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Tetracycline adsorption on steam alternative activated carbon: kinetic and thermodynamic parameters

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ABSTRACT

Water pollution by emerging pollutants, such as antibiotics like tetracycline (TC), is a worldwide environmental problem. To eliminate TC from water, the present study used an advanced water treatment technology (sorption) that has shown a very good relation between cost and effectiveness. To develop a sustainable and cheap activated carbon with acceptable sorption capacity for TC removal, it was proved a friendly environmental activation by using an agricultural waste like alternative precursor: pecan nut shells and water-like activating agent. Four different materials were used for the sorption test: pecan nut shell carbonised and water activated (NAC-850), commercial activated carbon as reference (GAC), and both materials were modified with citric acid (NAC-850-mod and GAC-mod). All the materials were characterised by S_{BET}, scanning electron microscopy, energy-dispersive X-ray and Fourier transform infrared. It was calculated that the sorption equilibrium time for the TC, kinetic parameters for pseudo-first-order, pseudo-second-order and Elovich models; the sorption isotherms for Langmuir, Freundlich and Temkin and thermodynamic parameters (ΔH, ΔS, ΔG and Ea) also were applied. It evaluated the effect of pH and temperature and the presence of competitive ions in the aqueous media. The prepared activated carbons that showed the best sorption capacity were those that followed a citric acid activation. The kinetics experiments fitted to pseudo-second-order equation and to isotherm Freundlich model. The efficiency to remove the TC increased with the modification of the surface with citric acid between 5% and 11%. The activation/modification method applied is simple and economical and improves the TC sorption capacity that is equivalent to the removal efficiencies of commercial activated carbons.

Keywords: Activated carbon; Adsorption; Citric acid; Pecan nut shells; Tetracycline

1. Introduction

Emerging pollutants are chemicals that persist in the environment; they bioaccumulate through the food chain and pose a risk of adverse effects on human health and environment [1]. The new contaminants include bioaccumulable, persistent and toxic substances; and products such as personal care, pharmaceuticals, surfactants, industrial additives and a variety of chemical compounds. However, the incidence and the health risks for most of these antibiotics often used in the treatment of infectious diseases are not known [2]. Pharmaceutical antibiotics such as tetracycline (TC) have been widely used in human or veterinary therapy and agriculture industry. TCs are considered important antibiotics in pharmaceutical area for treatment of a lot of kind of infections [3]. TC in general is used to fight again diseases or even is incorporated into animal feeding to improve the production. Therefore, TC has been detected in substrates, which lead to important pollution problems [3].

Moreover, antibiotics are part of the range of emerging contaminants, which are not included in the current monitoring programs of water treatment [4] nor in the legislation of any country worldwide, so there is no legal regulation

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to determinate the maximum permissible concentrations thereof in the environment [5]. During the last decade, there was a significant amount of researches focused on the elimination of pharmaceuticals in wastewater, which reveals that treatment like flocculation, filtration, activated sludge and chlorination are not effective in removing these compounds [6].

Recent researches show that TC antibiotics are classified second in the production and use of antibiotics worldwide; thus is one of the antibiotics most frequently detected in wastewater [7,8]. As with most antibiotics, TCs are poorly metabolised and absorbed by humans and animals treated. Therefore, a large fraction (90%) is excreted in the urine and faeces as unchanged parent compound [9]. It has been shown that TC residues are frequently detected in several samples of soil and environmental water as surface, ground and drinking water [10]. At the same time, in pharmaceutical wastewater, it has been reported TC concentrations from 10 to 1,000 mg L^{-1} [11].

The main technologies employed nowadays focus on advanced oxidation processes including ozonation, photo-Fenton, photolysis, photocatalysis and electrochemical processes [12]. However, these technologies have limitations such a high cost of equipment and maintenance and energy. They must be combined with other methods to make it more effective; in the process, they can produce intermediaries more toxic than the parent compound, and yield is affected by organic matter, suspended solids, carbonates and bicarbonates, chloride ions, pH and temperature [13].

The term adsorption is commonly used to describe the tendency of molecules in aqueous phase to adhere to a field strength of a solid surface. This technique has the advantage of eliminating the analytes instead of producing potentially dangerous metabolites [6,14] unlike to some of the advanced oxidation processes mentioned. Also, adsorption can be applied to water containing both high levels of organic matter and high concentrations of antibiotics. Regarding the characteristics that must have the adsorbent, there are two of them to consider: the porosity and pore morphology [15]. It is not only desirable to have a well-developed microporosity, which increases their surface area but also to have mesoporosity and macroporosity that work as channels to allow easy access to the micropores and surface chemistry. However, while adsorption is a well-known process, in recent years, there are not many studies on this technology applied to the removal of antibiotics. Pecan nut shells are cheap and available precursors for activated carbon production. In the present study, this kind of materials could improve their sorption capacities by modifying their surface in a sustainable way with innocuous organic molecules such as citric acid. The advantage of this method is the preparation of the pecan nut shells activated carbon by one-step carbonization/activation process using also non-dangerous activating agents such as water. On the other hand, to our knowledge, this is the first study where these materials are used to eliminate TC from aqueous media.

Therefore, the aim of this work was to determine the sorption behaviour of TC by using unmodified and citric acid modified activated carbons obtained from Mexican pecan nut shells.

2. Materials and methods

2.1. Raw material

The pecan nuts (*Carya illinoinensis*) shells were obtained directly from the local producers in the State of Chihuahua in northern Mexico, and they correspond to Wichita and Western varieties. The shells with a brown colouration were dried at 105°C ± 5°C using a Shel Lab oven, were cracked into fragments with diameters around 0.5 and 1 cm and were used in these conditions for carbonization or activation. A simple characterization of the raw material prior carbonization and activation process was performed.

2.2. Activated carbon production

The pecan nut shells, after being drying for 24 h, were heated at 10°C min^{-1} up to 850°C under a nitrogen flow rate of 0.5 L min^{-1}; this temperature was selected because the furnace stabilization was reached at 850°C, and it was a temperature closer to that reported for activated carbons prepared from agricultural by-products [16,17]. After the maximum temperature was reached, steam was introduced into the furnace equipped with a quartz reactor. The steam activation was performed by introducing water with a peristaltic pump at the entrance of the quartz vessel at 0.7 mL min^{-1} for 80 min; the water drops were carried into the reactor by the gas used to maintain the inert atmosphere (N_2). After all of this, heating was stopped, and the samples were left to cool under nitrogen atmosphere in the reactor. These conditions were optimised in a previous study [16] and designed to follow a sustainable production process with the utilization of local resources; a direct activation process was used; and the activating agent was totally innocuous (water). After the process previously mentioned, a fraction of the material was modified with a 1-M citric acid solution [18]. The same procedure was used to modify a commercially activated carbon (GAC). Likewise, the material GAC was used in original form without modification.

