



Research paper

Influence of pH and antibiotic solubility on the removal of ciprofloxacin from aqueous media using montmorillonite



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ABSTRACT

The ciprofloxacin (CPX) is a fluoroquinolone antibiotic that has been found in soils and aqueous media due to its vast use in both, human and veterinary health care. As a consequence the removal of this kind of compounds is widely studied. However, there are a few studies about the CPX removal from aqueous media by adsorption. This work is focused on the study of CPX removal by adsorption using an Argentinian montmorillonite (Mt). The influence of the pH media and the consequent antibiotic solubility in the adsorption process was analyzed. The experimental curve of CPX solubility versus pH media showed a strong correlation between them where the lowest value of solubility was obtained for the zwitterion species (CPX[±]). This result points out the fact that the solubility of the CPX species must be considered in adsorption experiments because of the antibiotic precipitation and the consequent overestimation of the adsorbent adsorption capacities. CPX adsorption kinetics and adsorption isotherms at different pH values showed that the adsorption processes obey pseudo-second order kinetics. The CPX adsorption capacity of the Mt, the affinity of the species towards its surface and the possible mechanisms involved in the adsorption process were assessed by Langmuir, Freundlich and Scatchard methods. The results showed that the adsorption mechanism of CPX on Mt is pH dependent, obtaining a negative cooperative mechanism at pH 3, 6 and 7.5 and a positive cooperative mechanism at pH 10. The highest CPX adsorption capacity on Mt was obtained at pH 6. Infrared spectroscopy and X-ray diffractograms of the complexes obtained after the adsorption process provided information about the interaction between the functional groups of CPX and the adsorption sites on Mt and the changes in the basal space related with the molecular arrangements of the CPX on the sample, respectively. The CPX removal by this clay mineral is remarkably higher when it is compared with other materials and quite similar to previous data obtained with other bentonites.

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1. Introduction

Many organic compounds as detergents, surfactants, pesticides, dyes, antibiotics and hormones, among others, can be found in the environment and their presence is mainly associated to human and veterinary pharmaceutical uses. These kinds of compounds, so-called emerging contaminants, have no control standard even though they represent an environmental risk. In addition, there is little information about their indirect effect on human health or species living in aquatic ecosystems (Sarmah et al., 2006; Kümmerer, 2009; Grassi et al., 2012).

Among these new contaminants, antibiotics have received much attention because thousands of tons are used in human and veterinary medicine as well as in agriculture and aquaculture activities. The residual wastes are thrown to water courses and soils which, even in low concentrations, could be hazardous for different species. The presence

of different antibiotics in the environment has been found in concentrations of the order of $\mu\text{g} \cdot \text{L}^{-1}$ and $\text{ng} \cdot \text{L}^{-1}$ showing that the conventional wastewater treatments are not effective for their removal. Different techniques have been proposed to remove antibiotics in low concentrations from water, but adsorption process has shown to be simple and efficient.

Although the adsorbents mainly used for the removal of organic compounds are the activated carbons, natural clay minerals are a feasible alternative in the large scale systems. These adsorbents have not only proved to be effective, but also widely distributed, affordable and environmentally friendly materials (Grassi et al., 2012). Consequently, clay minerals have been applied for the removal of many different organic compounds as dyes (Rytwo et al., 2000), pesticides (Polatti et al., 2006) and antibiotics (Putra et al., 2009; Molu and Yurdakoç, 2010; Genç et al., 2013). Particularly, the bentonites located in the Alto Valle de Río Negro–Neuquén, Argentina have showed to be good adsorbents for the removal of thiabendazole fungicide (Roca Jalil et al., 2013) and the tetracycline antibiotic (Parolo et al., 2008) from aqueous media.

The adsorption studies of antibiotics on clays have showed that the structure of the organic molecule has a direct influence on the

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adsorption capacity. This can be explained by the fact that antibiotics have molecules with protonable groups, dependent of the pH media affecting the interactions between the antibiotic species present at each pH and the adsorption sites on the surface clay mineral.

Ciprofloxacin (CPX) is an antibiotic from the group of the fluoroquinolones and its presence has been reported in wastewaters, soils and hospital effluents (Karthikeyan and Meyer, 2006; Githinji et al., 2011). It is considered an emerging contaminant, so studies that contribute to its removal from aqueous media are necessary. Different authors have reported adsorption capacity values of 1.55, 7.4, 33, 112, 135, and 300 mg of CPX per gram of adsorbent by modified coal fly ash, kaolinite, illite, carbon xerogel, rectorite, carbon nanotubes and activated carbon, respectively (Li et al., 2011; Wang et al., 2011; Zhang et al., 2011; Carabineiro et al., 2012). However, the results obtained for adsorption of CPX on montmorillonites showed higher adsorption capacities (Wang et al., 2011; Genç et al., 2013).

The protonable groups present in the CPX molecule are pH dependent, producing different ionic species. Thus, the CPX solubility in water also depends of the pH, decreasing with the increase of the percentage of neutral species (zwitterion). Despite this, most studies only analyze one acid and one basic pH values, and never use pH values around 7.5 where the zwitterion species is in the highest concentration. As a result, many of these studies have disregarded the effect of the pH on the CPX solubility, which can be significant in adsorption capacities.

Taking the above into consideration, in this work it is studied the CPX adsorption on a montmorillonite (Mt) from the Pellegrini Lake and the relationship with the pH media and CPX solubility. Different working conditions were evaluated to show the influence of the CPX species on the material adsorption capacities. The CPX-Mt interactions were studied by infrared spectroscopy (FTIR) and X-ray diffraction (XRD).

