

Influence of Ca^{2+} on tetracycline adsorption on montmorillonite

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ABSTRACT

The adsorption of tetracycline (TC) on montmorillonite was studied as a function of pH and Ca^{2+} concentration using a batch technique complemented with X-ray diffraction and transmission electron microscopy. In the absence of Ca^{2+} , TC adsorption was high at low pH and decreased as the pH increased. In the presence of Ca^{2+} , at least two different adsorption processes took place in the studied systems, i.e., cation exchange and Ca-bridging. Cation exchange was the prevailing process at $\text{pH} < 5$, and thus, TC adsorption decreased by increasing total Ca^{2+} concentration. On the contrary, Ca-bridging was the prevailing process at $\text{pH} > 5$, and thus, TC adsorption increased by increasing Ca^{2+} concentration. The pH 5 represents an iso-adsorption pH where both adsorption processes compensate each other. TC adsorption became independent of Ca^{2+} concentration at this pH. For TC adsorption on Ca^{2+} -montmorillonite in 0.01 M NaCl experiments, the ratio adsorbed TC/retained Ca^{2+} was close to 1 in the pH range of 5–9, indicating an important participation of Ca^{2+} in the binding of TC to montmorillonite. X-ray diffraction and transmission electron microscopy showed that TC adsorption induced intercalation between montmorillonite layers forming a multiphase system with stacking of layers with and without intercalated TC.

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1. Introduction

Montmorillonite is the most studied swelling clay mineral. It is a layered material with a structural negative charge due to isomorphous substitutions, which impart a cation exchange capacity (CEC) of about 100 mEq/100 g (1.00 Eq/kg) to the solid and hydrophilic properties to its surface [1]. In addition, this clay mineral presents colloidal particle size and high specific surface area. All these properties determine the adsorption and intercalation of various inorganic and organic substances on its constituting particles. Patagonian montmorillonites were extensively characterized [2–4]. These clay minerals provide materials to be used in pharmaceutical formulation [5] and as adsorbents of organic pollutants [6].

Tetracyclines (TCs) constitute a family of antibiotics which are used worldwide to treat many bacterial infections. They are also used as veterinary medicines and as animal growth promoters. TCs mainly enter the environment through land application of animal manure or direct deposition by livestock [7]. The extensive use of TCs has resulted in their recurrent detection in groundwater, wastewater, and soils [7,8]. They are becoming subject of growing concern because they are rather persistent in nature and can be hazardous to non-target organisms or be the cause of antibiotic resistance of microorganisms [9].

The so-called tetracycline (TC) is a compound from the TCs family, and its chemical properties were extensively studied [10–12]. TC may exist in either cationic, zwitterionic, or anionic forms at environmentally relevant pH values. Electron donor groups present in the TC structure permit complex formation with Ca^{2+} and Mg^{2+} cations [13,14]. These donor groups and the presence of electric charges in TC species also promote adsorption on various mineral surfaces, including clays.

The transport of TC in soils and natural waters is strongly affected by adsorption on soil minerals, making adsorption studies very important for the understanding of the environmental behavior of TC. Several authors have carried out studies of TC adsorption onto different clay minerals, including montmorillonite [15–17], rectorite [18], and palygorskite [19]. In the case of a Patagonian montmorillonite in aqueous NaCl solutions [15,16,20], it was shown that TC can intercalate into the interlayer space of montmorillonite and that not only the cationic species but also the zwitterionic, and the monoanionic TC species can adsorb on the negatively charged montmorillonite surface. In general, TC adsorption decreased by increasing the solution pH [15]. A similar behavior was shown for the adsorption of TC and oxytetracycline on the K-10 Sigma Aldrich montmorillonite in NaCl solutions [21] and for the adsorption of TC on a sodium-saturated montmorillonite from Wyoming [22]. Cation exchange together with non-electrostatic interactions such as hydrogen bonding or hydrophobic interaction was proposed as the main adsorption mechanisms [15,21–23].

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The adsorption of TC and other TCs on montmorillonite have been usually conducted on the Na⁺-exchanged form of the clay mineral in NaCl solutions. There is less information on the adsorption in the presence of a divalent cation such as Ca²⁺. This cation is ubiquitous in natural media and is implicated in many biological, edaphological, and environmental processes. In addition, Ca²⁺ is known to have both a relatively high affinity for the montmorillonite surface [24] and a significant capacity of forming complexes with TCs in solution [25]. Therefore, its presence in aqueous media may affect considerably the binding of TCs to montmorillonite. There are only a few articles where the participation of Ca²⁺ in the mechanism of TCs adsorption on clays was reported. Figueroa et al. [21], for example, found that a Ca²⁺-exchanged montmorillonite adsorbed less oxytetracycline than the Na⁺-exchanged clay at pH lower than 6.5. The behavior reversed at pH higher than 6.5, where the adsorption on the Ca²⁺-exchanged montmorillonite was larger. A rather similar behavior was informed by Browne et al. [22] for TC adsorption on Na⁺- and Ca²⁺-exchanged montmorillonites, except for the pH range 1–3, where the adsorption was equal on both samples. Pils and Laird [26], on the other hand, studied TC and chlortetracycline on whole soils and different soil components, which were previously exchanged with either Ca²⁺ or K⁺. They found that the adsorption of the studied antibiotics at pH 5.8 and 7 was larger on the Ca²⁺-exchanged systems than on the K⁺-exchanged ones. In all cases, cation exchange and cation bridging (where calcium acts as a bridge between the surface and TC) were proposed as the mechanisms that contributed to adsorption.

