

Tetracycline adsorption on montmorillonite: pH and ionic strength effects

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Abstract

The adsorption of tetracycline (TC) on a Patagonian montmorillonite is studied as a function of pH, ionic strength and TC concentration by using X-ray diffraction, UV–Visible spectroscopy, ATR–FTIR spectroscopy, batch experiments and adsorption modeling. X-ray diffraction reveals that TC species can intercalate into the interlayer space of montmorillonite as deduced from the change in the basal spacing from 12.6 Å to 19.5 Å, in the absence or presence of TC respectively. UV–Visible and ATR–FTIR spectroscopies show that the corresponding spectra of TC change upon adsorption, suggesting important montmorillonite–TC interactions in the adsorbed state. Batch experiments, on the other hand, reveal that there is an important adsorption of TC in a wide range of pH. Since at low pH (pH < 4) the prevailing species of TC is a cation with a net charge of +1, the adsorption is rather high at this pH, reaching nearly the cation exchange capacity of the mineral. The adsorption then decreases as the pH is increased and eventually becomes negligible at pH 11. Experiments and modeling suggest that not only the cationic species but also the neutral and monoanionic species of TC adsorb on the negatively charged montmorillonite surface. Although there is a significant electrostatic interaction between TC and montmorillonite, a rather strong non-electrostatic interaction also exists. At all pH values TC species compete with sodium ions for surface sites, and thus there is an important effect of ionic strength on the adsorption. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Clays are used in many industrial applications mainly because of their high specific surface, presence of structural negative charges, and colloidal dimensions. Chemical and surface characteristics enables clays to adsorb different kind of molecules, specially organic and

inorganic cations (Sposito, 1984; Sánchez-Camazano and Sánchez-Martín, 1991; Rytwo et al., 2002; Gürses et al., 2004; Lombardi et al., 2006). Clays are widely used, for example, for the adsorptive removal of dyes and colouring substances from wool, oils, wines, fruit juices, fats and waxes, as Ca²⁺ remover in water softening, and as adsorbent of many pollutants (Giese and van Oss, 2002). The use of clay minerals in pharmaceutical formulation have also been described by several authors (Gámiz et al., 1992; Viseras and López Galindo, 1999; Viseras et al., 2007; Lopez Galindo et al., 2007). The interaction between drug and clay, the latter acting as excipient in the formulation, can control the drug's release and

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therefore can improve its therapeutic profile (Carretero, 2002; Aguzzi et al., 2007).

Montmorillonite occurs in substantially pure deposits of bentonite in Argentina, mainly in the North Patagonia region (Vallés and Impiccini, 1999; Lombardi et al., 2003). Some of its potential applications in pharmaceutical uses were reported by Viseras et al. (2006).

Tetracyclines comprise a group of natural and semi-synthetic products that inhibit the synthesis of bacterial proteins. They show an important activity towards a variety of micro organisms and thus they are used as broad-spectrum antibiotics in human beings, animals and in some areas of agriculture (Chopra et al., 1992). The so-called tetracycline (TC) is one of these products. The chemical properties of TC have been extensively studied (Stephens et al., 1956; Stezowski and Prewo, 1977; Lambs et al., 1983). TC has three different groups of the molecule that can undergo protonation–deprotonation reactions and the possibility to adopt different ionic species and conformations depending on the pH of the aqueous solution in which TC is dissolved. Protonation of the amine group on TC allow its cation exchange with exchanged cations of montmorillonite. There are some reports in the literature regarding TC adsorption on clays. Browne et al. (1980), for example, studied the interaction between TC and montmorillonite (Wyoming bentonite), hectorite (Hector Calif.), attapulgite (Georgia palygorskite) and kaolinite (Hydrite-10). They concluded that the interaction was related to the surface charge of the clay particles. More recently, Aguzzi et al. (2005) studied the adsorption of several tetracyclines (TC, Chlortetracycline, Methacycline, Minocycline and Doxycycline) on two pharmaceutical-grade smectites containing mainly montmorillonite. They investigated the effects of contact time and the conditions used to disperse clay aggregates. They assumed that cation exchange was the main adsorption mechanism of TC, although they left open the possibility for another (secondary) adsorption mechanism. Although these studies give some insights into the processes that control the adsorption of tetracycline on montmorillonite, more research is still needed in order to have a better understanding of the process.

