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Removal of Mn(II) and Cd(II) from wastewaters by natural and modified clays

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Abstract The adsorption capacities of commercial and Brazilian natural clays were evaluated to test their applications in wastewater control. We investigated the process of sorption of manganese(II) and cadmium(II) present in synthetic aqueous effluents, by calculating the adsorption isotherms at 298 K using batch experiments. The influence of temperature and pH on the adsorption process was also studied. Adsorption of metals was best described by a Langmuir isotherm, with values of $\boldsymbol{Q}_0$ parameter, which is related to the sorption capacity, corresponding to 6.3 mg g^{-1} for K-10/Cd(II), 4.8 mg g^{-1} for K-10/Mn(II), 11.2 mg g^{-1} for NT-25/Cd(II) and 6.0 mg g^{-1} for NT-25/Mn(II). We observed two distinct adsorption mechanisms that may influence adsorption. At the first 5 min of interaction, a cation exchange mechanism that takes place at exchange sites located on (001) basal planes is predominant. This process is inhibited by low pH values. After this first and fast step, a second sorption mechanism can be related to formation of inner-sphere surface complexes, which is formed at edges of the clay. The rate constants and the initial sorption rates correlate positively with temperature in all studied systems, denoting the predominance of a physisorption process. The addition of complexing agents that are incorporated within the K10 structure, enhance metal uptake by the adsorbent. The results have shown that both Cd(II) and Mn(II) were totally retained from a 50 mg L^{-1} solution when K10 grafted with ammonium pyrrolidinedithiocarbamate (APDC) was used as adsorbent.

Keywords Modified clays · Brazilian clay · Toxic metals · Adsorption isotherm · Wastewater · Heavy metals

1 Introduction

Manganese and cadmium are commonly associated with water pollution and their presence in water can be the result of effluent discharge from many commercial activities, such as batteries, pigments, metal coatings, and plastic manufacturing. The toxicity of these metals is related to kidney, lung and intestinal damage and their compounds may reasonably be anticipated to be carcinogens (Gasselin et al., 1984; USEPA, 2004). Therefore, due to the potentially harmful effects on humans and animals it has became mandatory the removal of these cations from industrial effluents. The adsorption technique is more suitable than traditional solvent extraction in the removal of cations from dilute

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solutions. According to this rational, ion exchange processes, especially those using low-cost exchangers and sorbent materials, such as natural zeolites and laminar silicates, have been studied and are currently being used in a number of industries (Ahsan et al., 2001).

Smectite clays, as montmorillonite, are widely used as industrial adsorbents in the removal of liquid impurities and in the purification of gases. These clays possess a negative structural charge that results from isomorphic substitutions in the crystal lattice. Thus their applications as adsorbent are related to cationic exchange (Konta, 1995). Moreover, clays have stable and rigid structures, with high surface areas and good physico-chemical properties. In order to combine these optimal support characteristics with the affinity for cationic species, a great effort has been made towards the synthesis of new ion-exchangers containing metal complexing extractants, capable of improving the efficiency and selectivity for a wide range of metal species (Tavlarides et al., 1987). Many sequestrating agents towards metal cations, anchored in a variety of solid sorbents, have been used, including ammonium pyrrolidinedithiocarbamate (Hiraide et al., 1997; Liu and Huang, 1992), diethylenetriaminepentaacetic acid (Nagy et al., 1998) and ethylenediaminetraacetic acid (Lim et al., 2005). The efficiency and selectivity of these agents to remove heavy metal ions was already confirmed in many studies (Dabrowski et al., 2004). The chemical bonding of these complexing molecules to polymeric materials is difficult and expensive, however the use of macroporous supports impregnated with metal extractants offers a compromise, which is both effective and economical (Cecile and Casarci, 1991; Camel, 2003).

Although the use of clays and zeolites for the elimination of metals from wastewaters has been extensively studied (Schlegel et al., 1999; Zorpas et al., 2000), natural clays from Brazil have not been used either as adsorbent or support in such applications. The aim of this work was to study the effect of initial concentration, temperature and pH on the adsorption of manganese(II) and cadmium(II) from aqueous solutions by two clays, the Fluka K-10 commercial montmorillonite and the natural Brazilian bentonite NT-25. The studies also involved a modification of the commercial K-10 clay by addition of ammonium pyrrolidinedithiocarbamate (APDC), the disodium salt dihydrate of ethylenediaminetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). The modified supports were compared with the natural K-10 commercial montmorillonite for their affinities for manganese(II) and cadmium(II).

