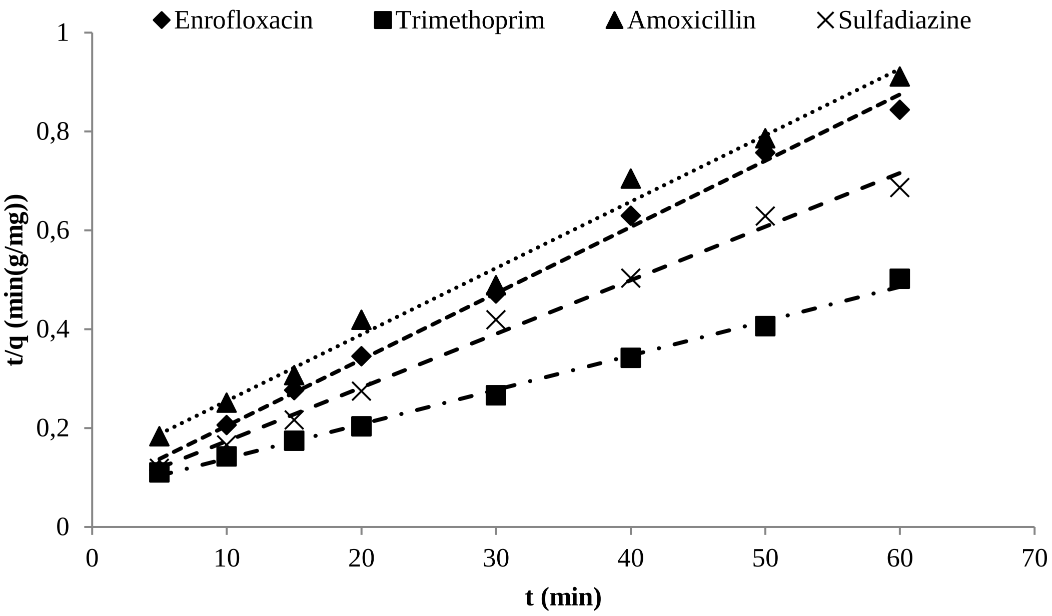

Fig 5 Variation of t/q [min (g/mg)] for amoxicillin, enrofloxacin, sulfadiazine and trimethoprim (initial concentration: amoxicillin= 50 mg/L, enrofloxacin= 50 mg/L, sulfadiazine=50 mg/L, trimethoprim = 50 mg/L, PAC dose=100 mg/L, pH=6.5).

4. Conclusions

A study of the adsorption of four antibiotics (sulfadiazine, trimethoprim, amoxicillin and enrofloxacin) over vegetal PAC was carried out, determining the influence of different parameters (antibiotic type, treatment time, initial concentration and pH) on the yield of the process. In addition, the isotherms and kinetics of the process were determined. The following conclusions can be drawn:

1. PAC adsorption is capable of removing from 28% (enrofloxacin) to 67% (sulfadiazine) of the selected antibiotics from water in one hour by applying a dose of 100 mg/L of PAC. The concentrations of antibiotics used in this experiment are higher than those usually found in natural waters and the process in these conditions has been shown to be effective. Therefore, the adsorption process will be effective in removing these emerging pollutants in a DWTP, where they are commonly present at trace levels.

2. The adsorption is enhanced in acidic conditions for sulfadiazine and amoxicillin due to the establishment of hydrogen bonds and the presence of a charged carboxyl group respectively, while trimethoprim performs better in basic environments, having a similar pKa to the point of zero charge which causes greater repulsion in low pHs. The adsorption of enrofloxacin is barely affected by variations in the pH due to the establishment of hydrogen bonds with the surface of the adsorbent.

3. Sulfonamides and trimethoprim show a higher affinity for vegetal PAC in the operating conditions in which the study was carried out due to the presence of aromatic ring in their structures and the establishment of hydrogen bonds. In comparison, the selected β-lactams and fluoroquinolones showed lower yields.

4. The kinetics of the adsorption process follows pseudo second-order kinetics for the four antibiotic families.

5. The equilibrium results obtained for the selected antibiotics fitted the Langmuir isotherm model, except in the case of amoxicillin, whose adsorption fitted both Langmuir and Freundlich isotherms.

6. FTIR characterization of PAC after amoxicillin adsorption as well as the simultaneous competitive adsorption essays of the target antibiotics showed that the antibiotics with structures capable of stablishing the higher number of π- π interactions tend to occupy easily the active sites of PAC.

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6. Supplementary material

Table S1. Frequency of bands found in the region between 1600 and 2000 cm^{-1} for amoxicillin-adsorbed PAC and their attribution.

Frequency (cm^{-1})	**Assignment**
1683-1695	Aromatic C-C
1697-1712	
1714-1729	
1731-1905	C=O (stretching)
1907-1914	Aromatic ring overtones
1916-1924	
1941-1949	

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