The aim of this article is to present a study of the adsorption of TC on an Argentinean montmorillonite. The effects of pH and ionic strengths are mainly investigated. The adsorption results are combined with X-ray diffraction (XRD) data, ATR–IR spectroscopy and UV–Vis spectroscopy in order to confirm the presence of TC on the montmorillonite surface and to obtain some molecular-level information of the montmorillonite–TC interaction. A simple theoretical model is also used to explain

the adsorption data and to find the optimum conditions for TC adsorption.

2. Materials and methods

2.1. Materials

The bentonite was obtained from La Pampa province, Argentina. The deposits of bentonite in this province are mainly located close to the margin of the Colorado River, Argentina. The sample used was taken from the Perito Moreno mine, which is located in that region. The chemical analysis and physicochemical properties of the studied clay sample were previously reported by Lombardi et al. (2003), Vallés and Impiccini (1999) and by Viseras et al. (2006). It contains 98% of montmorillonite and 2% of quartz, as measured by XRD. The structural formula, calculated from <2 μm fraction (Signin et al., 1994) is $[(\text{Si}_{3.92}\text{Al}_{0.08})(\text{Al}_{1.42}\text{Fe}^{3+}_{0.18}\text{Mg}_{0.41})\text{O}_{10}(\text{OH})_2]\text{M}^{+}_{0.49}$, where M^{+} is predominantly Na^{+} . The sample has a cation exchange capacity (CEC) of 104 mEq/100 g as measured by the ammonium acetate method, a specific surface of 607 m²/g as measured by the adsorption of ethylene glycol monoethyl ether, and an isoelectric point of 1.8 as measured by diffusion potential (Torres Sanchez et al., 1992).

Tetracycline hydrochloride was obtained from PARAFARM, and its purity (99%) was confirmed by XRD and IR spectroscopy. The structural formula of TC is given in Fig. 1. It is a yellow crystalline substance with a molecular weight of 480.9. In aqueous solutions three different groups of the molecule can undergo protonation–deprotonation reactions depending on the pH of the solution (Qiang and Adams, 2004) giving rise to the formation of four different species. The fully protonated species of TC, which exists at rather low pH values, is the one shown in Fig. 1, and is a monocationic species that will be called TCH_3^+ . As the pH increases, the first deprotonation step takes place involving the proton at O3 (pK_{a1} = 3.3), generating a species with a negatively charged group and a positively charged group. The net charge of this species is zero and will be called TCH_2 . The second deprotonation step takes place in the diketone system involving O11 and O12 (pK_{a2} = 7.7), generating a

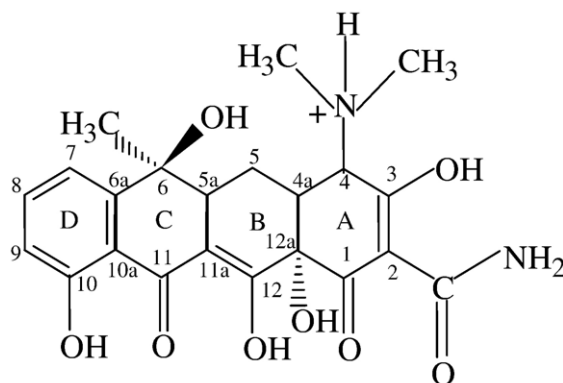


Fig. 1. Schematic drawing of the fully protonated tetracycline.

species with two negatively charged groups and a positively charged group. The net charge of this species is then -1 and will be called TCH^- . Finally, the third deprotonation step involves the proton at the dimethylamino group bound to C4 ($\text{pK}_{\text{a}3}=9.5$), giving rise to a species with two negatively charge groups (TC^{2-}) (Leeson et al., 1963).

TC stock solutions were prepared just before use to avoid degradation caused by oxygen and light (Oka et al., 1989). NaOH and HCl were used for pH adjustment and NaCl was used for ion strength adjustment.