2 Materials and methods

2.1 Starting material

Montmorillonite K-10 was obtained from Fluka and was tested without any treatment. The chemical composition obtained by X-Ray Fluorescence analysis correspond to 65.34% SiO_2, 12.89% Al_2O_3, 2.38% Fe_2O_3, 0.95% MgO, 0.52% TiO_2, 0.24% CaO, 0.53% Na_2O, 1.54% K_2O, 7.85% P_2O_5, and 8.06% LOI (loss on ignition at 1273 K). The B.E.T. surface area is 232 m^2 g^{-1}. This commercial clay is obtained by treatment with phosphoric acid, which removes part of the octahedral ions. Thus some phosphate anions are fixed at the edges of the SiO_4 layers or will substitute adsorbed hydroxyl anions (Mokaya and Jones, 1995). The formula of one half unit cell is $Na_{0.60}K_{0.12}Ca_{0.02}$-$(Al_{1.78}Fe_{0.12}Mg_{0.10})_{VI}(Si_{3.89}Al_{0.11})_{IV}O_{10}(OH)_2$. In this formula, Fe^{2+}, Mg^{2+} and Al^{3+} are the isomorphically substituting cations, and Na^+, K^+ and Ca^{2+} are the charge-compensating cations. The symbols VI and IV are related to the octahedral and tetrahedral layers, respectively. Based on the quantity of charge-compensating cations, the theoretical cation exchange capacity (CEC = 1.9 meq g^{-1}) was calculated.

Bentonit União Nordeste S.A. provided the bentonite clay mineral, identified as NT-25. This bentonite is originated from Campina Grande, Paraíba State, Brazil. The chemical composition obtained by X-Ray Fluorescence analysis is 57.85% SiO_2, 16.74% Al_2O_3, 8.78% Fe_2O_3, 2.73% MgO, 1.24% TiO_2, 1.08% CaO, 0.73% Na_2O, 0.43% K_2O, 0.27% P_2O_5, and 10.10% LOI. The B.E.T. surface area is 139 m^2 g^{-1}. The formula of one half unit cell is $Na_{0.10}K_{0.04}Ca_{0.08}(Al_{1.28}Fe_{0.45}Mg_{0.28})_{VI}(Si_{3.94}Al_{0.06})_{IV}$ $O_{10}(OH)_2$ with a theoretical cation exchange capacity (CEC) of 0.8 meq g^{-1}.

Powder diffraction data of K-10 and NT-25 samples were collected using a PHILIPS PW 3710 X-ray powder diffractometer, equipped with a graphite monochromator and a Cu tube, operating at 45 KV and 40 mA. The analyses were performed with Cu$K\alpha$ radiation, a step size of 0.02° 2θ, and a counting time of 0.4 s. Sample analysis consisted of in the collection of data in the 3°–40° 2θ range. In addition, the clay fraction was separated by centrifugation and analyzed according to the method of Moore and Reynolds Jr (1997) for the study of clays, which includes crystal oriented, thermally treated (823 K) and glycolated samples.

2.2 Reagents

Nitrates of cadmium(II), manganese(II) and sodium (analytical grade—Aldrich) were used as a source of metallic ions. Concentrated hydrochloric acid and sodium hydroxide (ACS grade, obtained from Merck and Aldrich, respectively) were used for pH adjustment. Copper(II) chloride and ethylenediamine (ACS grade—Aldrich) were used for experimental CEC determination. Ammonium pyrrolidinedithiocarbamate (APDC), disodium salt dihydrate of ethylenediaminetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) (analytical grade—Aldrich) were used in preparation of modified clays. Deionized water was used in all experimental work.

2.3 Preparation of modified clay

The chemical modification of the K-10 clay was carried out as follows. An aqueous suspension of 50.0 g of the clay in 2 L of ethanol:water 1:1 was added to 0.1 mol of complexing agent. The mixture was magnetically stirred for 1 h. The solid was separated by centrifugation and washed several times with deionized water to remove superficially held adsorbate. The amount of adsorbed complexing molecules was determined by thermogravimetric analysis in a Thermal Analyser Netzsch TG 209, with about 6 mg of sample at a heating rate of 10 K min^{-1} in air atmosphere.