The carbonaceous activated material obtained from pecan nut shells was called NAC-850, without any additional treatment. The modified materials with citric acid (CTR Scientific) were called NAC-850-mod and GAC-mod for the activated carbon obtained from pecan nut shells and for GAC, respectively. After the carbonization process, the materials were crushed in a hammer mill, and the particles were sieved reaching particle size between 0.5 and 1.0 mm; the particle sizes used for TC removal experiments were between 0.50 and 1.00 mm; this step was done to obtain similar particle sizes. This fraction was washed with distilled water (10 g L^{-1}) until the pH remained constant; finally, they were filtered and dried at 105°C ± 5°C. Mass yields were 23% for NAC-850 and NAC-850-mod. The total ash content as percentage w/w was calculated by the standard test method for activated carbon [19].

2.3. Activated carbon characterization

2.3.1. pH_{PZC} determination and total ash content

The pH_{PZC} was carried out by placing 100 mL of a 0.1-M NaCl solution in a closed Erlenmeyer flask, and the pH was adjusted to values between 3 and 11 by adding solutions of HCl or NaOH (0.1 M). Then, 0.05 g of each sample was added, and the final pH was measured after 5 d under stirring at 22°C. The pH_{PZC} is the point where the curve pH_{final} vs. $pH_{initial}$ crosses the line $pH_{final} = pH_{initial}$ [20].

2.3.2. Brunauer–Emmett–Teller surface area analysis

Some textural parameters of the carbonaceous materials, like surface area and porosity, were analysed by standard multipoint techniques of nitrogen adsorption. Non-modified and modified carbonaceous materials samples were heated at 373 K for 2 h before specific surface areas were measured. The N_2 isotherms were applied at 77 K in a Micromeritics Gemini 2360 instrument. The specific surface area (S_{BET}) and total pore volume (V_{total}) were obtained from the Brunauer–Emmett–Teller isotherm model. All the experiments were performed in duplicate.

2.3.4. Energy-dispersive X-ray and scanning electron microscopy

For scanning electron microscopy (SEM) observations, the material samples before contact with TC solutions were mounted directly on the aluminium holders and then observed. The carbonaceous materials were observed at 20 kV in a XL 30 Philips electron microscope. A magnification from 1,000× to 2,000× was used to obtain the images. At the same time, the microanalysis was done with an energy-dispersive X-ray (EDX) spectroscopy system to determine the elements contained on the surface of the carbonaceous materials.

2.3.5. X-ray diffraction

Powder diffractograms of the samples were obtained with a Siemens D500 diffractometer attached to a copper anode X-ray tube, operating at 20 kV with a scan range from 5° to 75°. The conventional diffractograms were used to identify the compounds to verify if any crystalline structure exists.

2.3.6. Fourier transform infrared analysis

The functional groups situated on the surface of the carbons were identified using the Fourier Transform Infrared (FTIR) analysis. The carbon samples were ground in a mortar prior to analysis. The analysis conditions were: a sample scan of 64 at a resolution of 4 cm^{-1} measured between 400 and 4,000 cm^{-1} using an FTIR Bruker Alpha Platinum-ATR instrument.

2.4. Tetracycline removal

2.4.1. Sorption kinetics

Batch contact time experiments were conducted at different temperatures (25°C, 35°C and 60°C) by stirring 0.5 g carbonaceous materials with 500 mL of TC solution (50, 100 and 300 mg L^{-1}), at 150 rpm; the initial concentration was established to have a representative and similar TC presence in water than those found in pharmaceutical and industry wastewaters. Initial pH values were carried out close to 4.0, 6.0 and 9.0, and were recorded at the end of the experiment. The test was done without light by using black polyethylene reactors. The equilibrium time was considered accomplished when no more changes occurred at the X-axis by plotting concentration versus time (t). The TC concentration in the solutions was determined using a Jenway® UV/Visible spectrophotometer Model 7315 at 355 nm. To investigate the mechanism of sorption, three kinetic models were tested: pseudo-first-order, pseudo-second-order and Elovich kinetic models.

2.4.2. Adsorption isotherms

Batch adsorption isotherms were conducted with 25 mL of synthetic solutions from 100 to 500 mg L^{-1} of TC and 0.05 g of carbonaceous materials. Black conical tubes were sealed and placed on an orbital shaker for 7 d at 25°C. After shaking, the equilibrium pH was measured and recorded; the samples were decanted; and the concentration of TC in the aqueous media was determined by UV/Vis spectroscopy with a spectrophotometer (7315, Jenway®).

3. Results and discussion

3.1. Activated carbon production

The prepared activated carbon by using Mexican pecan nut shells (NAC) has a yield of 23%. Other researchers where it was prepared activated carbons from different nut shells such as macadamia fruits showed yields between 20% and 25% [21]. In the same way, studies have been carried out using activated carbons prepared from macadamia nut shell, yielding around 30% [22].

3.2. Characterization of the prepared activated carbons

3.2.1. pH_{PZC} determination

The pH_{PZC} of the obtained materials tends to be slightly acidic (pH = 6) except for NAC 850 (pH = 8.5). This was probably because this parameter depends on electronic and chemical properties of the functional groups that are located on the surface of the activated carbon [17]. The determination of pH_{PZC} is known as the pH value required to give a net surface charge of zero; it is also designated as pH zero charge. This parameter is important because the net charge of the carbon is affected by the pH of the environment, causing the surface to be positive or negative by the loss or gain of electrons altering the adsorption capacity. Knowing the pH value of zero charge (where the positive and negative charges are equal) helps to know at what pH values the carbon would present positive or negative charge and increases its availability to trap molecules, depending on the conditions in which the medium is located. In a previous research [23], it was established this behaviour, where (i) at $pH < pH_{PZC}$, the global surface charge of the material is protonated and has a positive charge; (ii) at $pH = pH_{PZC}$, the surface has equal number of positive and negative charges; and (iii) at $pH > pH_{PZC}$, the overall surface of the material is mostly deprotonated and therefore has a negative charge [23].

The pH_{PZC} for NAC-850, GAC, NAC-850-mod and GAC-mod present a value of 8.5 for NAC 850; all the other materials had a zero-charge pH value of 6, which is considered a value slightly acid.

Observing these values, it can be established that the activated carbon from pecan nut shell modified with citric acid changed from a basic surface to a slightly acidic one. In the case of commercial activated carbon, its nature was acidic, and the modification did not cause changes in the net charge of the material; the same pH_{PZC} value has been observed before and after the modification by using citric acid. In a previous study, it was used a macadamia nut shell carbon [22] where a pH_{PZC} value of 8.74 was obtained indicating a predominance of basic groups, which is like the value obtained by NAC 850 (pH = 8.5).