2. Materials and methods

2.1. Materials

The natural clay mineral selected for this study is a bentonite extracted from the Pellegrini Lake deposits in the province of Rio Negro, Argentina. The X-ray diffraction showed that up to 99% of its mineralogical composition corresponds to Mt. The Cation Exchange Capacity (CEC) was determined according to the Chhabra method (Chhabra et al., 1975) and the total amount of cations was determined by atomic absorption. The Mt CEC obtained was $1.23 \text{ meq} \cdot \text{g}^{-1}$ of clay mineral being Na^+ the most predominant cation ($0.86 \text{ meq} \cdot \text{g}^{-1}$ of clay).

Textural properties of Mt were obtained from nitrogen adsorption-desorption isotherms at 77 K and are shown in Table 1. The specific surface area (BET area, S_{BET}) was assessed by the Brunauer, Emmet and Teller (BET) method. The micropore volumes (V_{up}) were calculated with the α -plot method using the calcined sample at 1000 °C as reference (Villarroel-Rocha et al., 2013). The total pore volume (V_{T}) was obtained by the Gurvich rule (at 0.97 of relative pressure) (Rouquerol et al., 1999). The values obtained from the textural characterization agree with the usually observed for this kind of materials. The Mt can be considered a mainly mesoporous material with a minimal contribution of micropores associated to its well-known structure. Its S_{BET} agrees with previous reports for clay minerals of the Pellegrini Lake region (Roca Jalil et al., 2013).

The ciprofloxacin hydrochloride used as adsorptive, was acquired from Romikim S.A (Argentina) and had a purity of 99.3%. The CPX

molecule has an almost planar configuration and its approximate dimensions are $13.5 \text{ \AA} \times 3 \text{ \AA} \times 7.4 \text{ \AA}$ (Carabineiro et al., 2012). A scheme of the chemical structure of CPX is shown in Fig. 1. The pK_a values for CPX are 5.90 ± 0.15 and 8.89 ± 0.11 and are associated to the carboxylic acid group and the amine group in the piperazine moiety, respectively. Fig. 2 illustrates the distribution of CPX species at different pH values, obtained by the method reported by Del Piero et al. (2006).

2.2. CPX adsorption studies

The adsorption experiments were conducted by mixing 0.01 g of Mt with 40 mL of CPX solution in tubes of 50 mL and stirring at 20 °C up to beyond the equilibrium time. The concentration of the adsorbent in the suspension was selected based on previous studies and the CPX concentration based on its solubility properties. The pH was adjusted to values between 3 and 12 using HCl or NaOH solutions. The tubes were wrapped in aluminum foils to prevent light-induced decomposition. The solution was then separated from the adsorbent using a Sorvall RC 5C centrifuge at 8000 rpm for 20 min. The CPX equilibrium concentrations in the resultant supernatant were measured using a T60 UV-vis spectrophotometer at the λ_{max} corresponding to the pH value, from the previously determined calibration curve. All the samples were measured in duplicate and the average value was used.

2.3. Analytical methods

The amount of CPX adsorbed on the clay mineral (q) was calculated from the initial and equilibrium CPX concentrations, according to the Eq. (1),

$$q = \frac{V(C_i - C_{eq})}{w} \quad (1)$$

where V is the CPX solution volume (L), C_i is the initial CPX concentration (ppm), C_{eq} is the equilibrium CPX concentration (ppm) and w is the mass of clay (g).

Among the solids obtained after centrifugation for each pH studied value, two of them were dried at room temperature and studied by X-ray diffraction (XRD) and infrared spectroscopy (FTIR) in order to evaluate the intercalation of CPX into Mt and the possible interactions. XRD diffractograms were obtained using a RIGAKU Geigerflex X-ray diffractometer with $\text{CuK}\alpha$ radiation at 20 mA and 40 kV. Scans were recorded between 2° and 10° (2θ) with a step size of 0.02° and scanning speed of 2° min^{-1} . The samples were prepared from montmorillonite suspension ($15 \text{ mg} \cdot \text{mL}^{-1}$) and the dispersions were deposited and oriented onto glass slides under constant relative humidity conditions. The FTIR spectra were acquired by Infracalum FT-08 FTIR spectrometer using KBr pressed pellet method. The KBr pellets were prepared by pressing mixtures of 3 mg of power and 300 mg of KBr. All spectra were collected at room temperature using 40 scans in the range of $3000\text{--}400 \text{ cm}^{-1}$.

Kinetics models were used to evaluate the adsorption mechanism. The adsorption kinetics data corresponding to CPX on Mt were fitted

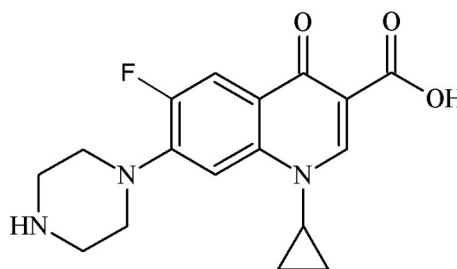


Fig. 1. Molecular structure of ciprofloxacin (CPX).

Table 1
Textural properties data for natural clay mineral.