Although all the investigations mentioned above give important insights into the effects of calcium on TC adsorption on clay minerals, the system was not extensively studied, and more information is still needed. Previous studies, for example, did not investigate calcium adsorption in order to support the proposed cation bridging mechanism. The aim of this article is to evaluate the effects of Ca²⁺ on the adsorption of TC on a Patagonian montmorillonite. TC adsorption studies in the pH range 2–12 in the presence of Ca²⁺ and Na⁺ ions are presented and analyzed. Ca²⁺ adsorption is also evaluated in a selected system to provide additional information on the adsorption process. X-ray diffraction (XRD) and transmission electron microscopy (TEM) are also used as complementary techniques.

2. Materials and methods

2.1. Materials

The studied montmorillonite was obtained from Northern Patagonia, Argentina. The mineralogical and chemical composition and some physicochemical properties of the naturally occurring sample were previously reported by Vallés and Impiccini [27] (identified as sample 714), Lombardi et al. [3] (identified as sample 9), and Viseras et al. [5] (identified as sample A8). It contains 98% of montmorillonite and 2% of quartz, as measured by XRD. Its structural formula, calculated for the <2 μm fraction, is [(Si_{3.92}Al_{0.08})(Al_{1.42}Fe³⁺_{0.18}Mg_{0.41})O₁₀(OH)₂]M⁺_{0.49}, where M⁺ is predominantly Na⁺ (>90%). The cation exchange capacity (CEC) is 104 mEq/100 g (1.04 Eq/kg) as measured by the ammonium acetate method, and the specific surface is 607 m²/g (0.607 m²/kg), as measured by adsorption of ethylene glycol monoethyl ether. This sample will be called Na⁺-montmorillonite.

Experiments were performed with the Na⁺-montmorillonite sample and with a Ca²⁺-exchanged form (Ca²⁺-montmorillonite) for comparison. In order to obtain this last sample, the Na⁺-montmorillonite was dispersed in a 1 N CaCl₂ solution during 24 h. Afterward, the dispersion was centrifuged at 10,410g during 30 min, the supernatant was removed, and the solid was washed with water

until negative chloride assay. The so-prepared Ca²⁺-montmorillonite was dried at 40 °C, ground, and stored until use.

Tetracycline hydrochloride was purchased from PARAFARM (99% purity). Stock solutions of TC were prepared just before use to avoid degradation caused by oxygen and light. NaCl or CaCl₂ was used for ionic strength adjustment and NaOH or HCl was used for pH adjustment. The pH was measured with an Altronix (SilverCap) glass electrode and an Altronix (TPX-II) pH meter.

2.2. X-ray diffraction

XRD patterns were obtained using a RIGAKU Geigerflex X-ray diffractometer with Cu Kα 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°/min.

Dispersions (15 mg/mL) of montmorillonite samples at pH 7 were deposited and oriented onto glass slides and let dry under constant relative humidity conditions (36%). Three types of dispersions were prepared for these analyses: Na⁺-montmorillonite in 0.01 M NaCl, Ca²⁺-montmorillonite in 0.01 M NaCl, and Ca²⁺-montmorillonite in 0.01 M CaCl₂. The same dispersions, but with addition of TC at the desired concentration, were prepared to investigate the effects of TC on the X-ray diffraction patterns.

2.3. Transmission electron microscopy

Dry samples of montmorillonites with and without adsorbed TC were embedded in Spurr's resin and treated overnight at 60 °C. Seventy nanometer thick sections were cut on a LKB microtome and observed in a JEOL 100 CXII transmission electron microscope operating at 100 kV. Images were analyzed using the software NIKON-NIS-Elements Basic Research, version 3.0, in order to estimate basal spacings.

2.4. TC adsorption

Before starting an adsorption experiment, a stock TC solution (2.78 × 10⁻³ M) and a stock montmorillonite dispersion (9.0 × 10⁻⁴ kg/L) were prepared by dissolving/dispersing the solids in the desired electrolyte solution (either 0.01 M NaCl or 0.01 M CaCl₂). After that, a series of 10 mL centrifuge tubes were filled with 2.2 mL of the stock TC solution, 4 mL of the stock montmorillonite dispersion of the desired pH, and 1.8 mL of electrolyte in order to obtain a final volume of 8 mL and a total TC concentration of 0.76 mM in all tubes. The pH was readjusted with NaOH and HCl solutions if necessary to cover the pH range 2–11. The tubes were closed and shaken in darkness during 24 h. Preliminary experiments showed that this time was enough to reach equilibrium. After that, the dispersions were centrifuged in a Sorvall RC 5C centrifuge at 7100g during 30 min and the supernatants were withdrawn. TC concentration in the supernatants was measured by UV-Vis spectroscopy using a SHIMADZU 240 spectrophotometer. Since TC absorption maxima depend on pH [20], a calibration curve was performed at each investigated pH to measure TC concentration. The amount of adsorbed TC was calculated as the difference between the initial TC concentration and the concentration that remained in the supernatant. All measurements were taken in triplicate at room temperature.

The following three series of (TC adsorption vs. pH) experiments were performed with the above methodology: (a) TC adsorption on Na⁺-montmorillonite using 0.01 M NaCl as supporting electrolyte; (b) TC adsorption on Ca²⁺-montmorillonite using 0.01 M NaCl as supporting electrolyte; and (c) TC adsorption on Ca²⁺-montmorillonite using 0.01 M CaCl₂ as supporting electrolyte. These experiments were designed to have constant concentrations of montmorillonite (4.5 × 10⁻⁴ kg/L) and TC (0.76 mM) in the three

series and different total concentration of Ca^{2+} (0 M for series a, 2.34×10^{-4} M for series b and 0.01 M for series c).