2.2. X-ray diffraction

XRD patterns 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 40° (2θ) with a step size of 0.05° and scanning speed of $2^\circ/\text{min}$. The samples were prepared from montmorillonite suspension (15 mg/mL) and TC-montmorillonite system (92.67 mmoles of TC per 100 g montmorillonite) at pH 3. The dispersions ($<2 \mu\text{m}$ fraction) were deposited and oriented onto glass slides under constant relative humidity conditions of 36%.

2.3. UV–Visible spectroscopy

UV–Visible spectra were performed to TC aqueous solutions (0.055 mM) at varying pH (between 2 and 11) and to TC-montmorillonite dispersions at pH 3, 4 and 7. The spectra were obtained with a SHIMADZU 240 spectrophotometer. To avoid interference due to light scattering by the clay particles, a reference sample for each pH condition was prepared with 2 mL of the montmorillonite dispersion and 2 mL of water.

2.4. ATR–FTIR spectroscopy

ATR–FTIR absorption spectra were performed with a NICOLET Magna 560 FTIR apparatus equipped with a DTGS detector, a Smart RK ATR accessory and a flat ZnSe crystal. A stock montmorillonite dispersion (10 g/L) was prepared by dispersing solid montmorillonite in water. The resulting dispersion was shaken during 1 h and its pH was adjusted to the desired value by adding HCl or NaOH solutions. Several drops of this dispersion were placed on top of the ZnSe crystal and let dry overnight in order to form a dry montmorillonite film. The film was then rinsed with water in order to eliminate the excess of solid particles that did not adhere well to the crystal. The film was then covered with a NaCl solution of the desired concentration and pH, and a blank spectrum was recorded. The electrolyte solution was withdrawn and new NaCl solution having the same pH and containing 7.27×10^{-4} M TC was added. Spectra were recorded as a function of time. Additional experiments were performed in absence of the montmorillonite film in order to record the spectra of the TC in NaCl solution. In this case a rather concentrated (0.02 M) TC solution was used. All the spectra were taken in the $1000\text{--}2000 \text{ cm}^{-1}$ region. Each spectrum was the result of 256 co-added interferograms, with a spectral resolution of 2 cm^{-1} .

2.5. Adsorption studies

Two types of adsorption studies were performed: adsorption isotherms at constant pH and varying TC concentration, and adsorption measurements at constant TC concentration and varying pH and ionic strength. Adsorption isotherms were performed at four different pH values (3, 4, 5, and 7). A series of 10 mL centrifuge tubes were filled with 4 mL of a 450 mg/L of the montmorillonite dispersion of the desired pH and NaCl concentration. Then, variable volumes of a stock TC solution of the same pH were added to the tubes to give total TC concentrations ranging between 0.08 and 0.9 mmol/L and the pH was readjusted if necessary. The tubes were capped and shaken in darkness during 24 h. Preliminary experiments showed that this time was enough to reach equilibration and that changes in pH (if existed) during equilibration were lower than 0.2 units. After equilibration, the dispersions were centrifuged in a Sorvall RC 5C centrifuge at 8000 rpm during 30 min and the supernatants were removed for UV–Visible analysis at 357 nm. The amount of adsorbed TC was calculated as the differences between the initial TC concentration and the concentration that remained in the supernatant. Similar procedures were applied to perform adsorption experiments at constant TC concentration and varying pH and ionic strength. The total concentration of TC in these experiments was 0.76 mmol/L in all centrifuge tubes, the pH was varied between 2 and 11 and ionic strength between 1×10^{-4} and 1 M.

All adsorption measurements were performed in duplicate at 20°C .

2.6. Modeling

The adsorption data were fitted with a mathematical model that takes into account the binding between the TC species and the montmorillonite surface. The binding is assumed to take place at localized sites S^- , whose surface density represents the density of structural charges of montmorillonite. According to the model, each TC species and Na^+ ions, which belong to the supporting electrolyte, are bound at these sites and compete for them.