2.4 Metal quantification

Perkin-Elmer model AA-300 atomic absorption spectrometer was used for cadmium and manganese analysis. Calibration curves were obtained from 1000 mg L^{-1} stock solutions (Titrisol, Merck). The speciation in the metal solutions was predicted using MINEQL, a chemical speciation prediction program developed to simulate equilibrium processes in aqueous systems.

2.5 Experimental cation exchange capacity–CEC_{exp}

CEC_{exp} of the original clays was determined by the Cu-ethylenediamine method described by Bergaya and Vayer (1997). Briefly, a sample containing 0.3 g of clay was suspended in 25.0 mL of 0.05 M Cu-ethylenediamine. The suspension at pH = 7 was stirred for 30 min and filtered through a 0.2 μm membrane filter (RC15). The concentration of copper remaining in solution was determined by atomic absorption spectrometry (AAS), as described above. The CEC_{exp} of the samples was obtained by the difference in copper concentration in the initial and final solutions, as determined by AAS. Thermogravimetric analysis was used to determine the amount of water in the samples.

2.6 Single-metal adsorption study

Experimental solutions with different metal concentrations were prepared in stopped Pyrex glass flasks, at 298 K. The sorption rate of the metals was investigated in bench-scale studies, by mixing 6.0 mL of a solution of the metal of interest with initial concentration (C_0) varying from 10 to 1000 mg L^{-1} and 0.1 g of clay, under magnetic stirring, at 298 K. After a time period of 60 min, the suspension was filtered through a 0.2 μm membrane filter (RC15) and the metal remaining in the solution was quantified by AAS. Sorption isotherms and other studies were made in solutions with an initial concentration of 50 mg L^{-1} that corresponds to the upper limit of concentrations observed in wastewater effluents originated from São Paulo Metropolitan industries (Casarini et al., 2001). The original pH values varied according to C_0: 6.9 to 6.1 for cadmium and 6.8 to 3.1 for manganese. Kinetic studies were carried out in systems with $C_0 = 50$ mg L^{-1} (other conditions as described above) and samples were taken at present time intervals.

Blank experiments, processed without addition of clay, confirmed that adsorption of cadmium(II) and manganese(II) on the walls of glass flasks and filtration systems were negligible.

2.7 Influence of temperature on the adsorption process

Isotherms describing the sorption mechanism were obtained by measuring the binding of metals from solutions containing 50 mg L^{-1} of each metal. Experiments were performed in three different temperatures (278, 288 and 298 K). After defined time intervals, the aqueous phase was separated by filtration and the remaining concentration of metal was quantified by AAS.

2.8 Influence of pH on adsorption process

The effect of pH was performed in the range 1.0–6.0 in systems containing 50 mg L^{-1} of each metal. The pH was adjusted to desired values by addition of hydrochloric acid or sodium hydroxide solutions and the sorption studies were performed as indicated. The digital pHmeter Analyser model 300 M was used for pH measurement.

3 Results and discussion

X-ray powder diffraction patterns are shown in Fig. 1. The data is typical of smectites with a broad 001 reflection. The characteristic montmorillonite peak is reduced in the K-10 sample, which is expected for materials submitted to both acidic and thermal treatments, as those applied to the commercial K-10 product. The samples also contain characteristic peaks of kaolinite, hydromica, cristobalite and quartz, as identified by Rodrigues et al. (2003).

After sample preparation for the fraction clay analysis, the diffractograms of the oriented, thermally treated and glycolated NT-25 sample had shown the following patterns, presented in Fig. 2.

The behavior observed in Fig. 2 shows a typical standard for smectites, whose diffractogram of the oriented sample presents the main reflection (001) in 15.73 Å. After glycolated, the sample expands and this peak moves to the left, reaching 18.65 Å. Upon heating the structure collapses, showing a reduction of the basal distance for about 9.3 Å. Finally, to determine the type of smectite present, a special preparation for measurement of the (060) reflection was carried out (Fig. 3).

The value of $d_{(060)} = 61.83$ Å (1.5005 2θ) confirms the presence of the montmorillonite in both samples. The Figure still shows the presence of quartz peaks (trace marked), more abundant in the K-10 sample, as previously shown.