3.2.2. Determination of total ash content

The ash percentages for all materials, in general had a high carbon content (>80%) and low ash content (<11%). This is a parameter used to quantify the amount of carbon that constitute the materials, since its structure can present inorganic compounds, which are reported as the total ashes percentage. Other prepared activated carbons from pecan nut shell showed a total ash content between 12% and 14% [17], which were considerably higher in comparison with those obtained in the present work, except for NAC-850 that was similar to reported values (10.25%).

3.2.3. Brunauer–Emmett–Teller surface area analysis

The solute adsorption depends on the surface area and on the porosity onto the adsorbent surface. Table 1 shows the specific surface areas for NAC-850, GAC, NAC-850-mod and NAC-850-mod. The GAC materials possess the highest surface area, and it is probably due to the chemical activation that follows the commercial activated carbons; on the other hand, the prepared activated carbons by physical activation have surfaces area slightly lower than GAC's materials due to the creation and opening of the restricted pores by steam water reaction effect. The surface area values obtained are in the same order of magnitude as those of other carbonaceous materials obtained from similar wastes [24]. NAC-850 exhibits a value for specific surface like NAC-850-mod indicating that the modification with citric acid does not affect this characteristic. For the GAC materials, this modification (citric acid addition) leads to a diminution of superficial area in 26.4%. Fig. 1 shows the nitrogen adsorption isotherm at 77 K for (a) NAC-850, (b) GAC, (c) NAC-850-mod and (d) GAC-mod. The mean pore for all the material has a measure between 2.4 and 2.6 nm that allows TC molecules penetrate into the pores of the activated carbons, since TC present sizes smaller than 2.16 nm [22]. The total pore volumes values for the activated carbons agreed with the values obtained for the surface areas. The mean pore diameters determined (Table 1) correspond to a mesoporous surface (from 2 to 50 nm).

Table 1
SSA, TPV, and MPD for the prepared activated carbons

Material	SSA ($m^2\ g^{-1}$)	TPV ($cm^3\ g^{-1}$)	MPD (nm)
NAC-850	524.1	0.322	2.458
GAC	828.3	0.539	2.600
NAC-850-mod	536.3	0.320	2.386
GAC-mod	610.0	0.403	2.634

3.2.4. Energy-dispersive X-ray and scanning electron microscopy

The SEM images of these materials are presented in Fig. 2. The elemental composition (EDX) of the NAC-850 shows that the major component was carbon with a total percentage of 74.65, followed by oxygen (17.71%) and potassium and calcium with similar values of 3.3%. Also, another minor percentage element was found: silicon, with a percentage <1%. In the same way, the elements founded in the NAC-850-mod were carbon (75.45%), oxygen (21.47%) and calcium (2.60%). Similarly, there are smaller constituents such as silicon and potassium with relatively low weights. The modified material (NAC- 850-mod) showed a slight increase in the composition of carbon and oxygen. In contrast, there was a notable decrease in the percentage of silicon, potassium and calcium. The elemental composition of the GAC showed that the largest constituent present is carbon (81.35%), followed by oxygen (15.76%) and silicon (1.02%); other elements in the material were in minority with a percentage <1%, such as aluminium, sulphur, potassium, calcium and iron. Comparing GAC-mod with GAC, it can be observed that most elements showed an increase in oxygen weight and a decrease in the percentage by weight of carbon when the material was modified with citric acid (GAC-mod), as well as the weight of silicon, and the other elements were practically maintained the same in both materials. However, iron doubled its weight after modification of the material.

Fig. 2 shows the SEM images of (a) NAC-850, (b) GAC, (c) NAC-850-mod and (d) GAC-mod. As can be seen, the surface of all the prepared materials presents roughness without any defined porous structure. The citric acid modified carbons surface appears to be a cleaner and more defined surface, indicating that the modification does not affect in important way the surface morphology.

3.2.5. X-ray diffraction

After the obtention of the X-ray diffraction images of the NAC-850 and GAC, it was observed that both materials do not present crystallinity; therefore, they are considered as amorphous materials. Despite this, two important peaks were observed principally in NAC-850, which correspond to calcite $Ca(CO_3)$ (JCPDS 47-1743) and quartz (JCPDS 33-1161), which are indicated by the red and green lines, respectively. Similar results were previously reported in another research where pecan nut shells were used as a precursor for activated carbon preparation [17].

3.2.6. Fourier transform infrared analysis

The functional groups of activated carbons usually govern the sorption processes. The FTIR spectra of the prepared carbons were realised to identify the groups on their surface. Fig. 3 shows the FTIR spectra of all the materials. In the particular case for NAC-850 and NAC-850-mod, absorption