2.5. Ca^{2+} released/retained during TC adsorption

For the case of TC adsorption on Ca^{2+} -montmorillonite in 0.01 M NaCl (series b), an extra experiment was performed aiming to quantify the amount of Ca^{2+} released/retained by the solid during TC adsorption. The experimental conditions were the same as the employed for that series of experiments, but the total volume in each centrifuge tube was 80 mL (using 22 mL of the stock TC solution, 40 mL of the stock Ca^{2+} -montmorillonite dispersion and 18 mL of 0.01 M NaCl). After centrifugation, the supernatants were analyzed for Ca^{2+} in order to determine the amount of Ca^{2+} released to the solution. In addition, the amount retained by the solid was calculated as the difference between total Ca^{2+} (which was initially as the exchange cation of the solid) and Ca^{2+} that appeared in solution. These data were compared with those obtained under the same conditions but in the absence of TC. Ca^{2+} concentration was measured with an atomic absorption spectrophotometer (METRO-LAB 250AA, $\lambda = 423$ nm). Before the analyses, supernatants were mixed with a lanthanum oxide solution to account for possible interferences during data acquisition. The aqueous detection limit of the used method was 1 ppm.

Similar calcium determinations were not performed for series a experiments, because the exchanging cation of this natural montmorillonite is mainly sodium (calcium is only present in low amounts), or in series c experiments, because calcium concentration in the supporting electrolyte is around 100 times higher than calcium concentration that could be released by the mineral, which impedes an accurate determination of the amount of calcium released to the solution.

3. Results and discussion

The structure of the TC molecule in its fully protonated form is shown in Fig. 1. This molecule (actually a cation, called TCH_3^+ here) possesses three dissociable proton centers namely C1–C3 tricarbonyl methane ($\text{pK}_a = 3.3$), O10 and O12 ketophenolic hydroxyl groups ($\text{pK}_a = 7.7$), and C4 dimethylammonium group ($\text{pK}_a = 9.5$) (Table 1). Dissociation reactions lead to the existence of four different species in aqueous media: a cationic (TCH_3^+), a zwitterionic (TCH_2^{\pm}), and two anionic (TCH^- and TC^{2-}) species under acidic, moderately acidic to neutral, and alkaline conditions, respectively.

Electron donor groups in the TC molecule (N4-OH12a and O10-O12) enable the formation of strong complexes with metal ions such as Ca^{2+} and Mg^{2+} [13,14,28]. Therefore, additional species of TC appear in the presence of Ca^{2+} . The formation constants of TC complexes with Ca^{2+} were reported by Lambs et al. [29] and are also listed in Table 1.

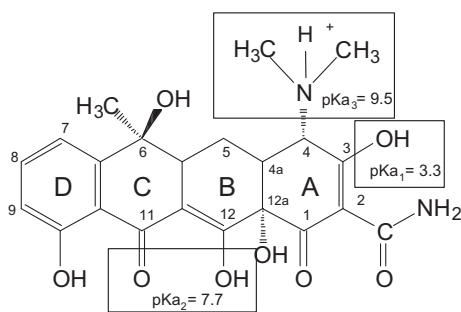


Fig. 1. Structure of fully protonated TC.

Table 1
Formation constants used in the calculations [29].

Formation reaction	Species	logK
$\text{TC}^{2-} + \text{H}^+ \rightleftharpoons$	TCH^-	9.052
$\text{TC}^{2-} + 2 \text{H}^+ \rightleftharpoons$	TCH_2^{\pm}	16.323
$\text{TC}^{2-} + 3 \text{H}^+ \rightleftharpoons$	TCH_3^+	19.485
$\text{TC}^{2-} + 2 \text{Ca}^{2+} \rightleftharpoons$	$\text{Ca}_2\text{TC}^{2+}$	8.671
$2 \text{TC}^{2-} + \text{Ca}^{2+} \rightleftharpoons$	CaTC_2^{2-}	8.731
$2 \text{TC}^{2-} + \text{Ca}^{2+} + \text{H}^+ \rightleftharpoons$	$\text{Ca}(\text{TC})(\text{TCH})^-$	17.618
$2 \text{TC}^{2-} + \text{Ca}^{2+} + 2 \text{H}^+ \rightleftharpoons$	$\text{Ca}(\text{TCH})_2$	25.540