Thermogravimetric curves of K-10 and NT-25 are shown in Fig. 4. The curves exhibited a first mass loss centred at 340 K (K-10) and 345 K (NT-25), which are related to the loss of physisorbed water and to water molecules that are bound to interlayer cations. Moisture in these samples corresponds to 9.80% and 14.17%, respectively for K-10 and NT-25 clays. The second peak, centred at 763 K (K-10) and 733 K (NT-25), is attributed to the dehydroxylation of the layer silicate and corresponds to a loss in mass of 6.00% and 8.36%, respectively for K-10 and NT-25.

3.1 Single-metal sorption experiments

In order to assess the cation exchange capacity of the clay samples, the experimental cation exchange

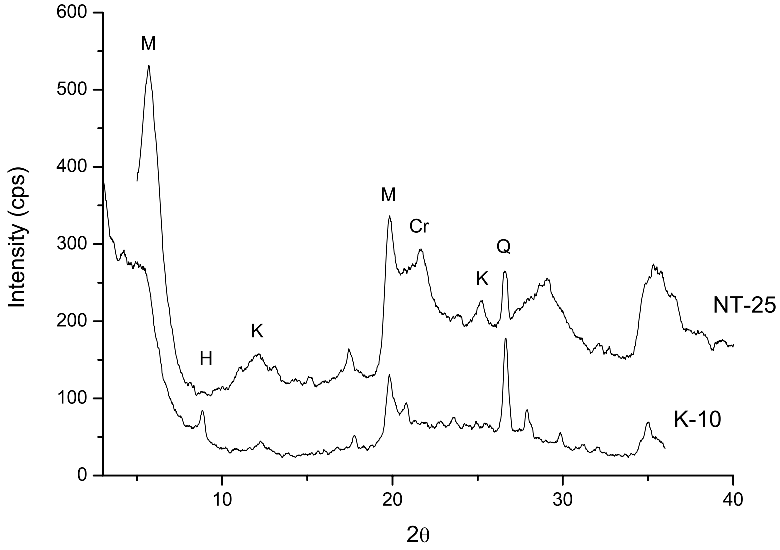


Fig. 1 X-ray diffractograms of K-10 and NT-25: M = montmorillonite, H = hydromica, K = kaolinite, Q= quartz, Cr = cristobalite

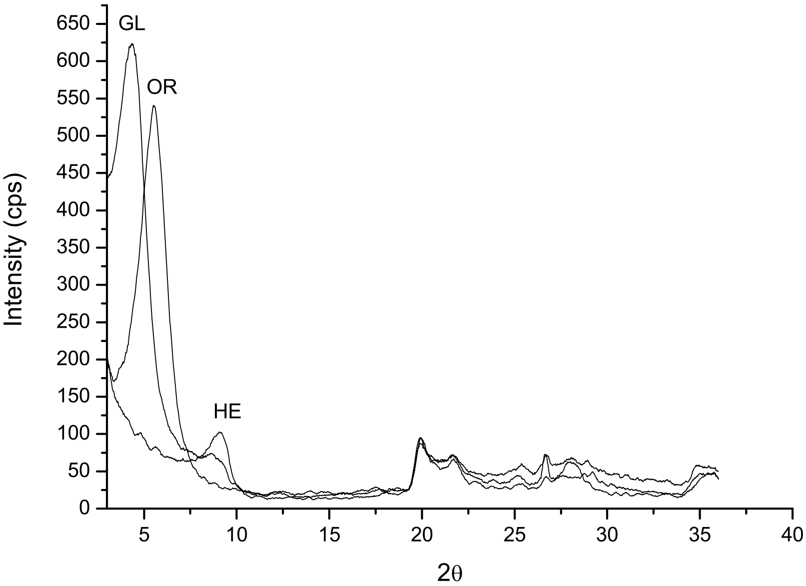


Fig. 2 X-ray diffractograms of NT-25: GL = glycolated, OR = oriented, HE = heated at 823 K