	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	V_{T} ($\text{cm}^3 \cdot \text{g}^{-1}$)	V_{up} ($\text{cm}^3 \cdot \text{g}^{-1}$)
Natural Clay	67	0.096	0.001

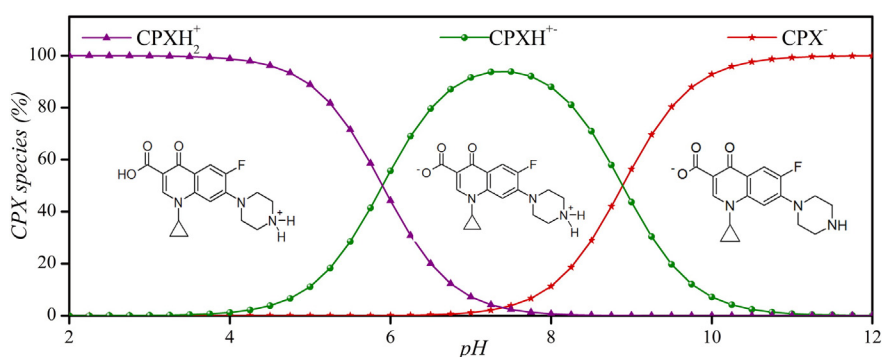


Fig. 2. Distribution of CPX species as a function of pH.

to both the pseudo-first-order and pseudo-second-order models (Ho and McKay, 1998; Azizian, 2004).

The Lagergren pseudo-first order equation can be expressed as:

$$\frac{dq}{dt} = k_1(q_e - q). \quad (2)$$

The integration of the Eq. (2) using the boundary conditions: $t = 0$ for $t = t$ and $q = 0$ for $q = q_t$, gives:

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

where q_t is the amount of CPX adsorbed at time t ($\text{mg} \cdot \text{g}^{-1}$), q_e is the equilibrium adsorption capacity of the adsorbent ($\text{mg} \cdot \text{g}^{-1}$) and k_1 is the rate constant of pseudo first-order kinetics (min^{-1}).

Similarly, if the mechanism is thought to be pseudo-second order kinetic, the equation can be expressed as:

$$\frac{dq}{dt} = k_2(q_e - q)^2. \quad (4)$$

Integrating Eq. (4) for the same boundary conditions: $t = 0$ for $t = t$ and $q = 0$ for $q = q_t$, gives:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (5)$$

where q_t is the amount of CPX adsorbed at time t ($\text{mg} \cdot \text{g}^{-1}$), q_e is the equilibrium adsorption capacity of the adsorbent ($\text{mg} \cdot \text{g}^{-1}$) and k_2 is the rate constant of pseudo second-order kinetics ($\text{g} \cdot \text{mg} \cdot \text{min}^{-1}$).

The CPX adsorption equilibrium data were fitted to Langmuir and Freundlich isotherm models (Febrianto et al., 2009; Wang et al., 2011). The Langmuir isotherm model assumes a monolayer adsorption on a surface with a finite number of identical sites. According to this model, all the sites are energetically equivalent and there are not interactions among the adsorbed molecules. The mathematical expression of the Langmuir isotherm model is showed in Eq. (6):

$$q = \frac{q_m k C_{eq}}{1 + k C_{eq}} \quad (6)$$

where q_m is the maximum adsorbed amount within a monolayer of adsorptive ($\text{mg} \cdot \text{g}^{-1}$) and k (ppm^{-1}) is the Langmuir dissociation constant, which is related to the adsorption energy.

The Freundlich equation is an empirical method that has been widely applied to adsorption on heterogeneous surfaces. This model uses a multi-site adsorption isotherm and its mathematical expression is defined in Eq. (7):

$$q = k_F C_{eq}^{1/n} \quad (7)$$

where k_F ($\text{L} \cdot \text{g}^{-1}$) and n (dimensionless) are the Freundlich characteristic constants, indicating the adsorption capacity and adsorption intensity, respectively.

The Scatchard model was applied to the adsorption data in order to obtain complementary information about adsorption phenomena. This method is known as independent site-oriented model and it involves the transformation of the data from the isotherm to obtain a plot of q/C_{eq} versus q (where q has the same sense indicated above). If the Scatchard plot is a straight line, it suggests that there is one type of sites for adsorption on the adsorbent. On the other hand, if a non-linear curve is observed in the Scatchard plot, its shape can be related to different phenomena indicating nonspecific or multi-type interactions between the adsorbate and adsorbent. A concave curve can be related to a negative cooperative phenomenon or to the presence of heterogeneity sites for the adsorption. However, if the result is a convex curve, a positive cooperative phenomenon can be associated, which means that the first adsorption takes place with low affinity and that the adsorbate becomes a possible site for the subsequent adsorption (Dahlquist, 1978; Gerente et al., 2000; Gezici et al., 2007; Anirudhan and Suchithra, 2010).

3. Results and discussion

3.1. Effect of medium pH and CPX solubility on CPX adsorption

It is known that CPX has high aqueous solubility under high and low pH conditions. Due this fact, most of the reported analyses are performed in these pH ranges, avoiding pH region near 7. To consider the CPX solubility in all pH range, an experimental curve was obtained from different saturated solutions of CPX adjusted at pH values between 4 and 11. The solutions were kept at 20 °C for about 12 h, considering that the equilibrium time was reached. After that, the solutions were filtered and the CPX concentration was determined by UV-vis spectroscopy.

The solubility curve for CPX is shown in Fig. 3. The lowest solubility values obtained were in the pH region around 7.5, in accordance to the values previously reported by Fallati et al. (1994). The behavior shown by the CPX solubility as a function of the pH can be explained by the species present within each pH range. At the lowest pH values, the soluble CPXH_2^+ species are present and its percentage decreases from pH 3 to 5.9. The pH range from 5.9 (pK_{a1}) to 8.89 (pK_{a2}) contains three different species, being the CPX zwitterion the least soluble, reaching the lowest solubility in water at pH 7.5 due to its neutral charge. The CPX became more soluble with every pH increase due to the presence of CPX^- species reaching 50% at pH 8.89 and increases for pH greater than this value. In other words, the CPX is more soluble when its molecule behaves as an ion (either cation or anion), which only occurs at a pH value different from 7.5. The significant variation with the pH adjustment can results in an inaccuracy measurement in the CPX concentration, with the consequent over- or under-estimation of the