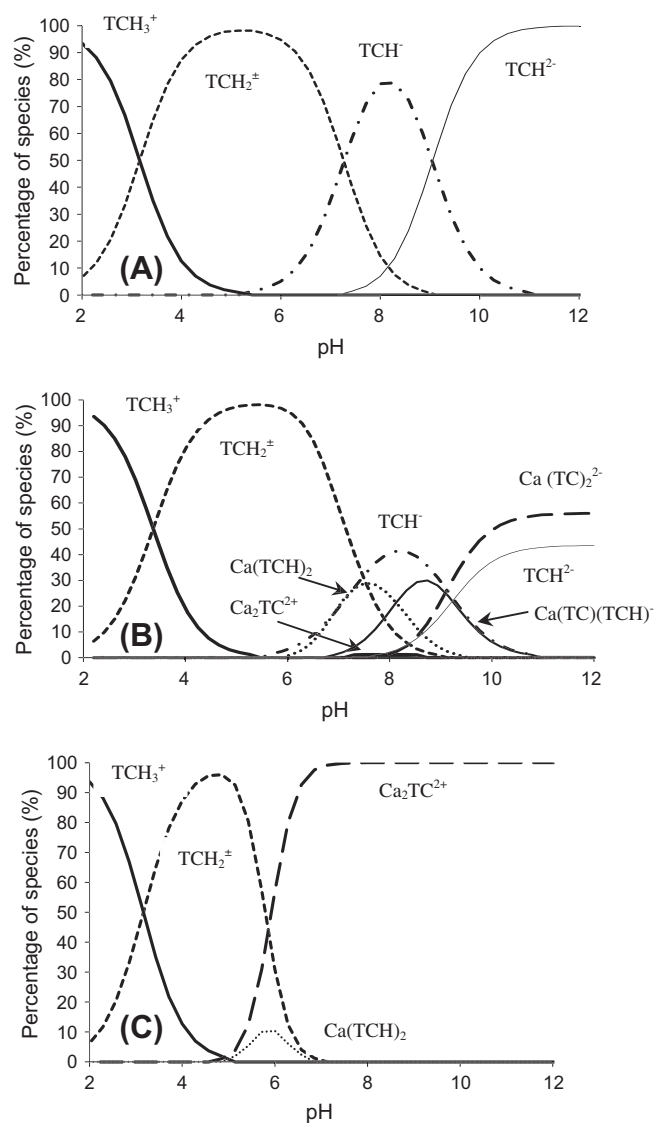


Fig. 2. Species distribution curves for TC and Ca^{2+} -TC complexes: (A) $[\text{TC}] = 0.76$ mM, (B) $[\text{TC}] = 0.76$ mM, $[\text{Ca}^{2+}] = 2.34 \times 10^{-4}$ M, and (C) $[\text{TC}] = 0.76$ mM, $[\text{Ca}^{2+}] = 0.01$ M.

Fig. 2 shows the distribution of species of a 0.76 mM TC solution as a function of pH in the absence of Ca^{2+} and at two different total concentrations of Ca^{2+} , 2.34×10^{-4} M and 0.01 M, corresponding to the maximum Ca^{2+} concentrations that could be obtained in solution in the experiments with Ca^{2+} -montmorillonite in 0.01 M NaCl and with Ca^{2+} -montmorillonite in 0.01 M CaCl_2 , respectively. In the absence of Ca^{2+} only TCH_3^+ , TCH_2^{\pm} , TCH^- and TC^{2-} species are present. In the presence of Ca^{2+} 2.34×10^{-4} M, $\text{Ca}(\text{TCH})_2$, $\text{Ca}(\text{TC})(\text{TCH})^-$, $\text{Ca}(\text{TC})_2^{2-}$ complexes with calcium appear at significant

concentrations at $\text{pH} > 6$, whereas in 0.01 M Ca^{2+} , the dominating Ca–TC complex is $\text{Ca}_2\text{TC}^{2+}$, which appears at $\text{pH} > 5$.

3.1. X-ray diffraction

The diffractograms of Na^+ -montmorillonite and Ca^{2+} -montmorillonite in different media and in the absence or presence of TC are shown in Fig 3. The pattern of Na^+ -montmorillonite in 0.01 M NaCl without TC (Fig 3A) shows a broad primary reflection at around $6.60^\circ 2\theta$ that correspond to a basal spacing d_{001} of 13.4 Å, indicating the coexistence of two hydration states, with one and two intercalated water layers [30–32]. The addition of TC to this sample leads to a pattern containing two primary reflections at $4.02^\circ 2\theta$ ($d_{001} = 22.0$ Å) and $6.71^\circ 2\theta$ ($d_{001} = 13.2$ Å). Since basal spacings of around 20 Å are rather common for monolayer TC intercalation in montmorillonite [15,17] and the other spacing is very similar to that of Na^+ -montmorillonite in the absence of TC, the results indicate that the layer stacking is not regular and that two different domains are occurring, one of them containing TC molecules in the interlayer and the other containing Na^+ ions. Similar results were found for TC intercalation in SWy-2 and SAz-1 montmorillonites [17].

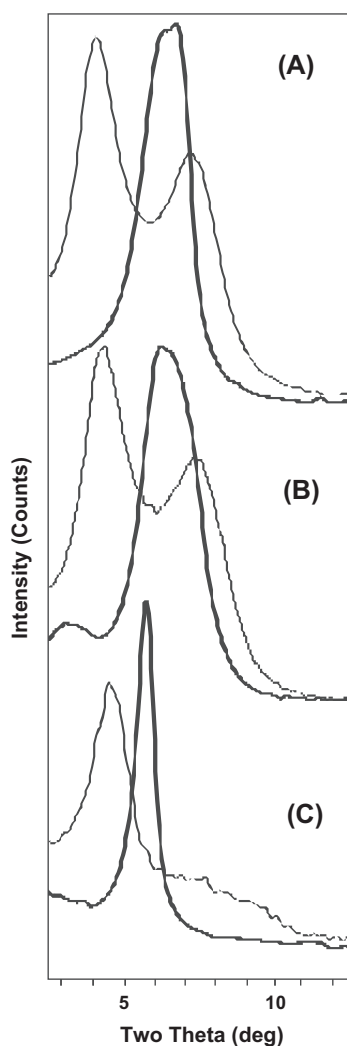


Fig. 3. XRD patterns of (A) Na^+ -montmorillonite in 0.01 M NaCl, (B) Ca^{2+} -montmorillonite in 0.01 M NaCl, and (C) Ca^{2+} -montmorillonite in 0.01 M CaCl_2 . In all cases, the patterns in the absence (thick line) and presence (thin line) of TC are compared.

The pattern of Ca^{2+} -montmorillonite in 0.01 M NaCl without TC (Fig. 3B) shows also a broad first order reflection, but now at around $6.28^\circ 2\theta$ ($d_{001} = 14.06$ Å). This increase in the basal spacing may be due to the coexistence of calcium and sodium ions in the interlayer. Upon the addition of TC, a second reflection appears at $4.06^\circ 2\theta$ ($d_{001} = 21.8$ Å) indicating TC intercalation.