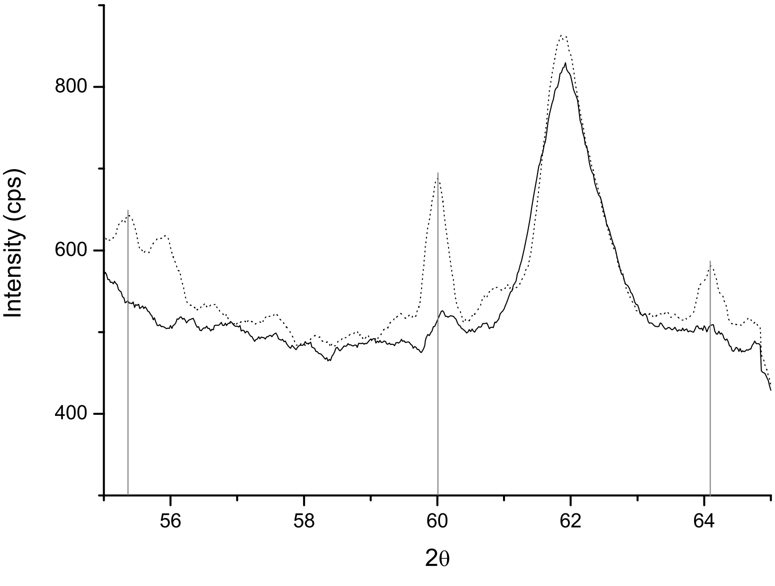


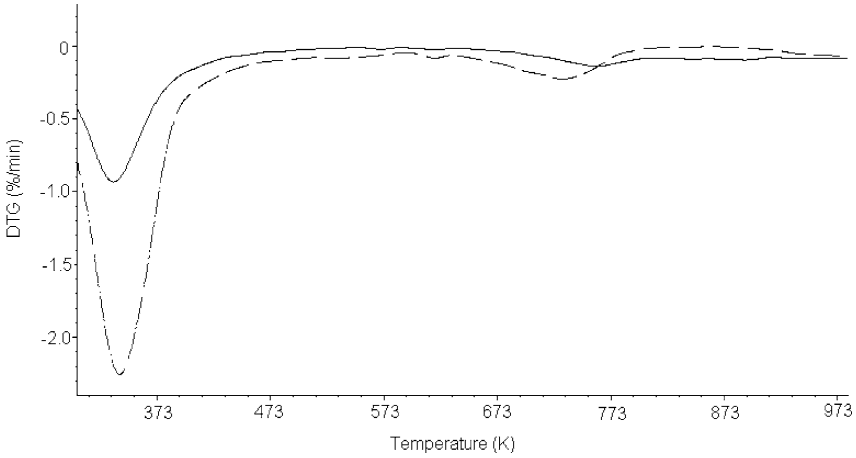
Fig. 3 X-ray diffractograms of K-10 (dashed) and NT-25 (solid)

capacity (CEC_{exp}) measurements were carried out according to the Cu-ethylenediamine method. The results demonstrated that the CEC_{exp} of K-10 is 0.451 meq g^{-1} and the value for NT-25 is 0.748 meq g^{-1}. While the theoretical and experimental CEC values are in agreement for NT-25 sample, we observed that the CEC_{exp} of K-10 (0.451 meq g^{-1}) is lower than the theoretically calculated (1.9 meq g^{-1}), which is probably due to the acid treatment to which this montmorillonite was submitted, that induces the removal of octahedral aluminum ions. The loss of aluminum can vary from 14% to 48.5%, in accordance with the acid force of the medium (Mokaya and Jones, 1995).

Kinetic studies were conducted in systems containing 50 mg L^{-1} of each metal using K-10 as the sorbent material. The results of such studies are shown in Fig. 5.

The removal of metal is a rather fast process in which metal uptake is attained within a few minutes. At the first 5 min, more than 95% of the cations present in solution were retained. Following this stage, a slow adsorption process takes place and the equilibrium is

Fig. 4 DTG curves of K-10 (solid) and NT-25 (dotted) clays



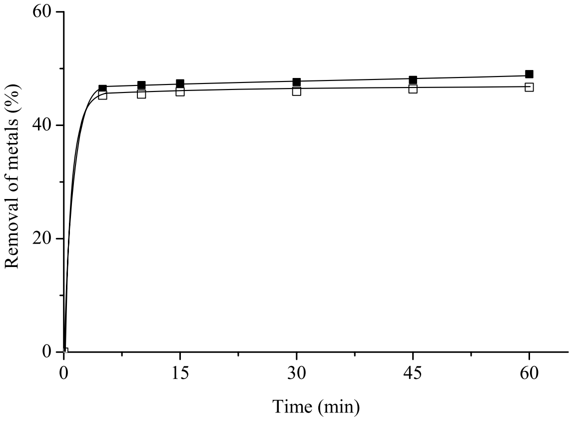


Fig. 5 Kinetic studies on the removal of metals by K-10: cadmium (■) and manganese (□)