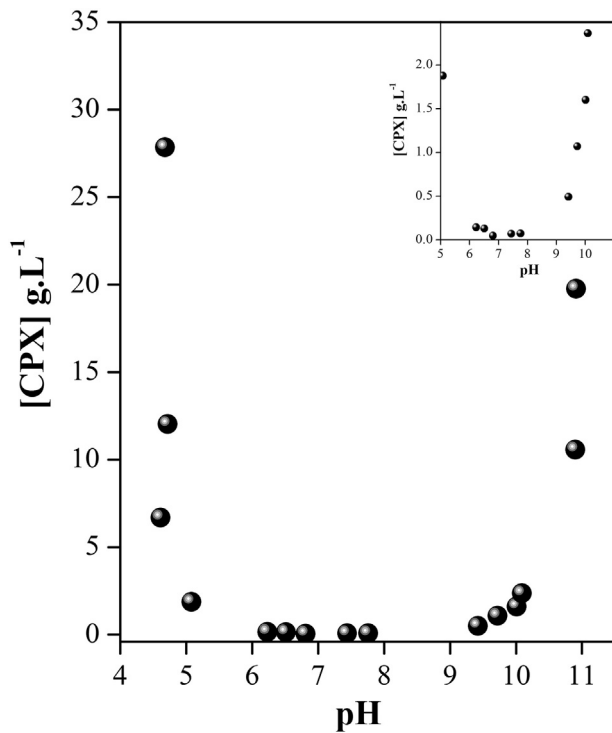


Fig. 3. Solubility curve for CPX in function of pH.

adsorption capacity for a determined adsorbent. Therefore it is crucial to consider the CPX solubility in adsorption studies.

The adsorption capacity of CPX on Mt at different pH values was assessed under the previously mentioned conditions with an initial fixed CPX concentration ($110 \text{ mg} \cdot \text{L}^{-1}$) according to the solubility results, to ensure that the CPX does not precipitate. Adsorption capacity of CPX on Mt at different pH values is shown in Fig. 4. The results exhibited high adsorption at low pH values and a fast decrease in adsorption at pH values starting at 7.5. This behavior can be explained by the relationship between the surface charge of Mt and the CPX total charge and by the presence of the cationic form (CPX^+) that favors a strong adsorption on the negative surface of the clay mineral. These results suggest that there is a cation exchange of this species for the natural cation within the Mt interlayer which is the usual adsorption

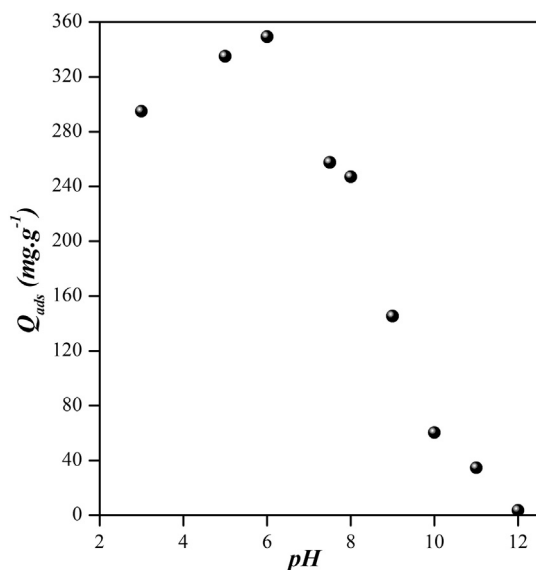


Fig. 4. Effect of solution pH on CPX adsorption.

mechanism proposed for this kind of natural clay minerals. The adsorption decrease is significant after a pH of 7.5. This behavior could be related to the presence of the negative molecule form (CPX^-), which can exhibit repulsive interactions with the clay mineral negative surface.

3.2. Adsorption kinetics

The adsorption kinetics of CPX on the Mt was evaluated at four different pH values, including cationic (pH 3), zwitterionic (pH 7.5), and anionic (pH 10) species. The fourth pH 6 was chosen because it showed the highest adsorption capacity. The experiments were performed using the same initial and fixed CPX concentration ($110 \text{ mg} \cdot \text{L}^{-1}$) with contact times varying between 0.5 and 24 h. Adsorption kinetic curves are shown in Fig. 5, where it is plotted the amount of adsorbed CPX ($\text{mg} \cdot \text{g}^{-1}$) as a function of the contact time. The results show that the adsorption is extremely fast at pH values up to 7.5 (with a contact time of roughly 30 min), indicating a cation exchange mechanism for the adsorption. Regarding the adsorption kinetics at pH 10, the time to reach the equilibrium was longer in comparison to other pH values, which could suggest a different adsorption mechanism. The adsorption kinetics parameters were estimated by nonlinear regression of pseudo-first and pseudo-second order equations (Azizian, 2004; Kumar, 2006). The obtained values agree with the previously showed results obtained for the CPX adsorption vs pH (Fig. 4) and are summarized in Table 2. In spite of the fact that the regression coefficients for the two models are higher than 0.90 for all pH values, the pseudo second-order model is more appropriate than the pseudo first-order one, according to the theoretical analysis proposed by Azizian (2004).

For the results shown in Fig. 5, an equilibrium time of 4 h was chosen to perform the CPX adsorption isotherms for the four chosen pH values.