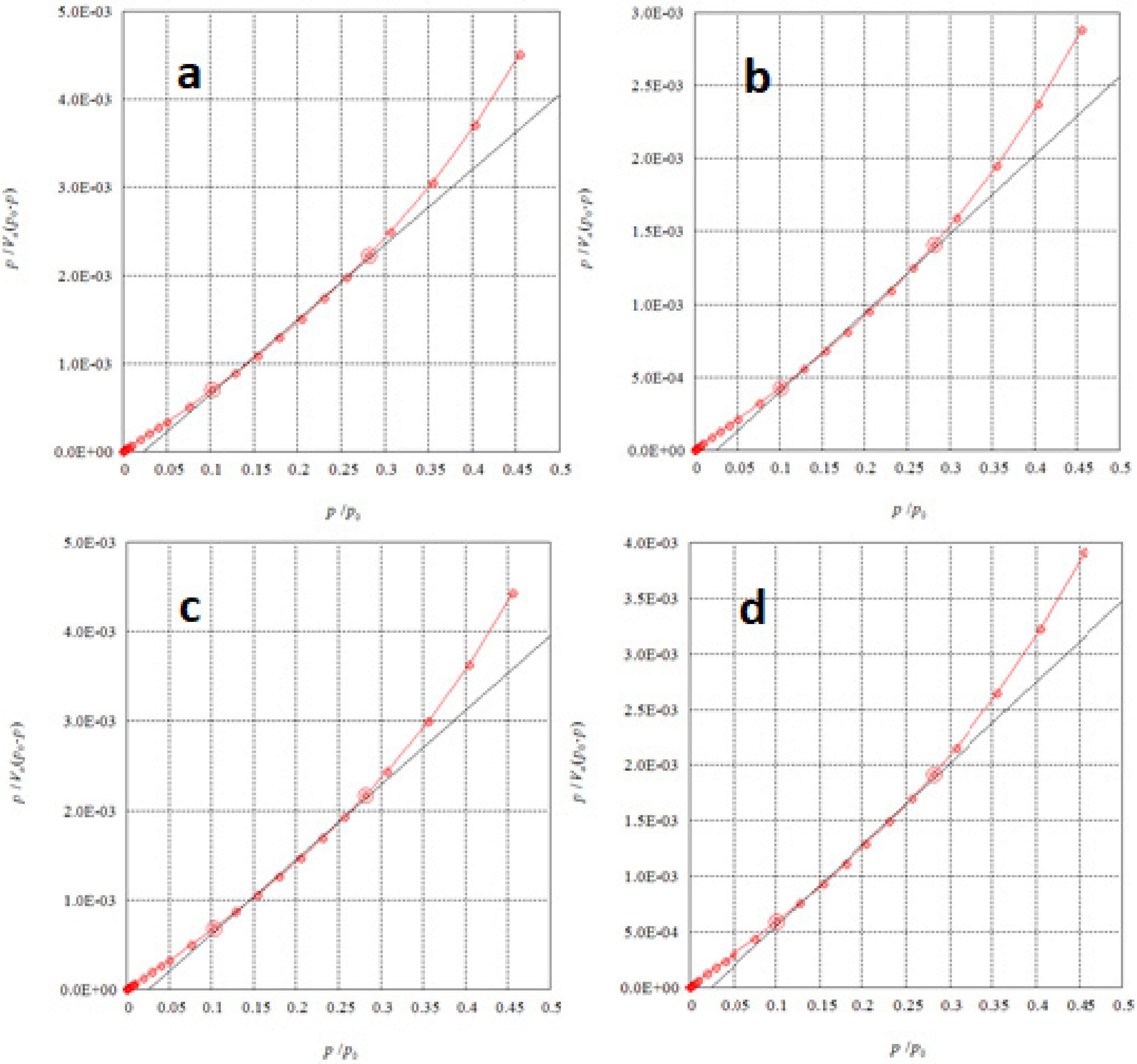

Fig. 1. Nitrogen adsorption/desorption isotherm at 77 K for: (a) NAC-859, (b) GAC, (c) NAC-850-mod, and (d) GAC-mod.

bands around 2,300 cm^{-1} are characteristic of vibrations in C–C bonds of alkane groups [25]. Also, absorption bands at 1,653 cm^{-1} represent vibrations at C=O bond of the carbonyl group from an aromatic ring of lignin, and at 1,517 cm^{-1} band, there are vibrations of C=C bond in the same aromatic ring. Absorption bands between 1,000 and 1,200 cm^{-1} indicate vibrations on C–O bonds of alcohols, phenols, carboxylic acids or ethers [26]. As can be seen, the spectrum of the unmodified material showed less intensity in the absorption bands compared with the modified material; absorption bands at 1,050 and 1,200 cm^{-1} indicate that some functional groups appeared after modification probably because of the alcohols and carboxylic acids from the citric acid. However, for the unmodified nut shell material (NAC-850), the absorption band was present at 1,050 cm^{-1} at lower intensity due to the vibration at C–OH bond of cellulose and hemicellulose (Fig. 3).

The FTIR spectra of the GAC and GAC-mod show absorption bands at 1,050 and 1,200 cm^{-1} corresponding to vibrations at C–O bonds of primary alcohols and carboxylic acids [26]. On the other hand, vibrations of C=C aromatic rings are observed at 1,517 cm^{-1} corresponding to the carbonyl group of the aromatic ring of lignin and at 1,653 cm^{-1} from the aromatic ring of the same molecule [27]. The bands in the 1,400 cm^{-1} regions represent vibrations of C–H bond in CH_3 groups of the aromatic rings [28]. Bands around 2,300 cm^{-1} are characteristic of C–C bonds vibrations of alkaline groups [25]. Finally, the 2,936 cm^{-1} band represents vibrations at the CH bond of the lignocellulosic components indicating the presence of methyl and

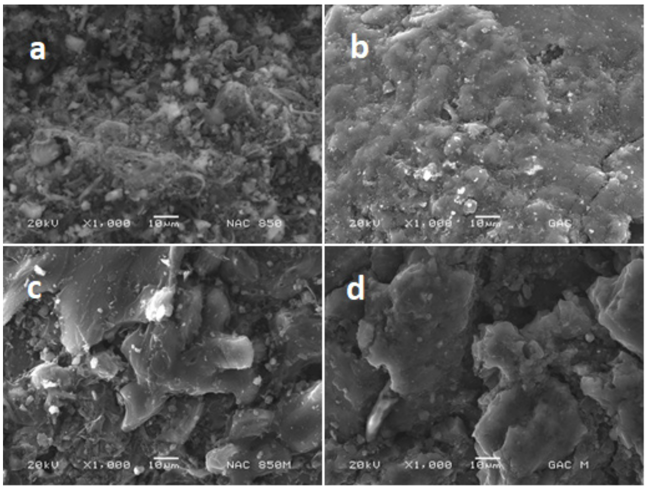

Fig. 2. SEM image of: (a) NAC-850, (b) GAC, (c) NAC-850-mod, and (d) GAC-mod.

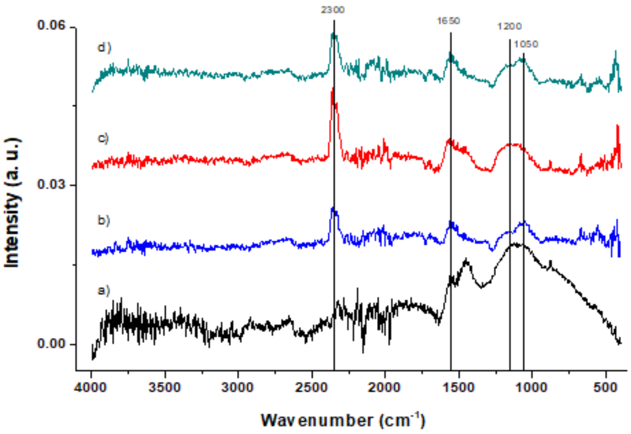

Fig. 3. FTIR analysis of: (a) NAC-850, (b) GAC, (c) NAC-850-mod, and (d) GAC-mod.

methylene groups that were observed only in the spectrum of the non-modified material, indicating that the hydrogen was removed during the modification process with citric acid (Fig. 3).

3.3. Tetracycline removal

3.3.1. Sorption kinetics parameters

Kinetic studies are very important to have an idea of the adsorption dynamics (rate constant) of the materials [29]. To evaluate the adsorption kinetics of TC onto the prepared activated carbons, the models of pseudo first order, pseudo second order and Elovich were fitted to experimental results (Fig. 6), and the kinetic parameters are shown in Table 4. In the kinetic tests, the sorption rate of the materials was determined to remove TC per time, starting from three different initial concentrations: 50, 100 and 300 mg L^{-1}. The TC concentrations in the remaining liquid were gradually decreased while the contact time between the activated carbons and the solutions went forward. The obtained data were plotted to calculate the TC removal percentages of the materials at different initial concentrations (Fig. 4).