then attained within 60 min. Diffusional restrictions are extremely important in these processes. One or more mechanistic steps may be involved: (i) external mass transport, (ii) diffusional mass transfer within the internal structure of the adsorbent particle, and (iii) adsorption at sites located in the surface. The first step is not rate-limiting since the effect of transport in the solution can be eliminated by efficient mixing. The second step must be deeply reduced in clay minerals, because these materials expand completely in the presence of large amounts of water, promoting complete separation of the unit layers. McKay et al. (1980) tested an intraparticle diffusion model for sorption systems and showed that the plots of x/m (mass of solute adsorbed per gram of adsorbent) *versus* $t^{1/2}$ may present multi-linearity, as shown in Fig. 6. The first portion of the curve describes the sorption occurring at the external surface, while the second portion describes a sorption mechanism that is limited by restrictions in mass transference. Panayotova (2001) and Brigatti et al. (2000) had already applied this model for other adsorbents. As shown in Fig. 6, a straight line describes each of the sorption mechanisms. The major difference between these lines is given by their slope. While the first presents a pronounced slope, the second process shows almost no slope. These results indicate that all exchange sites are located on a surface readily accessible to the exchange ions, either at external or expanded interlayer surfaces. Therefore, these data suggest a limited contribution of diffusional steps (i) and (ii) in the retention process.

Single-metal sorption is strongly influenced by the initial concentration. It was found that a high percentage of metal ions is removed from solutions with low C_0 values (10–100 mg L^{-1}), when compared to high C_0 values (100–1000 mg L^{-1}). When K-10 was used as the sorbent material, 60 min contact time results in the retention of 49.0% of cadmium(II) present in a solution with $C_0 = 50$ mg L^{-1}, which corresponds to a removal of 1.46 mg g^{-1}. When C_0 is 250 mg L^{-1}, the removal of cadmium(II) was 30.8% (4.28 mg g^{-1}), and with $C_0 = 1000$ mg L^{-1}, the removal was 10.4% (5.90 mg g^{-1}). The removal performance of manganese(II) ions is quite different. When C_0 is 50 mg L^{-1}, the retention of manganese was 48.4% (1.24 mg g^{-1}); similarly, with $C_0 = 250$ mg L^{-1}, it was 28.1% (3.87 mg g^{-1}), and with $C_0 = 1000$ mg L^{-1}, it was 8.1% (4.48 mg g^{-1}). This behaviour is best visualised in the sorption isotherms presented in Fig. 7. The isotherms were plotted using

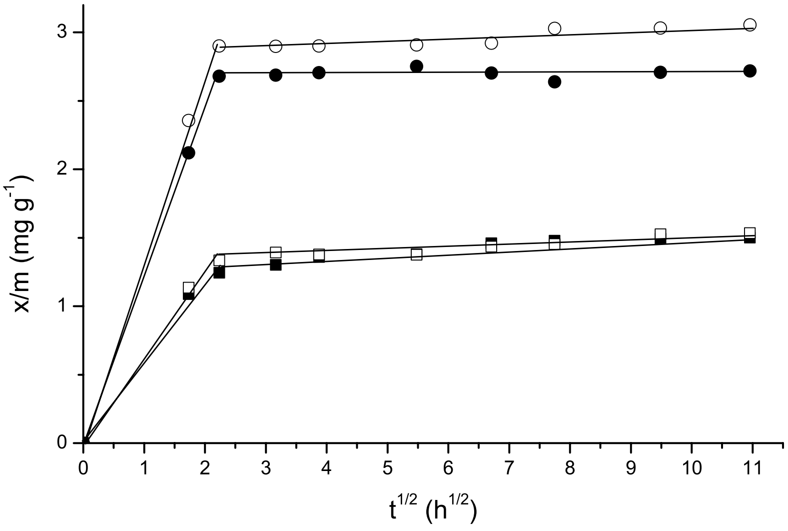


Fig. 6 Intraparticle diffusion model for the sorption of metals in K-10 (cadmium (■), manganese (□)) and NT-25 (cadmium (○), manganese (●))