As an example, the binding of TCH_3^+ to the montmorillonite surface is represented by the reaction:



Where S^- is the binding site at the montmorillonite surface, TCH_3^+ is the fully protonated species of TC in solution and $\text{S}^- \text{TCH}_3^+$ is the surface species formed by the binding between S^- and TCH_3^+ . The mass action law of this reaction is written as:

$$K_{\text{TCH}_3} = \frac{(\text{S}^- \text{TCH}_3^+)}{(\text{S}^-) [\text{TCH}_3^+]} \quad (2)$$

Where K_{TCH_3} is the adsorption constant, symbols within parentheses represent surface concentration in (mmol/100 g) and symbols within square brackets represent concentration in solution (mol/L).

By analogy, the adsorption reactions of TCH_2 and TCH^- (TC^{2-} was found to do not interact significantly with the montmorillonite surface and thus was not considered in the model) can be formulated to give the formation of the surface species $\text{S}^- \text{TCH}_2$, and $\text{S}^- \text{TCH}^-$, and the reaction of S^- with Na^+ to give the surface species $\text{S}^- \text{Na}^+$. This cation is present in the studied system as a consequence of both, the sodium added as NaCl to control the ionic strength, and the natural sodium that acts as exchange cation of the clay. The mass action laws for these reactions are respectively:

$$K_{\text{TCH}_2} = \frac{(\text{S}^- \text{TCH}_2)}{(\text{S}^-)[\text{TCH}_2]} \quad (3)$$

$$K_{\text{TCH}} = \frac{(\text{S}^- \text{TCH}^-)}{(\text{S}^-)[\text{TCH}^-]} \quad (4)$$

$$K_{\text{Na}} = \frac{(\text{S}^- \text{Na}^+)}{(\text{S}^-)[\text{Na}^+]} \quad (5)$$

The total concentration of Na^+ was calculated as the sum of sodium added with the supporting electrolyte plus the sodium initially present in the solid montmorillonite as the exchanging cation.

The reaction between TCH_3^+ and S^- , and that between Na^+ and S^- will surely take place to a significant extent because the positively charged TCH_3^+ and Na^+ species are electrostatically attracted by the negatively charged clay mineral. In addition to electrostatic attraction, some non-electrostatic (sometimes called specific) interactions such as hydrogen bonds or hydrophobic interactions can also take place, contributing to the overall interaction (Schwarzenbach et al., 1993; Sparks, 2003). If these contributions are different for each adsorbing species, they will be reflected in different values of the respective adsorption constants.

The model needs to be completed with the mass balance for surface sites, N_s :

$$N_s = (\text{S}^-) + (\text{S}^- \text{TCH}_3^+) + (\text{S}^- \text{TCH}_2) + (\text{S}^- \text{TCH}^-) + (\text{S}^- \text{Na}^+) \quad (6)$$

Which indicates that structural charge sites should be either present as free S^- sites or bonded to sodium ions or to TC species.

Surface speciation can be easily calculated at any pH with the model if Eqs. (1–6) are combined to obtain the surface concentration of all adsorbed species:

$$(\text{S}^- \text{TCH}_3^+) = \frac{N_s K_{\text{TCH}_3} [\text{TCH}_3^+]}{D} \quad (7)$$

$$(\text{S}^- \text{TCH}_2) = \frac{N_s K_{\text{TCH}_2} [\text{TCH}_2]}{D} \quad (8)$$

$$(\text{S}^- \text{TCH}^-) = \frac{N_s K_{\text{TCH}} [\text{TCH}^-]}{D} \quad (9)$$

$$(\text{S}^- \text{Na}^+) = \frac{N_s K_{\text{Na}} [\text{Na}^+]}{D} \quad (10)$$

Where the denominator D in the equations is:

$$D = 1 + K_{\text{TCH}_3} [\text{TCH}_3^+] + K_{\text{TCH}_2} [\text{TCH}_2] + K_{\text{TCH}} [\text{TCH}^-] + K_{\text{Na}} [\text{Na}^+] \quad (11)$$

The calculations were performed in an Excel spreadsheet. For this, the aqueous concentrations of the different TC species at any pH were calculated using the three pKa of TC. The value of N_s , which represents the density of charged sites at the montmorillonite surface, was assumed to be equal to the CEC of the sample. The values of the reaction constants K_{TCH_3} , K_{TCH_2} , K_{TCH} and K_{Na} were found by trial and error until the best data fit that was possible to be obtained.