In the kinetics, starting from C_0 = 50 mg L^{-1}, at 120 h of contact, 57.7% of TC was removed by NAC-850, and the percentage of elimination was slightly higher for NAC-850-mod with 62.6% of TC eliminated, indicating that the modification with citric acid was beneficial for the sorption process. The difference between the adsorption capacities of the materials can be attributed to the number of adsorption sites between them, which could have been increased with the modification of the material. For GAC and GAC-mod, both removal percentages were similar; 80.3% and 80.7% of TC were eliminated, indicating that the modification with citric acid did not show a significant improvement over the prepared activated carbon. When the initial TC concentration was 100 mg L^{-1}, the behaviour was similar; the modification increased the sorption capacity of the materials. When the TC concentration was increased to 300 mg L^{-1}, the modification of the surface did not improve the sorption capacity being lower than the unmodified materials.

3.3.1.1. Pseudo-first-order model. The results obtained from experimental sorption were adjusted to the pseudo-first-order model. This model refers that the sorption rate is proportional to the solute concentration according to the equation reported elsewhere [30].

The experimental data were correlated by the Lagergren equation using the software Statistica 8.0. R. The kinetic parameters obtained from the model application are shown in Table 2.

3.3.1.2. Pseudo-second-order model. The data obtained from experimental sorption process was fitted to the pseudo-second-order model that in general is applied to the adsorption system where a chemisorption mechanism takes place [31]:

Table 2 shows *k* and *R* values for the prepared materials. In a general, the experimental results present a good fit to the pseudo-second-order model. This model is generally used for heterogeneous adsorbents and chemical sorption [32].

3.3.1.3. Elovich model. The Elovich equation describes the kinetics of chemisorption of a gas phase on a solid phase. However, some researchers have applied this model to solid–liquid sorption systems [33]. Elovich model has been used widely in chemisorption on materials that present heterogeneous surfaces. Table 2 shows *a*, *b* and *R* for the adjustments of the experimental data to this model. The equation considers that the sorption sites on the surface of the material have different energies; perhaps, the experimental results could be adjusted also to this model for this reason.

As can be seen in Fig. 4, for the TC concentration tested (50, 100 and 300 mg L^{-1}), the equilibrium was reached around 96 h for 50 and 100 ppm and for 300 ppm after 120 h. Table 2 describes the kinetic parameters obtained from the application of the pseudo-first-order, pseudo-second-order and Elovich models to the experimental data. The Elovich model presents the lowest *R* (0–0.77) when the highest TC concentration was used. The models of pseudo first order and pseudo second order were well-fitted to experimental data in general for all the TC concentrations. The pseudo-first-order

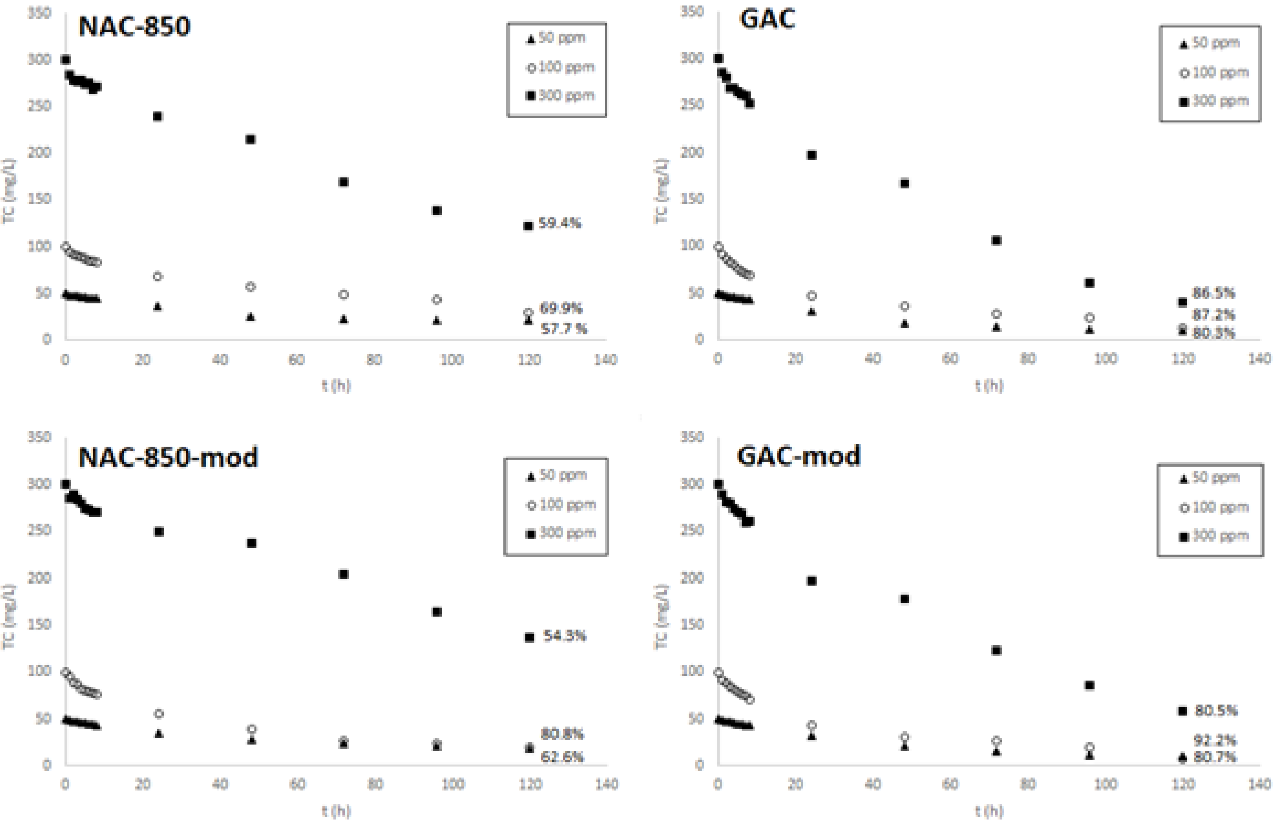

Fig. 4. TC removal by NAC-850, GAC, NAC-850-mod, and GAC-mod (C_0 = 50, 100, and 300 mg L^{-1}).

model presents q_e values very close to $q_{e,\exp}$ and high R values (0.95–0.99). For pseudo-second-order model, the adsorption rate (K) was proportional to the increase of TC initial concentration [34]. Therefore, for lower TC concentrations, Elovich model was defined as being the best model to describe the kinetic data of the adsorption of TC onto prepared activated carbons, presenting the highest R values (0.97–0.99); this model assumes that the adsorbent surface is heterogeneous considering the energy on its surface, and it does not present desorption or interactions between the adsorbed species that could affect the TC sorption at low surface coverage [35].