3.3. Adsorption isotherms

The batch adsorption experiments were performed in a range of CPX concentrations between 18 and $110 \text{ (mg} \cdot \text{L}^{-1})$. The adsorption isotherms obtained for CPX on Mt at each studied pH and their best fits (dot lines) are shown in Fig. 6. Different adsorption behaviors can be associated to the isotherm shapes taking into account the Giles et al. classification (1974). According to this system, the isotherm at pH 3 can be classified as high affinity type (H-type), where the adsorption increases abruptly, suggesting a high affinity of the adsorptive molecule towards the surface of the solid. The isotherms

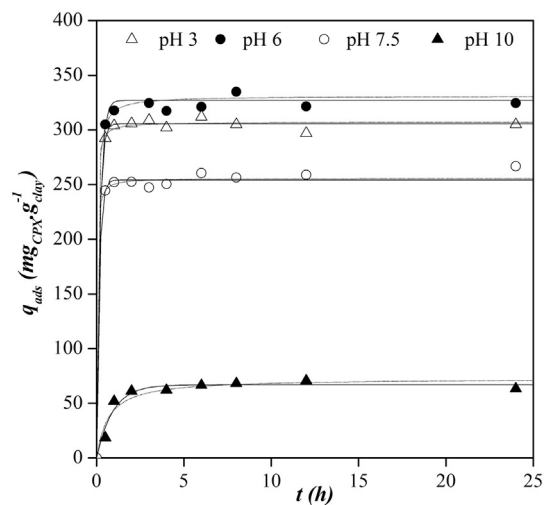


Fig. 5. Kinetic adsorption data for CPX on Mt as function of pH. The solid lines represent a pseudo-first-order model and dot lines represent pseudo-second order model.

Table 2
Pseudo-first- and pseudo-second-order parameters for CPX on Mt at four pH values.

		pH 3	pH 6	pH 7.5	pH 10
Pseudo first order	q_e ($\text{mg} \cdot \text{g}^{-1}$)	305.63	343.80	254.17	66.90
	k_1 (min^{-1})	6.26	5.28	6.57	1.09
	R^2	0.99	0.98	0.99	0.96
Pseudo second order	q_e ($\text{mg} \cdot \text{g}^{-1}$)	307.20	347.80	255.90	72.76
	k_2 ($\text{g} \cdot (\text{mg} \cdot \text{min})^{-1}$)	0.16	0.067	0.17	0.02
	R^2	0.99	0.99	0.99	0.92

obtained at 6 and 7.5 pH can be classified as a Langmuir type (L-type) and are associated to a progressive saturation of the solid surface due to the occupancy of the adsorbent surface sites. The H-type isotherm is usually considered a singular case within the L-type isotherms and both of them are associated to the ionic solute adsorption, where there is no strong competition between adsorptive and solvent molecules towards the surface of the solid (Giles et al., 1974; Limousin et al., 2007). These behaviors can be explained by taking into consideration the CPX species present in each case. At pH 3, 99.8% of the CPX molecules are in their cationic form (CPX^+), which higher affinity for the clay mineral negative surface than the one observed at pH 6, where the percentage of the cationic form is only 55.7%. These results suggest that there is a predominant cationic exchange mechanism at low pH values, due to the existence of electrostatic interactions between the positive charge of the molecule and the negative surface charge on the adsorbent. The decrease in the affinity seen at pH 6 could be related to the presence of the CPX zwitterionic form (44.2%). The maximum percentage for the zwitterionic form is obtained at pH 7.5, showing a lower affinity for the surface clay mineral than the previously studied pH value. The isotherm obtained at pH 10 exhibited a point of inflection and this is the reason why it is considered as a sigmoidal type isotherm (S-type). This type of isotherm indicates a cooperative adsorption, suggesting an initial low affinity of the adsorptive towards the adsorbent surface that increases as the surface is covered by the adsorbed molecules. This behavior supports the fact that, at pH 10, there are mainly CPX^- anions (92.8%) present in the

solution. At first, these anions could show a repulsive interaction with the negative Mt surface, but once adsorbed on the surface, they might become new adsorption sites, increasing the adsorption. The adsorption of the negative species suggests the presence of other adsorption mechanisms such as complexation, hydrogen bonding or hydrophobic interactions, previously reported for similar systems (Dahlquist, 1978; Lagaly et al., 2006; Parolo et al., 2008; Genç et al., 2013).

Adsorption data obtained for each studied pH were fitted to the Freundlich and Langmuir equations. Table 3 summarizes the fitting parameters as well as their correlation coefficients. The parameters obtained at pH 10 were not included because they showed a high error percentage, probably due to the fact that the adsorption behavior at this pH does not agree with the assumptions proposed by Langmuir and Freundlich models. Good fittings were obtained using the Langmuir equation for pH values of 3 and 6, suggesting that the adsorption under these conditions takes place in specific sites onto the solid surface, corresponding to negative charged sites. However, at pH 7.5 the best fit was obtained with the Freundlich equation indicating the presence of different adsorption sites on the solid surfaces (or non-specific sites). The highest adsorption capacity for the Mt took place at pH 6 while the lowest one was seen at pH 10. The results suggest that the CPX species present at each pH are mainly responsible for determining the adsorption mechanism, since the sites on the surface of the solids did not exhibit significant modifications. On the other hand, the lower adsorption capacity obtained at pH 3 with the increase of the CPX concentration might be explained as the result of a competitive adsorption of the H^+ against the CPX^+ species towards the surface sites. In addition, the highest adsorption values expressed in meq CPX adsorbed per g of clay mineral are 0.90 and 1.21 at pH 3 and 6, respectively. This proves that a cation exchange mechanism is very likely these pH values.