3. Results and discussion

Fig. 2 shows the XRD data of the montmorillonite sample and compares it with that of a montmorillonite that was previously dispersed in a TC solution at pH 3. The diffractogram of montmorillonite shows the primary reflection at $7.00^\circ 2\theta$ that corresponds to a basal spacing d (001) of 12.6 Å, the second and fourth order reflections: d (002) of 6.2 Å and d (004) of 3.1 Å.

X-ray pattern obtained match with samples having a water monolayer in the interlayer space of montmorillonite (Raussell-Colom and Serratos, 1987). After the contact with the TC solution the primary reflection shifts to $4.43^\circ 2\theta$ corresponding to a basal spacing of 19.5 Å, giving the evidence of the TC intercalation in the interlayer space. Since the thickness of each 2:1 layer in montmorillonite is about 9.6 Å, the interlayer spacing results to be around 9.9 Å. According to the size of the TC molecule (length 12.9 Å, height 6.2 Å and thickness 7.5 Å) (Gambinossi et al., 2004) this interlayer spacing suggests that TC is located as a monolayer between two 2:1 montmorillonite layers together with a monolayer of water molecules and perhaps some sodium ions.

Fig. 3 shows the UV–Visible spectra of a 0.069 mM TC solution at pH 3.

This is the typical spectrum of TC at this pH, with bands at around 275 nm produced by the tricarbonyl system of ring A (see Fig. 1) and at around 357 nm produced by the BCD-ring system (Mitscher, 1978). Fig. 3 also shows the spectrum of a TC solution of the same concentration and pH in the presence of 450 mg/L of clay. Under these conditions around 90% of TC is adsorbed on the montmorillonite particles and thus the spectrum corresponds mainly to adsorbed TC. Although this spectrum shows absorption at wavelengths higher than 420 nm, which is due to some turbidity caused by

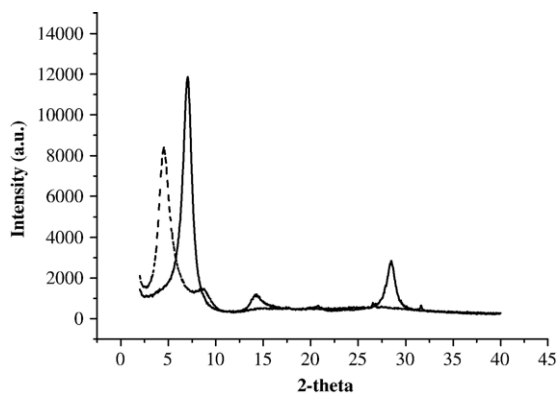


Fig. 2. XRD patterns of montmorillonite (solid line) and of montmorillonite with adsorbed TC (dashed line) at pH 3.

the montmorillonite dispersion, it also shows the typical absorption bands of TC. By comparing both spectra, it can be observed that adsorbed TC has the 357 nm band shifted to 364 nm. This shift is a good evidence for TC–montmorillonite interaction and reveals that this interaction is mainly affecting the UV–Visible absorption properties of the BCD-ring system. The same spectral changes and therefore the same kind of interaction takes place at pH 4 and 7 (not shown). According to Duarte et al. (1999) these spectral changes are caused by the conformational changes of the TC molecule from a flat conformation to a folded conformation. The results, therefore, suggest that these conformational changes are also taking place when TC interacts with montmorillonite. Similar conformational changes and spectral shifts were also reported for the interaction between TC and phospholipids (Caminati et al., 2002).