3.4. Effect of temperature on tetracycline sorption and thermodynamic parameters

The effect on TC removal for each material was evaluated at different temperatures (25°C, 35°C and 60°C) at C_0 = 50 mg L^{-1}. Fig. 5 shows the sorption kinetics and the influence of the temperature on the TC removal percentage. For NAC-850, the largest removal of TC was at 35°C (92%), followed by 60°C (83%), and finally, the lowest removal was given at room temperature (25°C), removing 57%. The NAC-850-mod showed the same behaviour. The effect of the modification of the material can be seen since the elimination percentages at all temperatures were slightly higher compared with NAC-850. The kinetics for the GAC material showed the same behaviour like the materials obtained from pecan nut shells; at 35°C, it has 97% TC removal; at 60°C, it obtained 92% TC removal, and at room temperature, it showed the lowest removal (80%). The GAC-mod also follows the behaviour described above. The increased sorption at higher temperatures can be explained due to the increase of active sites of the materials with the change of temperature [36]. Likewise, it is observed that increasing the temperature also increases the q_e, which indicates that the sorption in the materials is given by chemisorption. If this value decreases with the increase of temperature, it occurs a desorption process because the presence of involved forces that usually are weaker [37].

Important thermodynamic parameters, like the enthalpy change ($\Delta H^{\ominus}_{\text{ads}}$) and the entropy change ($\Delta S^{\ominus}_{\text{ads}}$), were obtained by van't Hoff method [38,39] and the Gibbs change in free energy of the adsorption, $\Delta G^{\ominus}_{\text{ads}}$, is given by $\Delta G^{\ominus}_{\text{ads}} = \Delta H^{\ominus}_{\text{ads}} - \text{T}\Delta S^{\ominus}_{\text{ads}}$.

The $\Delta H^{\ominus}_{\text{ads}}$ and $\Delta S^{\ominus}_{\text{ads}}$ values obtained in some cases could be ascribed to a single process together with sorption process (conformational changes, multiple equilibria and retention mechanisms) [40]. The $\Delta H^{\ominus}_{\text{ads}}$ data in Table 3 indicate endothermic events favoured by temperature increment. Positive $\Delta H^{\ominus}_{\text{ads}}$ values have been calculated in other researches using van't Hoff equation, specifically for cationic dyes adsorbed on clay [41]. Moreover, positive values of ΔH shown in Table 3 indicate that the adsorption of TC molecules on the surface of the materials is given by a chemical reaction. This may occur because of a protonation of hydrogen bridges or Van der Waals forces. Positive values of ΔS also indicate that entropy during TC sorption

Table 2
Kinetic parameters from models applied to sorption of TC onto activated carbons at different initial TC concentration (50, 100, and 300 mg L^{-1})

Kinetic models	Kinetic parameters	NAC-850	NAC-850-mod	GAC	GAC-mod
50 ppm					
Pseudo-first-order	q_e (mg g^{-1})	28.84	31.29	40.13	40.42
$q_t = q_e\ (1–e^{(K_L)\times t})$	$q_{e,\exp}$	26.53	28.92	37.64	37.78
	K_L (h^{-1})	0.028	0.028	0.028	0.026
	R	0.997	0.999	0.999	0.999
Pseudo-second-order	K (g mg h^{-1})	1,124.7	1,330.1	2,703.9	2,372.9
$\frac{t}{q_t} = \frac{1}{K(q_e)^2} + \left(\frac{t}{q_e}\right)$	R	0.935	0.919	0.896	0.850
Elovich	a	2.328	2.522	2.985	2.754
$q_t = \left(\frac{1}{b}\right)\left(\text{Ln}^{1+(a)(b)}\right)$	b	0.036	0.032	0.023	0.022
	R	0.999	0.999	0.998	0.998
100 ppm					
Pseudo-first-order	q_e (mg g^{-1})	69.89	80.77	87.27	92.24
$q_t = q_e\ (1–e^{(K_L)\times t})$	$q_{e,\exp}$	58.87	73.02	78.17	90.65
	K_L (h^{-1})	0.023	0.040	0.044	0.051
	R	0.972	0.987	0.965	0.983
Pseudo-second-order	K (g mg h^{-1})	17,641.9	55,618.5	40,361.8	69,119.9
$\frac{t}{q_t} = \frac{1}{K(q_e)^2} + \left(\frac{t}{q_e}\right)$	R	0.970	0.990	0.981	0.979
Elovich	a	7.653	13.33	19.94	17.17
$q_t = \left(\frac{1}{b}\right)\left(\text{Ln}^{1+(a)(b)}\right)$	b	0.021	0.018	0.020	0.016
	R	0.992	0.999	0.998	0.967
300 ppm					
Pseudo-first-order	q_e (mg g^{-1})	178.21	162.97	259.40	241.43
$q_t = q_e\ (1–e^{(K_L)\times t})$	$q_{e,\exp}$	126.39	113.13	196.46	181.68
	K_L (h^{-1})	0.018	0.017	0.021	0.020
	R	0.954	0.950	0.982	0.984
Pseudo-second-order	K (g mg h^{-1})	205,388	147,373	658,275	490,389
$\frac{t}{q_t} = \frac{1}{K(q_e)^2} + \left(\frac{t}{q_e}\right)$	R	0.853	0.841	0.897	0.883
Elovich	a	0.402	0.435	0.311	0.323
$q_t = \left(\frac{1}{b}\right)\left(\text{Ln}^{1+(a)(b)}\right)$	b	0.021	0.019	0.027	0.026
	R	0.555	0.766	0	0.601

process onto activated carbons increases, as well as a change in energy distribution occurs [42].

The Arrhenius equation was used to calculate the activation energy [43], and other thermodynamic parameters such as ΔH and ΔS was calculated with the Eyring equation [43].

The Arrhenius method considers a series of values for the sorption kinetics determined at different temperatures. Table 3 shows that the thermodynamic parameters (ΔH and ΔS) were also calculated by the Eyring equation. In the case of the van't Hoff equation, the values of the solute distribution on the adsorbent and in the solution were obtained at 24 h.