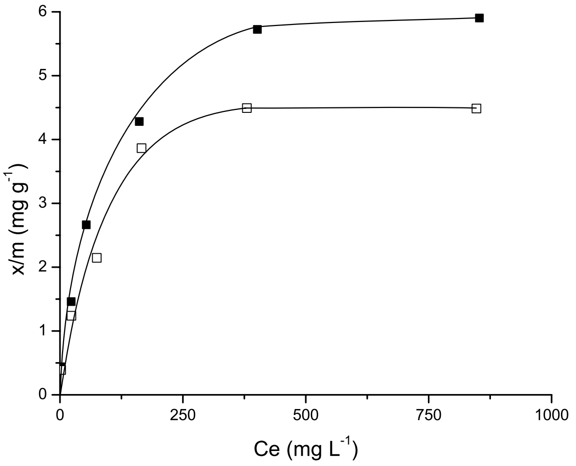


Fig. 7 Metal sorption isotherms for the binding of metals in K-10 at 298 K: cadmium (■) and manganese (□). x/m and Ce represent the in-going ion on the clay and the solution concentration in equilibrium, respectively

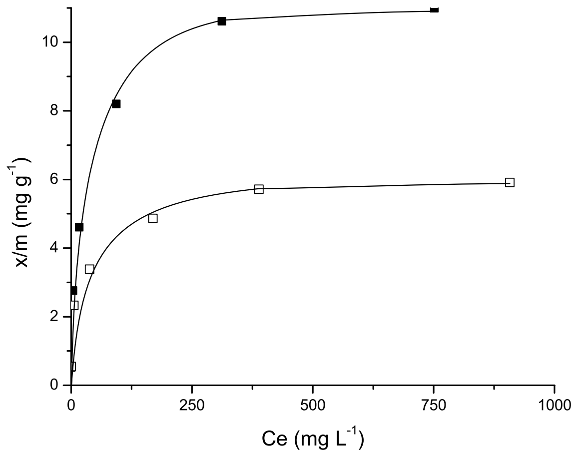


Fig. 8 Metal sorption isotherms for the binding of metals in NT-25 at 298 K: cadmium (■) and manganese (□)

a mass-based solid concentration, x/m (in mg of solute adsorbed per gram of adsorbent) as a function of concentration in solution, Ce (in mg of solute per litre of solution) in equilibrium conditions.

The sorption isotherms using NT25 as the sorbent are presented in Fig. 8.

The results show that the order of retention capacity is given by manganese(II) > cadmium(II) for both commercial and natural clays. The uptake capacities in more concentrated solutions reached 0.050 meq g^{-1} for cadmium(II) and 0.152 meq g^{-1} for manganese(II). The charge/radius ratio for cadmium(II) is slightly higher than that of manganese(II) (0.469 and 0.456, respectively) (Nightingale, 1959; Wulfsberg, 1987), which complicates the interpretation of the binding process. Puls and Bohn (1988) explained the sorbent properties of montmorillonite using the hard-soft acid base principle. Hard Lewis acids and bases tend to form outer-sphere complexes and their adsorption occurs preferably in surfaces with an excess of negative charges. Papelis and Hayes (1996) found that, in an adsorption study using X-ray absorption spectroscopy, two mechanisms were responsible for divalent metal ion adsorption on smectites. The first one, which is predominant at low electrolyte concentrations, was attributed to complexes formed on the siloxane ditrigonal cavities of the permanent charge interlayer. At high electrolyte concentrations, adsorption was attributed to

Table 1 Characteristic parameters obtained from Langmuir and Freundlich equations, where r is the correlation coefficient

		Langmuir Isotherm				Freundlich Isotherm		
Clay	Cation	Q_0 (mg g^{-1})	b (L mg^{-1})	R_L	r	n	Kf (mg g^{-1})	r
K-10	Cd(II)	6.3	0.0180	0.100	0.9978	2.33	0.42	0.9876
	Mn(II)	4.8	0.0190	0.103	0.9967	2.27	0.31	0.9803
NT-25	Cd(II)	11.2	0.0598	0.033	0.9992	3.20	1.74	0.9930
	Mn(II)	6.0	0.0531	0.037	0.9991	3.09	0.85	0.9358

metals complexed on the hydroxyl edge sites where the crystal structure is interrupted. Based on this interpretation and considering that significant metal uptake take place within the first 5 min contact time, we can suppose that a cation-exchange mechanism, that takes place at exchange sites located on (001) basal planes, is predominant and is responsible for this fast uptake of cations. After this first and fast step, a second sorption mechanism must be considered, since it is too slow to be attributed to cation exchange. This second step can be related to the inner-sphere surface complexes, that could be formed at the clay edges (Sposito, 1994).