Fig. 4 shows the ATR-FTIR spectrums of a 7.27×10^{-4} M TC solution in contact with the mont-

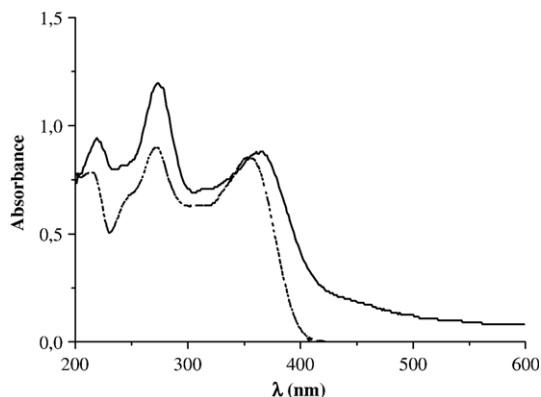


Fig. 3. UV–Visible spectra of TC aqueous solution (dashed line) and TC adsorbed on montmorillonite (solid line) at pH 3.

morillonite film at pH 4.5. For comparison, the inset of the figure shows the spectrum of the same TC solution in the absence of montmorillonite.

The bands obtained in the presence of montmorillonite correspond mainly to TC adsorbed or to TC interacting with montmorillonite since the spectrum in absence of clay shows much weaker bands in the explored IR region. The bands at 1647, 1607 and 1586 cm^{-1} can be assigned respectively to Amide I, the C=O stretching at ring A and the C=O stretching at ring C. The spectrum shows also bands at 1505 and 1456 cm^{-1} which can be assigned to the Amide II and C–C stretching (Caminati et al., 2002). Although it is difficult to elucidate the state of adsorbed TC from these data, the fact that the spectrum changes upon adsorption is also a good evidence for montmorillonite–TC interaction.

The adsorption is relatively high at pH 3 and 4 and decreases significantly at pH 5 and 7 (Fig. 5) indicating that the affinity of TC for the montmorillonite surface is higher at low pH.

The significant effects of pH on the adsorption can be better visualized in Fig. 6, where adsorption data at a given initial concentration of TC are shown for the pH range 2–11.5. The adsorption is high at pH between 2 and 4, decreases significantly between pH 4 and 5, remains nearly constant between pH 5 and 7, and then there is a less marked but continuous decrease at pH higher than 7. Eventually, the adsorption becomes negligible at pH 11.5.

Similar pH effects were reported in the literature for the adsorption of TC on several clay minerals (Browne et al., 1980). Figs. 5 and 6 also show model predictions with K values listed in Table 1. Considering the model simplicity, the fit is satisfactory in the major part of the analyzed conditions, even though an important model overestimation is detected in the initial parts of the isotherm at pH 4.

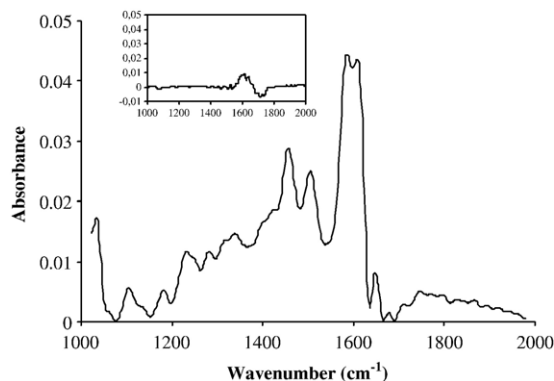


Fig. 4. ATR-FTIR spectrum of 7.27×10^{-4} M TC solution (inset) and adsorbed on montmorillonite at pH 4.5.

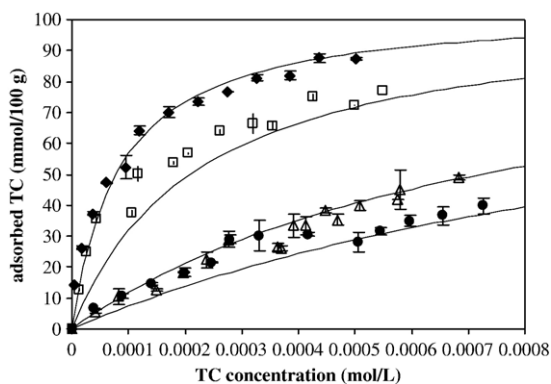


Fig. 5. Adsorption isotherms of TC on montmorillonite in 10^{-2} M NaCl. Experimental data: \blacklozenge pH 3, \square pH 4, \triangle pH 5 and \bullet pH 7. Lines: Theoretical curves obtained from the model at pH values indicated in the figure, $r=1.00$ ($p<0.05$) for pH 3, $r=0.98$ ($p<0.05$) for pH 4, $r=0.98$ ($p<0.05$) for pH 5 and $r=0.96$ ($p<0.05$) for pH 7.