Negative values of ΔH indicate an exothermic process, and positive values show an endothermic process. Values <84 kJ mol^{-1} indicate a physical sorption process, and values between 84 and 420 kJ mol^{-1} correspond to a chemical sorption process. The adsorption of TC in the materials indicates chemisorption and an endothermic process. The positive values of ΔG indicate that the process is not spontaneous [39], as in the case of the adsorption of TC at 25°C, otherwise at 35°C and 60°C, a spontaneous process occurs, except for NAC-850 (Table 3). On

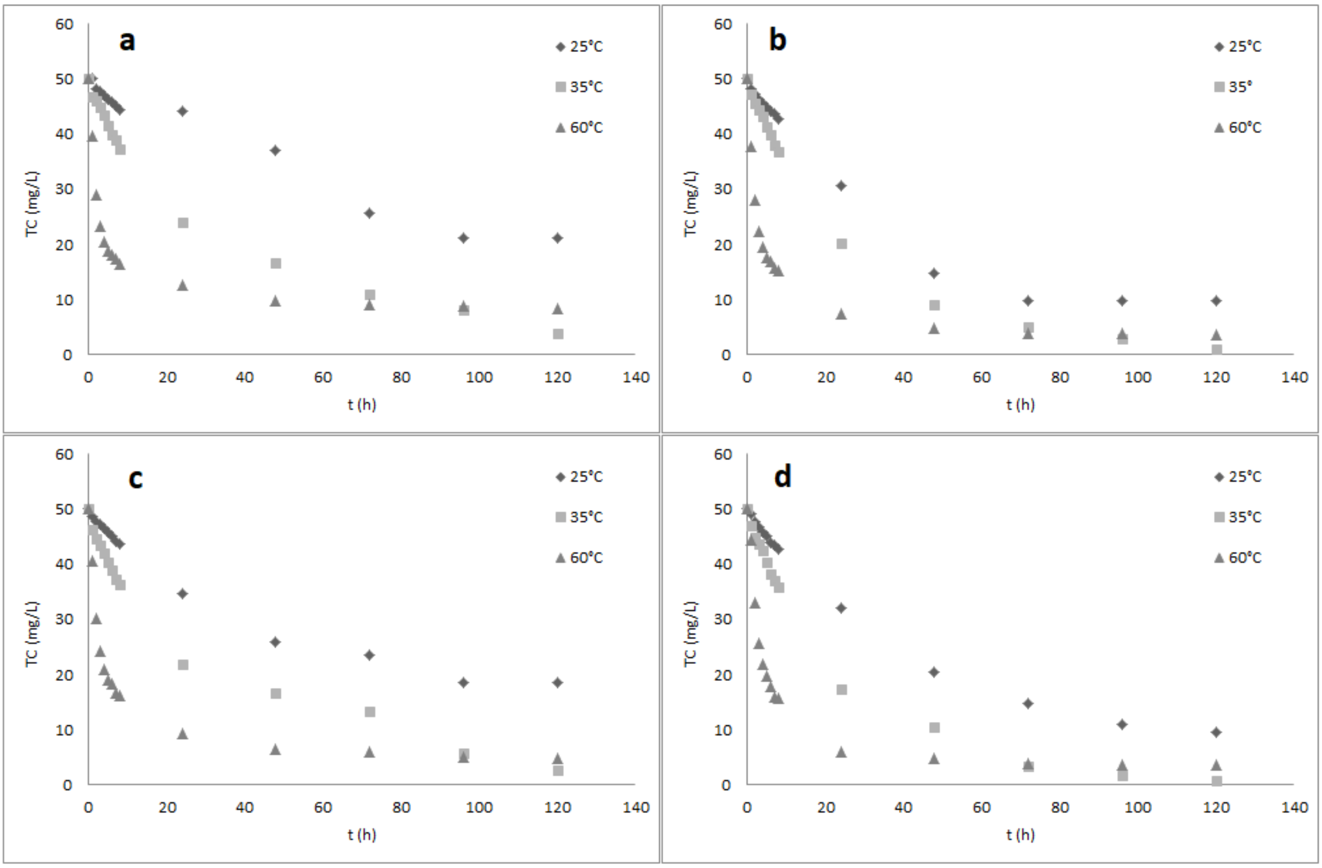

Fig. 5. Effect of temperature onto TC removal by (a) NAC-850, (b) GAC, (c) NAC-850-mod, and (d) GAC-mod (T = 25°C, 35°C, and 60°C).

Table 3
Thermodynamic parameters from van't Hoff and Eyring equations

Thermodynamic parameters (kJ mol^{-1})	NAC-850	GAC	NAC-850-mod	GAC-mod
van't Hoff method				
ΔH	48,487	50,724.5	51,496.9	58,444
ΔS	155.089	166.87	167.33	192.66
ΔG (25°C)	2,247.21	969.68	1,604.80	1,002.42
ΔG (35°C)	696.32	–699.09	–68.55	–924.18
ΔG (60°C)	–3,180.9	–4,870.7	–4,251	–5,740.7
Eyring method				
ΔH	72,286	60,147	71,889	60,770
ΔS	226.41	191.76	226.5	192.95
Ea	74,912.4	62,773.1	74,515.8	63,395.9

the other hand, thermodynamic studies performed with carbon nanoparticles for TC removal showed that the adsorption process occurred in spontaneously and endothermic way [44].

3.5. Adsorption isotherms

Langmuir, Freundlich and Temkin isotherm models were applied to describe the sorption process and to obtain the isotherm parameters for the prepared materials (NAC-850, GAC, NAC-850-mod and GAC-mod; Table 4).

3.5.1. Langmuir isotherm model

In this model, the adsorption process occurs in a monolayer coverage characterised by the q_m value, on homogeneous adsorption sites of constant energy; there are no interactions between the TC adsorbed molecules [45].

From the application of the model to experimental results, it was calculated the Langmuir constant (b_L; Table 4). The experimental results do not fit very well the Langmuir model for the prepared activated carbons, yielding to a

Table 4
Adsorption constants for Langmuir, Freundlich and Temkin isotherm models

Material	Langmuir			Freundlich			Temkin		
	q_m (mg g^{-1})	b (L mg^{-1})	R	K_F (mg g^{-1})	n	R	K_T (L g^{-1})	B (J mol^{-1})	R
NAC-850	139.68	0.035	0.959	25.63	0.297	0.990	4.158	0.003	0.745
GAC	202.89	0.144	0.972	61.10	0.256	0.997	1.774	0.034	0.972
NAC-850-mod	257.07	0.006	0.752	0.372	1.572	0.892	3.602	0.008	0.932
GAC-mod	212.36	0.022	0.902	32.98	0.313	0.966	0.315	0.033	0.738

Table 5
Adsorption capacity of TC by various adsorbents

Adsorbent	TC sorption capacity (mg g^{-1})	Reference
NaOH-AC from macadamia husks	455.8	[22]
Tyre char	455.0	[44]
Tomato waste	500.0	[45]
AC from beet pulp	288.3	[46]
AC from peanut hulls	28.0	[46]
Bio-char	58.8	[47]
Graphene oxide	313.0	[48]
Petroleum-coke	1,121.5	[49]
Hydrochar from *Salix P.*	25.4	[50]
AC from pecan nut shell	139.68	This work
Commercial activated carbon	202.89	This work
AC from pecan nut shell modified with citric acid	257.07	This work
Commercial activated carbon modified with citric acid	212.36	This work

very poor correlation value (R) principally for the commercial activated carbons (GAC and GAC-mod). The values of monolayer adsorption capacity (q_m) for the prepared activated carbons were 139.7, 202.9, 257.1 and 212.4 mg g^{-1} for NAC-850, GAC, NAC-850-mod and GAC-mod, respectively. This behaviour indicates that the citric acid modification would enhance the adsorption capacity compared with the unmodified material. The adsorption capacities of TC over a variety of adsorbents are reported [22,46–52], and they are compared in Table 5.