The Scatchard plots obtained for each pH value are shown in Fig. 7. The deviation from the linearity in the Scatchard plot (taking R^2 values) could be considered as an indication of the presence of nonspecific or multi-type interactions of the adsorbate molecules towards the surface sites. The R^2 values obtained were 0.95, 0.96, 0.84 and 0.72 at pH 3, 6, 7.5 and 10, respectively. This suggests that nonspecific interactions increase along with the pH. In addition, the slope obtained for the Scatchard plot linearization in the whole range of data, called the binding constant

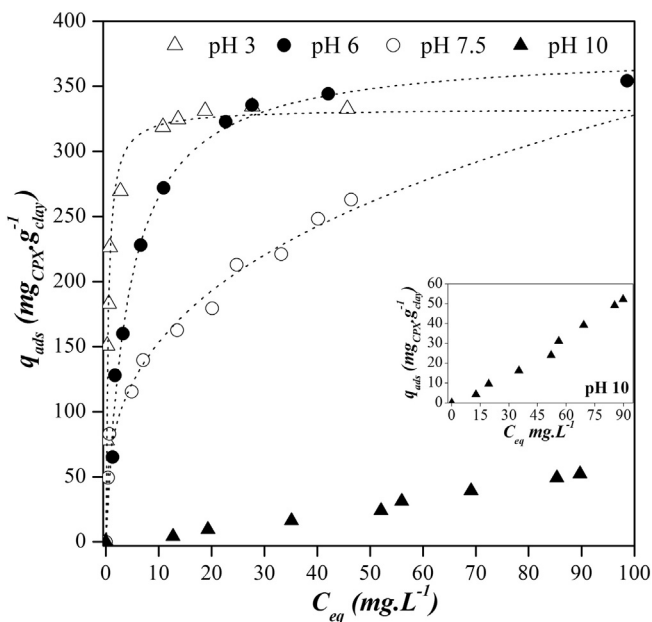


Fig. 6. Experimental isotherms (symbols) and their best adjustments (dot) for the equilibrium adsorption data of CPX on Mt.

Table 3
Freundlich and Langmuir parameters for CPX adsorption on Mt.

		pH 3	pH 6	pH 7.5
Freundlich model	k_F ($\text{mg g}^{-1}(\text{mg} \cdot \text{L}^{-1})^n$)	263.35	138.86	71.62
	n	14.49	4.57	3.03
	R^2	0.93	0.88	0.99
Langmuir model	q_m (mg g^{-1})	332.82	377.55	271.76
	k ($\text{L} \cdot \text{mg}^{-1}$)	2.50	0.24	0.15
	R^2	0.99	0.99	0.90

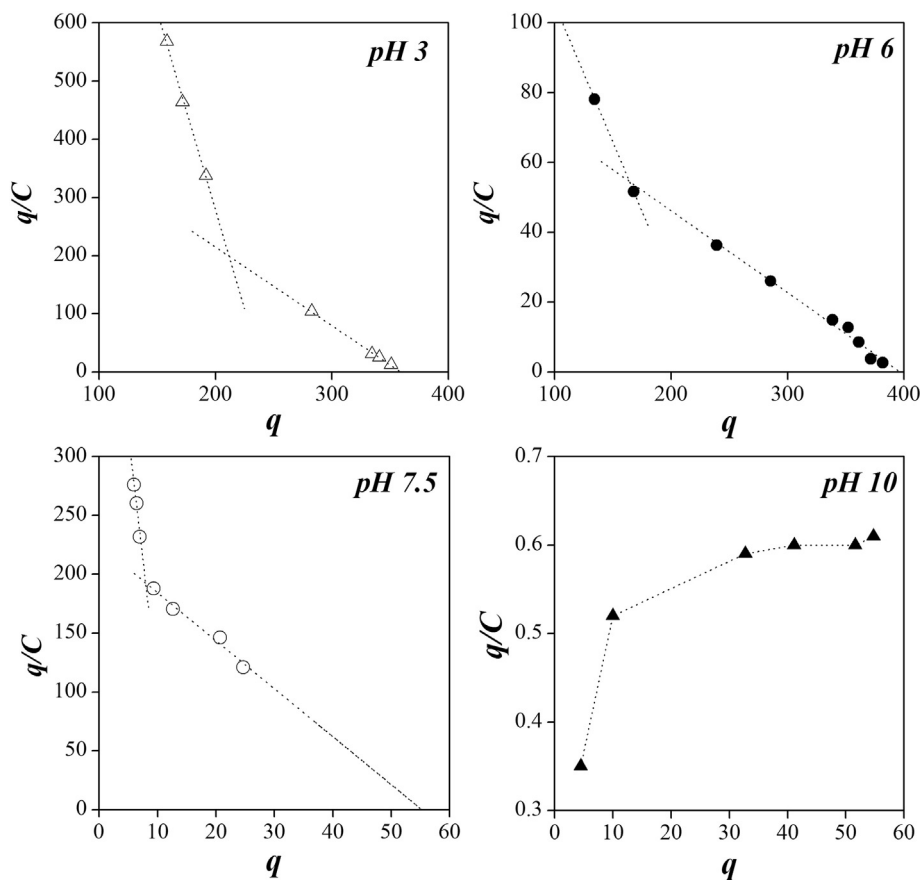


Fig. 7. The Scatchard plots derived for the adsorption data obtained at pH 3, 6, 7.5 and 10.