This fit indicates that the proposed model describes reasonably well the adsorption of TC on montmorillonite. According to Browne et al. (1980), the effects of pH on the adsorption of TC are due to the interaction between montmorillonite and the cationic species TCH_3^+ , whose concentration decreases by increasing the pH. However, if only adsorption of TCH_3^+ and Na^+ is assumed in the modeling, the fit results to be very poor and adsorption at pH higher than 6 cannot be predicted.

According to the data in Table 1, the affinity of TC species for montmorillonite decreases in the order $\text{TCH}_3^+ > \text{TCH}_2 > \text{TCH}^-$ as can be deduced from the decrease of their adsorption constants ($K_{\text{TCH}_3^+} > K_{\text{TCH}_2} > K_{\text{TCH}^-}$). The adsorption of TCH_3^+ is easy to be understood since electrostatic attraction should drive the cationic species to the negatively charged montmorillonite

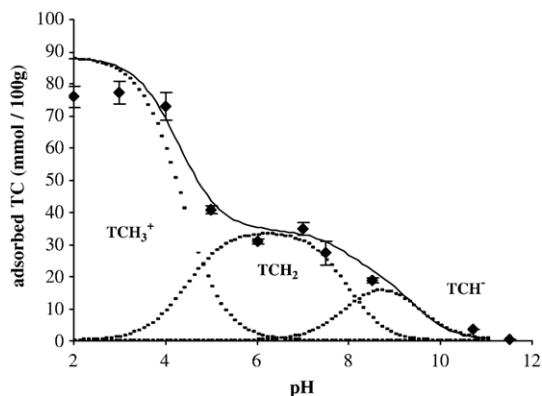


Fig. 6. Effect of pH on TC adsorption by montmorillonite in 10^{-2} M NaCl: \blacklozenge Experimental data. Solid line: Overall adsorption as predicted by the model, $r=0.99$ ($p<0.05$). Dashed lines: contribution of the different TC species to the overall adsorption.

ite surface. The case of TCH_2 and TCH^- is somewhat different since the net charge of the molecules is respectively 0 and -1 . A simple electrostatic analysis considering only the net charge of these species indicates that TCH_2 should not be electrostatically attracted by montmorillonite and that TCH^- should be repelled by the clay. However, since both species contain a positively charged group in their structure, it is likely that the molecules arrange at the surface so that the positively charged group is located very close to the surface, leading the negatively charged one(s) as far as possible from the surface. This analysis reveals that electrostatic may play an important role in the adsorption of not only TCH_3^+ but also TCH_2 and TCH^- . The analysis is also in agreement with the fact that the affinity for the surface decreases in the order $\text{TCH}_3^+ > \text{TCH}_2 > \text{TCH}^-$.

As indicated in Section 2.6, there may also exist non electrostatic interactions between TC species and the montmorillonite surface. By combining Eqs.(2) and (5) the following equation can be obtained $K_{\text{ex}} = \frac{K_{\text{TCH}_3^+}}{K_{\text{Na}^+}} = \frac{(S^- \text{TCH}_3^+) [\text{Na}^+]}{(S^- \text{Na}^+) [\text{TCH}_3^+]}$ which allows to evaluate the constant, K_{ex} , of the following cation exchange process $S^- \text{Na}^+ + \text{TCH}_3^+ \rightleftharpoons S^- \text{TCH}_3^+ + \text{Na}^+$.

If Na^+ and TCH_3^+ ions are assumed to be bound only by electrostatic attraction to the surface, $K_{\text{TCH}_3^+}$ and K_{Na^+} would be very similar and thus K_{ex} would be around 1. This is not the case in the studied system, since the value of $K_{\text{TCH}_3^+}$ is much higher than K_{Na^+} giving $K_{\text{ex}}=4000$. Thus, the much higher affinity of TCH_3^+ for the surface can only be explained if important attractive non-electrostatic interactions are also operating in the adsorption process of TCH_3^+ . These interactions, such as hydrogen bonding or hydrophobic interactions, are likely to operate not only with TCH_3^+ but also with TCH_2 and TCH^- , and they will surely contribute to drive the adsorption of these species. This seems to be rather common for ionic organic substances adsorbing at mineral surfaces (Russell-Colom and Serratos, 1987; Rodríguez et al., 2003; Ötker and Akmehmet-Balcioğlu, 2005).