The pattern of Ca^{2+} -montmorillonite in 0.01 M CaCl_2 without TC (Fig. 3C) shows the characteristic narrow reflection of calcium montmorillonite at $5.75^\circ 2\theta$ ($d_{001} = 15.4$ Å). After addition of TC, the primary reflection shifts to $4.50^\circ 2\theta$ (19.6 Å), indicating also TC intercalation.

3.2. Transmission electron microscopy

Fig. 4 displays TEM micrographs of Ca^{2+} -montmorillonite in 0.01 M NaCl with and without TC. For the case of Ca^{2+} -montmorillonite (Fig. 4A), clay layers are seen as relatively aligned and ordered lines. Basal spacing of 13.0 Å was measured in the sample. In some regions of the micrograph, a random arrangement is also noticeable, probably due to edge-to-edge and edge-to-face particle aggregation. For the case of Ca^{2+} -montmorillonite in the presence of TC, domains showing spacings of 13 Å mixed with other domains showing spacings of 22.0 Å were detected. TEM images support the findings from XRD, indicating that montmorillonite in the presence of TC forms, a multiphase systems consisting of stackings of montmorillonite layers without intercalated TC, mixed with stackings of layers with intercalated TC.

3.3. Adsorption studies

The effect of pH on TC adsorption at the three investigated total Ca^{2+} concentrations is shown in Fig. 5.

TC adsorption on Na^+ -montmorillonite in 0.01 M NaCl (series a, 0 M total Ca^{2+}) is relatively high at pH 2 and 3 and then decreases continuously with increasing pH and becomes very low at pH values above 10. Similar results were reported by other authors [22,33]. The adsorption of TC under these conditions was analyzed with some detail in a previous publication by using a simple adsorption model [15]. It was concluded that not only the cationic species TCH_3^+ but also the zwitterionic species TCH_2^\pm and the anionic species TCH^- adsorb on montmorillonite. Electrostatic interaction is favorable for TCH_3^+ adsorption on negatively charged montmorillonite and thus TCH_3^+ compete with Na^+ ions for the adsorption sites, competition that can be interpreted as a cation exchange process [15]. Besides electrostatic attraction, important non-electrostatic interactions (such as hydrogen bonding and hydrophobic interactions) were also proposed for the adsorption of TCH_3^+ since the affinity of this cationic species for the montmorillonite surface resulted to be much higher than the affinity of Na^+ (a similar affinity would be expected if the adsorption is mainly driven by electrostatics). These non-electrostatic interactions are also contributing to the adsorption of TCH_2^\pm and TCH^- , with the aid of some electrostatics. Even though the net charge of these two last species is 0 and -1 , respectively, both species contain a positively charged group in their structure, the dimethylammonium group, and thus, the molecules can arrange at the surface locating the positively charged group close to the surface and the negatively charged group(s) as far as possible from the surface [15].

TC adsorption on Ca^{2+} -montmorillonite in 0.01 M NaCl (series b, 2.34×10^{-4} M total Ca^{2+}) is also pH dependent. In the pH range 2–5, the adsorption is relatively high and very similar to that of the previous case. This can be well understood since no Ca–TC complex appears at significant concentrations under these conditions; thus, TC species adsorb as in the previous case. It is possible that some competition between TCH_3^+ and Ca^{2+} for surface sites is

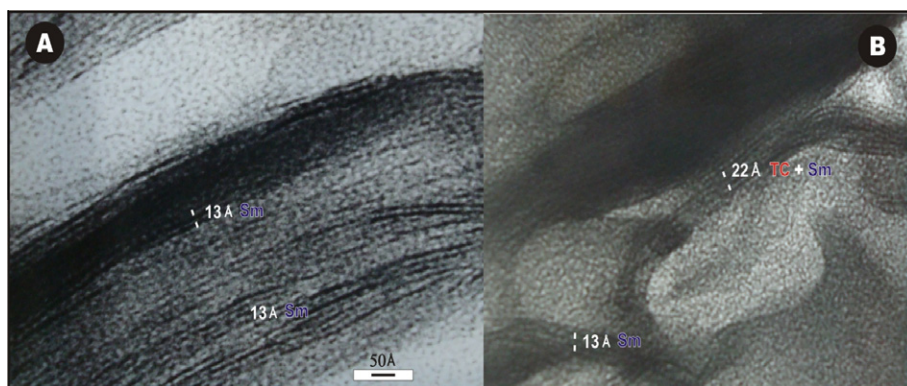


Fig. 4. TEM micrograph of (A) Ca^{2+} -montmorillonite and (B) Ca^{2+} -montmorillonite with adsorbed TC (60 mmol/100 g).