(K_d), is related to the adsorbate affinity for the adsorption sites. K_d values of 2.67, 0.27, 0.12 and 0.004 were obtained for pH values of 3, 6, 7.5 and 10, respectively showing an expected decrease in the affinity of the CPX species towards the surface sites. The highest deviation from linearity was obtained at pH 10 and its Scatchard plot is a convex curve associated to a positive cooperative phenomenon (Dahlquist, 1978; Gerente et al., 2000). This fact confirms the previous results and indicates that the adsorption process takes place adsorbing the first molecules with low affinity and then they become new adsorption sites favoring the subsequent adsorption. Additionally, the Scatchard plots obtained for the other pH values showed deviations from the linearity that can be considered as concave curves. These latter are associated to negative cooperative adsorption phenomena or surface heterogeneity, either of which show two kinds of affinity. Assuming the negative cooperative adsorption phenomena, the surface changes because the first adsorbed molecules decrease the affinity to the subsequent adsorption. On the other hand, the surface heterogeneity involves active sites with different affinities. These observations are consistent with the fact that the Scatchard plot exhibits two independent linear combinations, each one attributed to high-affinity (H) or low-affinity binding sites (Dahlquist, 1978; Gerente et al., 2000; Gezici et al., 2007; Anirudhan and Suchithra, 2010). At these pH values, the H binding sites may be considered as the ionic interactions of the CPX⁺ with the negative surface sites on the Mt according to the cationic proposed exchange mechanism, where the L binding sites suggest the presence of non-ionic interactions between the CPX species and other surface sites on the clay mineral surface.

3.4. Evidences of CPX intercalation into Mt: adsorption complexes

In order to evaluate the interactions between the CPX species and the clay mineral surface, FTIR spectra of adsorbed CPX on the clay

mineral (adsorption complex) were obtained. The results were compared with those obtained for the CPX (pure), the clay mineral (Mt) and a physical mixture of them (CPX-Mt). Table 4 summarizes the main bands showed by CPX, Mt and CPX-Mt which are in accordance with previous reports (Madejová, 2003; Al-Omar, 2004). Fig. 8 shows the spectra obtained for all samples CPX, Mt, CPX-Mt and the adsorption complexes. The vibration bands showed for the CPX-Mt are a combination of previous observations for the CPX and Mt, where the bands at 1640 and 1040 cm^{-1} are related to the Mt and the bands at 2840, 1701, 1480, 1387 and 1264 cm^{-1} are related to the presence of CPX. Regarding the complexes, the vibration bands of Mt are not influenced by the presence of the adsorbed CPX, but those vibration bands of CPX were modified. The bands at 1267 and 1701 cm^{-1} found in CPX and CPX-Mt spectra are assigned to the protonation of the carboxylic group and the stretching of its carbonyl group (C=O), respectively. After the adsorption, this band shifted to 1280 and 1713 cm^{-1} for the complexes of adsorption lower than the one at

Table 4
FTIR band positions (cm^{-1}) and suggested assignments for CPX, Mt and physical mixture (CPX-Mt).

CPX	Mt	CPX-Mt	Band assignment
2840	–	2840	Stretching of N–C
1701	–	1701	Stretching of C=O in carboxyl group
–	1640	1640	Deforming of O–H of water adsorbed
1621	–	–	Stretching C=O of quinoline
1605	–	–	Stretching C=O of quinoline
1480–1435	–	1480–1435	Stretching of C–N
1387	–	1387	Protonation of amine group in piperazinyl moiety
1264	–	1264	Coupling of carboxylic acid C–O stretching and O–H deforming vibrations
–	1040	1040	Stretching Si–O of di and trioctahedral smectites

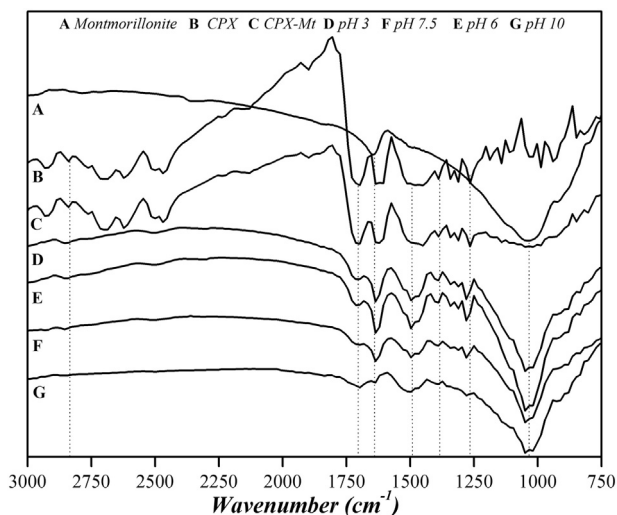


Fig. 8. FTIR spectra of Mt, CPX, CPX-Mt and the adsorption complexes obtained for pH 3, 6, 7.5 and 10.

pH 10 suggesting that the carboxylic group is involved in the adsorption process. At low pH values (3 and 6), this shift might be explained by the carboxylic group protonation and subsequent adsorption on the negative sites of the adsorbent surface. At pH 7.5, where the CPX^{\pm} and CPX^{-} species are present, the shift could be related to the presence of hydrogen bonding of the carboxylate group to the oxygen present in siloxanic surface (Li et al., 2011). The ketone $\text{C}=\text{O}$ stretching was found at 1621 cm^{-1} for CPX, but it has a high proximity with the $\text{O}-\text{H}$ deformation band of the clay mineral and it produces that this band was not considered in the analysis. The band at 1387 cm^{-1} is associated to the protonation of the amine group and it shifted to 1403 cm^{-1} in all the complexes suggesting the presence of electrostatic interactions between the protonated amine group and the negative sites on the clay mineral surface. Supporting this assumption is the shift exhibited by the band between 1480 cm^{-1} to 1494 cm^{-1} , related to the $\text{C}-\text{N}$ bond in this amine group.