3.5.2. Freundlich isotherm model

The Freundlich equation is an empirical model [53]. For Freundlich model, it has been established that (i) the adsorption sites have different energies; (ii) the adsorbed molecules could interact between them; and (iii) there is no upper limit to adsorption which restricts its use to diluted media. In this model, the constant (K_F) decreased when the materials were modified with citric acid. The n constant was higher in the cases which the activated carbons were also treated with citric acid (Table 4).

3.5.3. Temkin isotherm model

The Temkin isotherm model contains a factor that takes into account the interactions between adsorbate and adsorbent [54]. The heat of adsorption of the molecules in the layer decreases linearly with the coverage involved in this interaction. All the studied constants and the R values are shown in Table 4. The R values suggest that this model does not fit well with the experimental data. Therefore, the data were best adjusted to the Freundlich model.

There are various studies where the adsorption capacity of different prepared activated carbons is used to remove TC from water. Table 5 shows the sorption capacity of some materials in recent time, and it is appreciated that the activated carbons obtained from pecan nut shells have an acceptable performance in sorption tests. The adsorption capacity of the materials used in this study was better than those reported in literature used for TC removal but also less effective than other materials that followed chemical activation.

3.6. Effect of pH on the tetracycline sorption

The pH value is an important parameter into sorption process to have an effective interaction between TC molecule and activated carbon. Fig. 6 shows the pH effect on the percentage removal of TC. NAC-850 had a removal of 69.9% at pH = 4.3, 69.4% at pH = 6.1, and 59.3% at pH = 9.1. In general, for all the materials, the TC removal capacity was independent of pH values. At pH = 4.1, the TCH^{3+} and $TCH^{2\pm}$ species are present in solution [55], which promote a higher TC adsorption onto the activated carbons, while TCH^{-} and TCH^{2-} species inhibit its adsorption. Some mechanisms can be occurred in the sorption process onto activated carbons: electrostatic interaction, electron donor-acceptor, removal by hydrogen bonds formation and π–π dispersion interaction [56]. The hydrogen bonding could be an adsorption mechanism that can contribute to TC adsorption in this conditions because the zwitterion molecule is predominant at acid pH values [55].

3.7. Effect of competing ions on tetracycline sorption process

The ion content may affect sorption behaviour of organic pollutants on adsorbent materials in water systems. The effect of ions on the sorption capacity of TC in the used materials is shown in Fig. 7. It was used spring water with a specific ions content: Ca^{2+} (17 mg L^{-1}), Mg^{2+} (13 mg L^{-1}), Na^{2+} (18 mg L^{-1}), K^{+} (5 mg L^{-1}), Si (35 mg L^{-1}), HCO^{3-} (140 mg L^{-1}), SO_4^{2-} (<2 mg L^{-1}), Cl^{-} (9 mg L^{-1}) and NO_3^{-} 0.24 (mg L^{-1}). The results of this study

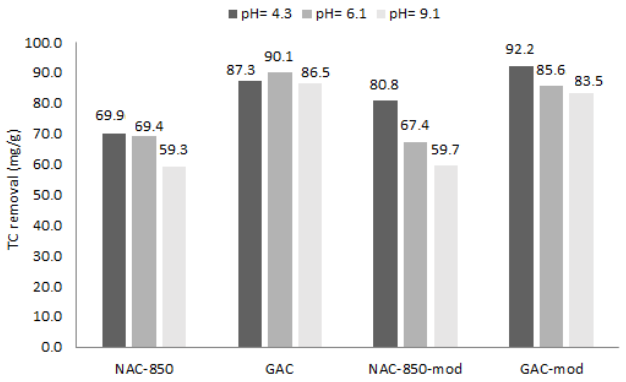

Fig. 6. Effect of pH of the solution onto TC sorption (C_0 = 100 mg L^{-1}, contact time = 120 min).

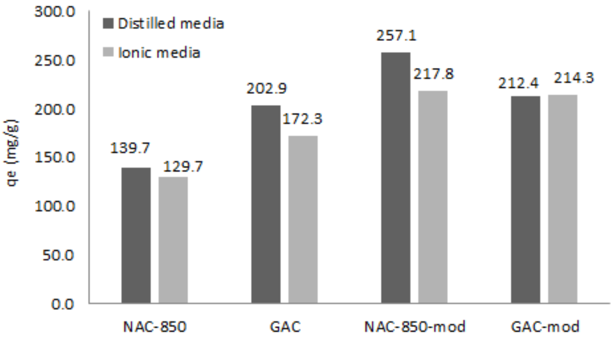

Fig. 7. Effect of competing ions (Ca^{2+}, Mg^{2+}, Na^{2+}, K^+, Si, HCO_3^-, SO_4^{2-}, Cl^-, and NO^{3-}) onto TC removal by the NAC-850, GAC, NAC-850-mod, and GAC-mod.

revealed that in all materials, TC sorption did not was significantly affected when the sorption process is carried out in the presence of ions in the solution. In these cases, the initial pH value was situated between 6.2 and 7.0, and the final pH between 7.0 and 7.5, indicating that the main TC species were $TCH^{2\pm}$ and subsequently, TCH^-. It is possible to distinguish that the presence of ions did not affect the sorption capacity of the materials, except for GAC where TC sorption decreased, and this phenomenon can be explained by the cation exchange. Most surfaces of adsorbent materials carry a net negative charge, and when the ion content increases, cations such as Na^+, Mg^{2+} or Ca^{2+} are attracted electrostatically by the negative carbon surface [57]. At the final pH value for the TC-GAC system (pH ≈ 7), the groups of the TC molecule are slightly positive; therefore, cations in solution can compete with TC in the sorption process.

4. Conclusions

Activated carbon from the walnut shell was obtained by physical activation with steam, and it was efficient for TC removal. The efficiency to remove the antibiotic increased with the modification of the surface with citric acid (1 M) between 5% and 11% in concentrations of 50 and 100 mg L^{-1}, presenting an adjustment to the kinetic models of pseudo second order (materials with heterogeneous surface). The activation/modification method is useful, simple and more economical to improve TC sorption capacity, and is comparable with the removal efficiencies of a commercial carbon under the described conditions. The main effect of the modification with citric acid was to increase the surface functional groups.

Both pH and temperature influenced the sorption capacity of the materials, and it was found that the optimum conditions for the sorption process are at pH = 4.3 and T = 35°C together with the addition of citric acid. Ions in solution or other components present in treated wastewater did not represent competence for TC sorption efficiency, which indicates that the materials could be suitable for use in advanced wastewater treatment.

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Conflicts of interest

The authors declare that there are no conflicts of interest.

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