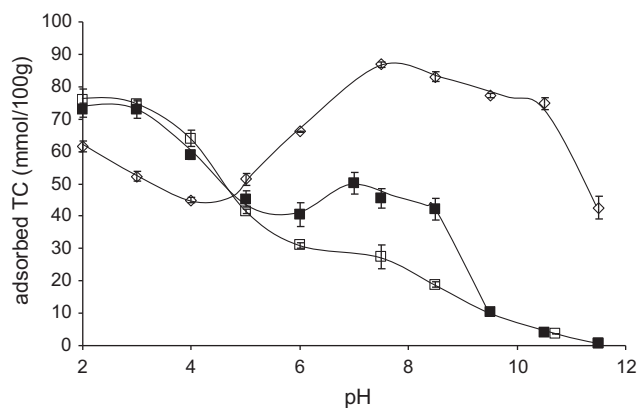


Fig. 5. Effect of pH on TC adsorption by Na^{+} -montmorillonite in 0.01 M NaCl (□), Ca^{2+} -montmorillonite in 0.01 M NaCl (■), and Ca^{2+} -montmorillonite in 0.01 M CaCl_2 (◇). TC concentration: 0.76 mM.

taking place in this pH range, accounting for the slight decrease in the adsorption with respect to adsorption in the absence of Ca^{2+} . From pH 5, and especially from pH 6 to around pH 9, TC adsorption is higher than in the absence of Ca^{2+} . TC is able to form several complexes with Ca^{2+} in this pH range (Fig. 2), such as the neutral complex $\text{Ca}(\text{TCH})_2$ between pH 6 and 9, the monoanionic complex $\text{Ca}(\text{TCH})(\text{TC})^{-}$ between pH 7 and 10, the dicationic complex $\text{Ca}_2\text{TC}^{2+}$ at low concentrations between pH 7 and 9, and the dianionic complex $\text{Ca}(\text{TC})_2^{2-}$ above pH 8. The distribution of species and their electrical charges suggest that $\text{Ca}(\text{TCH})_2$ and $\text{Ca}_2\text{TC}^{2+}$ are the best candidates for adsorption. Even though the exact nature of the adsorbed complexes cannot be known from these data, it is clear that Ca^{2+} is playing a key role in the adsorption, probably acting as a bridge between the montmorillonite surface and TC (calcium interacting simultaneously with the surface and TC), as was suggested by Figueroa et al. [21] and Pils and Laird [26].

TC adsorption on Ca^{2+} -montmorillonite in 0.01 M CaCl_2 (series c, 0.01 M total Ca^{2+}) is significantly lower at pH 2–5 and significantly higher at pH > 5 than in the other two cases (Fig. 5). Similar results were found for TC adsorption on a Ca^{2+} -montmorillonite in sodium bicarbonate solutions by Figueroa et al. [21]. The distribution of species in Fig. 2 indicates that TC is not able to form Ca–TC complexes to a significant extent at pH 2–5. The results suggest that competition between TCH_3^{+} and Ca^{2+} for the surface is taking place. Ca^{2+} has more affinity for the montmorillonite surface than Na^{+} , thus TCH_3^{+} adsorption is lower in 0.01 M Ca^{2+} than in 0.01 M Na^{+} . At pH > 5, Ca–TC complexes appear, being $\text{Ca}_2\text{TC}^{2+}$ the dominant complex in solution. Since this is a dication that should have a relatively high affinity for the montmorillonite surface, one is

tempted to conclude that the high adsorption at pH > 5 is due to purely electrostatic interaction between $\text{Ca}_2\text{TC}^{2+}$ and the surface. There is, however, one important fact that impedes to achieve this conclusion. TC adsorption at pH 7.5–11.0 is between 80 mmol/100 g and 90 mmol/100 g (0.80 Eq/kg and 0.90 Eq/kg). If it is assumed that $\text{Ca}_2\text{TC}^{2+}$ is the adsorbed complex, these adsorption values correspond respectively to 160 mEq/100 g and 180 mEq/100 g (1.60 Eq/kg and 1.80 Eq/kg), values that largely exceed the CEC of the solid and impede a simple electrostatic interpretation of the process. Unfortunately, there is no information about the structure of the adsorbed species under these conditions. In all previous published articles, a rather simple electrostatic interaction is postulated, but it seems to be more complicated than that. What is clear from adsorption data is that Ca^{2+} is playing a key role in promoting TC adsorption at pH > 5. It is likely that calcium bridges are formed, but the exact nature of the adsorbed complex is still unknown.

The overall analysis of the three adsorption curves in Fig 5 indicates that at least two different adsorption processes are taking place in the studied system, i.e., cation exchange and Ca-bridging. Cation exchange prevails at pH < 5, and thus, TC adsorption decreases by increasing total Ca^{2+} concentration. On the contrary, Ca-bridging prevails at pH > 5, and thus, TC adsorption increases by increasing Ca^{2+} concentration. Therefore, pH 5 represents an isoadsorption point or isoadsorption pH, which can be clearly seen as a crossing point of the curves. The two adsorption processes compensate each other at this pH, and thus, TC adsorption becomes independent of total Ca^{2+} concentration.

3.4. Ca^{2+} released/retained during TC adsorption

Fig. 6 shows the supernatant concentration of Ca^{2+} in equilibrium with montmorillonite in the presence and absence of

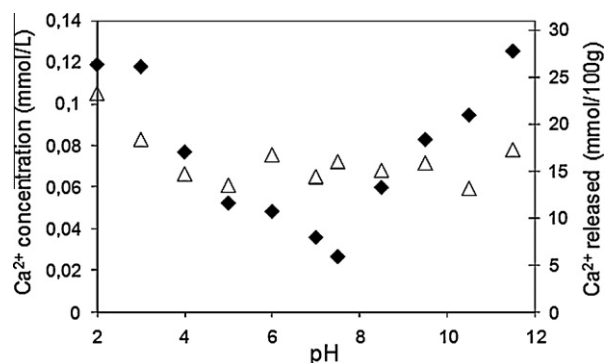


Fig. 6. Effect of pH on Ca^{2+} release from Ca^{2+} -montmorillonite in the absence (Δ) and presence (◆) of 0.76 mM TC. Supporting electrolyte: 0.01 M NaCl.