2:1 type clay minerals as the Mt usually show an expansion in their interlayer region when there are molecules within their layers, as it may be seen from the increase in the basal distance (d_{001}). In order to assess the presence of the CPX within the layers of the clay mineral, XRD patterns were obtained for Mt and the adsorption complexes (Fig. 9). As it can be seen, the Mt exhibits a basal distance (d_{001}) of 12.6 \AA , typical of a natural sodium montmorillonite. The diffractograms for the adsorption complexes were obtained for two representative regions in the adsorption isotherms: at unsaturated and saturated adsorption points, with CPX concentration of $55\text{ mg}\cdot\text{L}^{-1}$ and $110\text{ mg}\cdot\text{L}^{-1}$, respectively. Two different basal distances (d_{001}) were found for these two points at each pH values. The first value was lower than the second

in all samples. In the unsaturated adsorption complex the basal distances indicate that the CPX species are present in the interlayer of the Mt. On the other hand, for the sample where the adsorption process reached the highest adsorption capacity ($110\text{ mg}\cdot\text{L}^{-1}$), d_{001} values of 16.4, 17.5 and 16.9 were obtained at pH 3, 6 and 7.5, respectively.

The peak widths observed at pH 3 for the two samples under study suggest that the CPX molecules are relatively disordered inside of the clay mineral interlayer region. This supports the assumption that the two main functional groups in CPX molecule are protonated at this pH and the molecules interact through both of them. On the other hand, XRD patterns at pH 6 and pH 7.5 showed more symmetric peaks and higher values of d_{001} suggesting that, in these particular cases, the CPX adsorbed molecules are more ordered in the interlayer. These results could suggest a different orientation at these pH values likely due to the presence of the zwitterion form of CPX in which the protonated amine group and the carboxylate group are both present. For pH 10 complex, the found d_{001} value was the lowest among the adsorption complexes and nearest to the value of the Mt. This result could suggest that the CPX molecules are not being adsorbed inside of the Mt interlayer or the adsorption is very low according to the negative species present in the solution. In addition, the obtained d_{001} value could be explained by the hydration of the interlayer cations. The analysis of the basal space obtained and the vibration bands showed for FTIR may indicate that at this pH the CPX molecule is being adsorbed on the adsorption sites present on the exposed surface of the clay mineral.

4. Conclusions

This work shows that the montmorillonite from the Pellegrini Lake can be a feasible adsorbent for CPX removal. The studied Mt showed to be the best adsorbent (adsorption capacity up to $330\text{ mg}\cdot\text{g}^{-1}$) in comparison to some carbon materials, kaolinite and rectorite which showed adsorption capacities of $135\text{ mg}\cdot\text{g}^{-1}$, $7.4\text{ mg}\cdot\text{g}^{-1}$ and $112\text{ mg}\cdot\text{g}^{-1}$, respectively. Adsorption data proves the influence of the working conditions on the adsorption mechanism among the studied conditions. The medium pH showed to be a determinant variable since it is directly related to the CPX solubility and their species. Therefore, disregarding the relationship between the CPX solubility and pH media could lead to an overestimation of the resulting adsorption capacity.

Adsorption studies of ciprofloxacin onto Mt showed that at pH values lower than 10 the predominant adsorption mechanism is a cationic exchange with the presence of electrostatic interactions between the molecule and the surface. Additionally, the adsorption behavior at pH 10 suggested the presence of other adsorption mechanisms such as complexations, hydrogen bonding or hydrophobic interactions. The CPX adsorption on Mt was more favorable at pH 6 due to the adsorption of positive and zwitterion forms of CPX. At pH 3, although the concentration of CPX^{+} is pretty high, there might be

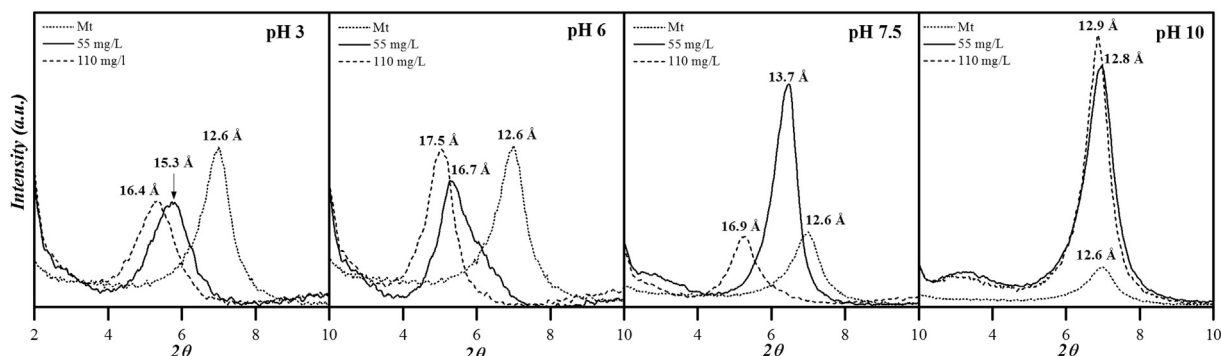


Fig. 9. XRD patterns of Mt and adsorption complexes obtained for pH 3, 6, 7.5 and 10 at two CPX initial concentrations.

some kind of competition between this species and the H^+ for the adsorption sites on the Mt, resulting in a lower adsorption capacity than the one obtained at pH 6. The results obtained at pH 7.5 suggest that the zwitterion species is also adsorbed on Mt even though the two species present at this pH value are CPX^\pm and CPX^- . For pH 3, 6 and 7.5 a negative cooperative mechanism is proposed as the first molecules adsorbed occupy the sites on the surface and affect the subsequent adsorption. At pH 10, the results suggest that the adsorption capacity is considerably low and a positive adsorption mechanism is proposed in accordance with the presence of the CPX^- . The FTIR spectra and DRX patterns obtained for all pH values show that the CPX is being adsorbed on the clay mineral surface by ionic interactions between the CPX ionizable groups and the adsorption sites on the Mt surface.

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