Experimental data indicate that the adsorption is nearly constant at low electrolyte concentration but

Table 1
Adsorption constants of TC species and Na^+ on montmorillonite

TC species	$\log(K)^a$
TCH_3^+	4.20 ± 0.05
TCH_2	2.93 ± 0.05
TCH^-	2.60 ± 0.05
Na^+	0.60 ± 0.05

^a the units of K are L/mol.

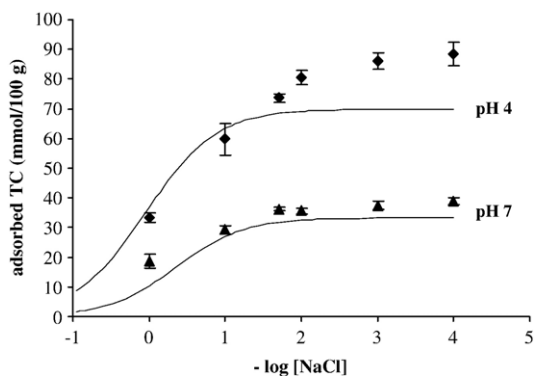


Fig. 7. Effect of ionic strength on the TC adsorption by montmorillonite. Experimental data: \blacklozenge pH 4, \blacktriangle pH 7. Lines: Theoretical curves obtained from the model at pH values indicated in the figure, $r=0.94$ ($p<0.05$) for pH 4 and $r=0.98$ ($p<0.05$) for pH 7.

decreases at high electrolyte concentration at pH 4 and 7 (Fig. 7). Although the model underestimates somewhat the adsorption at low electrolyte concentrations at pH 4, the general trends of the fits are in agreement with the experimental data. The results are good evidence for a competition between TC species and Na^+ ions for surface sites. In NaCl solutions having a concentration around 10^{-2} M or higher, the concentration of Na^+ is high enough to compete with TC species and occupy surface sites, decreasing the adsorbed amount of TC. On the contrary, when the NaCl concentration decreases, Na^+ ions are no longer important competitors and thus the maximum adsorption of TC is reached. Since the initial concentration of TC in the experiments of Fig. 7 was 7.6×10^{-4} M, it can be deduced that Na^+ ions need to be 100 to 1000 times more concentrated than TC to produce significant displacement of adsorbed TC species. This result also points toward a much stronger affinity of TC than Na^+ for surface sites.

4. Conclusions

XRD, ATR-IR and UV-Visible data show that TC species adsorb on montmorillonite. The adsorption leads to the intercalation of molecules in the interlayer spaces of the clay mineral, and probably to conformational changes of the adsorbed molecules.

The pH of the aqueous solution largely affects the amount of adsorbed TC. The adsorption is relatively high at low pH (2–4), where important electrostatic attraction takes place between the negatively charged montmorillonite and the prevailing positively charged TCH_3^+ species. The adsorption is so high under these conditions that it nearly reaches the CEC of the mineral. As the pH increases, the adsorption becomes lower.

The adsorption constants of the different TC species decrease in the order TCH_3^+ , TCH_2 , and TCH^- . This trend can be understood by taking into account electrostatic and non-electrostatic interactions between TC species and the montmorillonite surface. Important non-electrostatic interactions are demonstrated by the fact that the affinity of TCH_3^+ by montmorillonite is much higher than that of Na^+ .

From a practical viewpoint, the studied montmorillonite appears to be a very good adsorbent of TC. Although the optimum adsorption pH range is 2–4, the adsorption capacity of this clay mineral between pH 5 and 7 is still rather high. Thus montmorillonite could be used in this pH range as a purifying agent of waste waters containing TC and excipient in pharmaceutical formulations.

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