TC in the pH range 2–11.5. Data correspond to series b experiments, where Ca^{2+} -montmorillonite was the studied solid and 0.01 M NaCl was the supporting electrolyte. Since all Ca^{2+} in the system was initially present as the exchange cation, Ca^{2+} concentration in solution represents calcium ions that were released by montmorillonite in the experiments. This information is also given as a secondary axis in the figure (right-hand axis).

In the absence of TC, the concentration of Ca^{2+} in the supernatant is around 0.07 mmol/L or 15 mmol/100 g (0.15 mmol/kg) of Ca^{2+} released and rather independent of pH between pH 3 and 11.5. Only at pH close to 2, the concentration is somewhat higher, which could be attributed to some exchange with proton ions. In the presence of TC, on the contrary, the concentration of Ca^{2+} is dependent on pH. At pH below approximately 5 and above approximately 9, the concentration in the presence of TC is higher than in the absence of TC, whereas in the pH range 5–9, the opposite behavior is observed. The increase in Ca^{2+} concentration at pH below 5 is in agreement with the proposed cation exchange process under these conditions, where TCH_3^+ adsorbs on montmorillonite promoting Ca^{2+} desorption. On the other hand, the pH range 5–9, where it is observed a decrease in Ca^{2+} concentration, is nearly coincident with the pH range where an adsorption maximum of TC is observed (Fig. 5). This is in agreement with the proposed Ca-bridging interaction between TC and montmorillonite, showing that Ca-TC complexes should be present in the interlayer. These two processes compensate each other at pH around 5, and thus, calcium concentration in solution is the same in the absence and presence of TC. The increased Ca^{2+} concentration at pH above 9 is a consequence of the very low TC adsorption under those conditions. The relatively high concentration of TC that remained in solution induces an increased release of Ca^{2+} to form dissolved Ca-TC complexes. These two processes compensate each other at pH around 9, and thus, calcium concentration in solution is the same in the absence and presence of TC.

The analysis of Ca^{2+} concentration in solution for series b experiments allows also to quantify the amount of Ca^{2+} retained by the solid and to compare it with adsorbed TC. This comparison is given in Fig. 7. At pH below 5, TC adsorption is relatively high and Ca^{2+} retention is relatively low. This is rather well understood since cation exchange is the prevailing process under these conditions, and therefore, the high adsorption of a cation (TCH_3^+) is accompanied by the low retention of other cation (Ca^{2+}). It is interesting to note, however, that the sum adsorbed TC plus retained Ca^{2+} is between 125 mEq/100 g and 131 mEq/100 g (1.25 Eq/kg and 1.31 Eq/kg) under these conditions, which exceeds the CEC of the solid. This indicates that a fraction of adsorbed TC may not be in its cationic form and that TC species other than TCH_3^+ may be also adsorbing at pH below 5 by a less preponderant process, such as Ca-bridging. The

results could be also explained if chloride coadsorption is assumed, although there are no data to discriminate between one process and the other. At pH between 5 and 9, adsorbed TC is very similar to retained Ca^{2+} . In fact, the ratio adsorbed TC/retained Ca^{2+} is 1.19 for pH 5, 1.02 for pH 6, 1.14 for pH 7, 1.02 for pH 7.5, and 1.03 for pH 8.5. The prevailing adsorption process here is Ca-bridging, and it is possible that a mixture of $\text{Ca}(\text{TCH})_2$ and $\text{Ca}_2\text{TC}^{2+}$ species are being adsorbed. Finally, at pH above 9, TC adsorption is very low but Ca^{2+} retention is higher. This significant Ca^{2+} retention is mainly because Ca^{2+} should be acting as montmorillonite counterion together with Na^+ and not because Ca^{2+} is adsorbed as TC-Ca complexes.

4. Conclusions

The adsorption of TC on montmorillonite is significantly affected by pH and Ca^{2+} concentration. In the absence of Ca^{2+} , the adsorption is high at low pH and decreases as the pH increases. The presence of Ca^{2+} decreases TC adsorption at low pH and increases it at high pH. At least two different adsorption processes take place in the presence of Ca^{2+} : cation exchange and Ca-bridging, the formed prevailing at low pH and the later prevailing at high pH. The cationic TCH_3^+ species participates in the cation exchange process, whereas different TC species are believed to participate in the Ca-bridging process. The exact nature of the adsorbed complexes cannot be unambiguously determined with adsorption measurements, and other techniques as molecular spectroscopies are necessary.

XRD and TEM data indicate that TC adsorption leads to the intercalation of molecules in the interlayer spaces and to the formation of a multiphase system consisting of stacking of montmorillonite layers with and without intercalated TC.

On a practical basis, in the absence of Ca^{2+} , the studied montmorillonite is a good TC adsorbent only under acidic conditions. The presence of calcium improves considerably the adsorption at high pH and decreases only slightly the adsorption at low pH, resulting in a solid with important TC adsorption capacity in an ample range of pH.

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References

- [1] F. Bergaya, G. Lagaly, in: F. Bergaya, B.K. Theng, G. Lagaly (Eds.), Handbook of Clay Sciences, Oxford, 2006, p. 1.
- [2] A. Impiccini, Mineralogía de la fracción no arcillosa de las bentonitas del Cretácico superior de la región Norpatagonia. Tesis doctoral, La Plata, 1995.
- [3] B. Lombardi, M.T. Baschini, R.M. Torres Sánchez, Appl. Clay Sci. 22 (2003) 309.
- [4] T.B. Musso, K.E. Roehl, G.R. Pettinari, J.M. Vallés, Appl. Clay Sci. 48 (2010) 438.
- [5] C. Viseras, G. Cultrone, P. Cerezo, C. Aguzzi, M.T. Baschini, J.M. Vallés, A. López-Galindo, Appl. Clay Sci. 31 (2006) 272.
- [6] B. Lombardi, M.T. Baschini, R.M. Torres Sánchez, Appl. Clay Sci. 24 (2003) 43.
- [7] A.K. Sarmah, M.T. Meyer, A.B. Boxall, Chemosphere 65 (2006) 725.
- [8] H. Zhang, Y. Luo, Q.X. Zhou, J. Agro-Environ. Sci. 27 (2008) 407.
- [9] J. De-An, Z. Dong-Mei, W. Yu-Jun, Z. Hao-Wen, C. Jin-Lin, Geoderma 146 (2008) 224.
- [10] C.R. Stephens, K. Murai, K.J. Brunings, R.B. Woodward, J. Am. Chem. Soc. 78 (1956) 4155.
- [11] J.J. Stezowski, R. Prewé, J. Am. Chem. Soc. 99 (1977) 1117.
- [12] L. Lambs, M. Brion, G. Berthon, Inorg. Chim. Acta 106 (1983) 151.
- [13] A.A. Mackay, B. Canterbury, J. Environ. Qual. 34 (2005) 1964.
- [14] C. Gu, K.G. Karthikeyan, S. Sibley, J.A. Pedersen, Chemosphere 66 (2007) 1494.
- [15] M.E. Parolo, M.C. Savini, J.M. Vallés, M.T. Baschini, M.J. Avena, Appl. Clay Sci. 40 (2008) 179.
- [16] M.E. Parolo, M.J. Avena, G. Pettinari, I. Zajonkovsky, J.M. Vallés, M.T. Baschini, Appl. Clay Sci. 49 (2010) 194.
- [17] Z. Li, P. Chang, J. Jean, W. Jiang, C. Wang, J. Colloid Interface Sci. 341 (2010) 311.

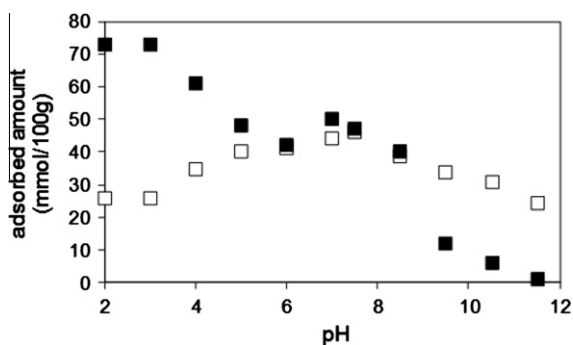


Fig. 7. Effect of pH on TC adsorption (■) and Ca^{2+} retention (□) by Ca^{2+} -montmorillonite. TC concentration: 0.76 mM TC. Supporting electrolyte: 0.01 M NaCl.

- [18] P. Chang, J.-S. Jean, W.-T. Jiang, Z. Li, *Colloids Surf., A: Physicochem. Eng. Asp.* 339 (2009) 94.
- [19] P. Chang, Z. Li, T.-L. Yu, S. Munkhbayer, T.-H. Kuo, Y.-C. Hung, J.-S. Jean, K.-H. Lin, *J. Hazard. Mater.* 165 (2009) 148.
- [20] M.E. Parolo, *Minerales Arcillosos de la NorPatagonia Argentina en la Retención de Compuestos Orgánicos que Impactan sobre la Salud Humana y el Medio Ambiente*, Tesis doctoral de la Universidad Nacional del Sur, Bahía Blanca, 2010.
- [21] R.A. Figueroa, A. Leonard, A.A. MacKay, *Environ. Sci. Technol.* 3 (2004) 476.
- [22] J.E. Browne, J.R. Feldkamp, J.L. White, S.L. Hem, *J. Pharm. Sci.* 69 (1980) 811.
- [23] L.S. Porubcan, C.J. Serna, J.L. White, S.L. Hem, *J. Pharm. Sci.* 67 (1978) 1081.
- [24] D. Penner, G. Lagaly, *Clays Clay Miner.* 48 (2000) 246.
- [25] L. Jin, X. Amaya-Mazo, M.E. Apel, S.S. Sankisa, E. Johnson, M.A. Zbyszynska, A. Han, *Biophys. Chem.* 128 (2007) 185.
- [26] J.R. Pils, D.A. Laird, *Environ. Sci. Technol.* 41 (2007) 1928.
- [27] J.M. Vallés, A. Impiccini, In: E.O. Zappettini (Ed.), *Recursos Minerales de la República Argentina*, Anales, La Plata, 1999, p. 1113.
- [28] J.M. Wessels, W.E. Ford, W. Szymczak, S. Schneider, *J. Phys. Chem.* 102 (1998) 9323.
- [29] L. Lambs, B. Decock-Le Reverend, H. Kozłowski, G. Berthon, *Inorg. Chem.* 27 (1988) 3001.
- [30] M.F. Brigatti, E. Galan, B.K.G. Theng, in: F. Bergaya, B.K.G. Theng, G. Lagaly (Eds.), *Handbook of Clay Sciences*, Amsterdam, 2006, p. 19.
- [31] M. Pantanetti, M. dos Santos Afonso, R.M. Torres Sánchez, in: M. Gonzalez, E. Iglesias, A.F. De Iorio, M.R. Torres Sanchez (Eds.), *La Contaminación en Ibero América: Xenobióticos y metales pesados*, Salamanca, 2008, p. 139.
- [32] W. Oueslati, H.B. Rhaïem, A.B.H. Amara, *Desalination* 271 (2011) 139.
- [33] B.B. Sithole, R.D. Guy, *Water, Air, Soil, Pollut.* 32 (1987) 315.