As observed in Figs. 7 and 8, the uptake values are lower than experimental CEC, suggesting that most metal ions are retained by cation exchange at specific surface sites. However, a discrete increase in cation uptake after 5 min must be related to the occupation of edge sites by cations that migrated from exchange sites at basal planes. Schlegel et al. (1999) already identified this sorption mechanismusing hectorite as sorbent.

Equilibrium uptake data found at room temperature and 60 min contact time were processed according to linear Langmuir and Freundlich isotherms (Hinz, 2001). For the traditional Langmuir isotherm, Eq. (1) was used.

$$\frac{Ce}{x/m} = \frac{1}{bQ_0} + \frac{Ce}{Q_0} \tag{1}$$

Where Ce is the equilibrium concentration of the solute, x is the mass of the solute adsorbed, m is the mass of the adsorbent, b and Q_0 are Langmuir constants.

For the Freundlich isotherm, Eq. (2) was used.

$$\log(x/m) = \log K_f + \frac{1}{n}\log Ce \tag{2}$$

Where K_f and n are Freundlich constants, x, m and Ce are defined as mentioned above.

The analysis of equilibrium data according to Langmuir and Freundlich-type equations allowed us to obtain the parameters presented in Table 1.

The data in Table 1 confirms that the equilibrium is best described by a Langmuir-type isotherm, with correlation coefficients above of 0.99, suggesting that equilibrium has been reached for at least one surface site. The Q_0 parameters are related to the sorption capacity with respect to a specific solute, and they are closed to experimental data.

The equilibrium parameter R_L indicates the type of isotherm (irreversible $R_L = 0$, favorable $0 < R_L < 1$, linear $R_L = 1$ or unfavorable $R_L > 1$) (Lin and Huang, 2002). This parameter can be calculated as indicated in Eq. (3).

$$R_L = \frac{1}{(1 + bC_0)} \tag{3}$$

Where C_0 is the highest initial solute concentration. The values of R_L show that the sorption of cadmium(II) and manganese(II) is favorable for both clays tested.

Two different kinetic models were used to adjust the experimental data of metal sorption. The pseudo-first order and the pseudo-second order Lagergren models were tested according to the equations presented by Ho and McKay (1998). The pseudo-first order Lagergren model can be expressed according Eq. (4).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4}$$

Where q_e and q_t (mg g^{-1}) are the amounts of sorbed metal ions on the clay surface at equilibrium and at any time t, respectively; and k_1 is the Lagergren first order rate constant. Integrating (4) between the limits, $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$, it gives the expression

Table 2 Kinetic parameters related to the sorption of metals on K-10 at 298 K, where r is the correlation coefficient

		Pseudo-first order		Pseudo-second order			
Metal	$q_{e,\exp}$ (mg g^{-1})	k_1 (min^{-1})	r	k_2 (g mg^{-1}min^{-1})	q_e (mg g^{-1})	h_0 (mg g^{-1} min^{-1})	r
Mn	1.24	0.119	0.7222	2.51	1.41	4.97	0.9990
Cd	1.46	0.082	0.8646	2.01	1.44	1.38	0.9998

showed in Eq. (5).

$$\log(q_e - q_t) = \log\ q_e - \frac{k_1}{2.303}t \tag{5}$$

The linear plots of log $(q_e - q_t)$ *versus t* indicate the applicability of this kinetic model. The pseudo-second order model can be expressed as indicated in Eq. (6).

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{6}$$

Where k_2 is the second order rate constant. Integrating (6) between the same limits, we have Eq. (7).

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e}t \tag{7}$$

Where q_e and k_2 values can be obtained respectively from the intercept and slope of the linear plot of t/q_t *versus t*. The initial sorption rate h_0 was obtained according to Eq. (8), as q_t/t approaches zero (Ho and McKay, 1998).

$$h_0 = k_2 \cdot q_e^2 \tag{8}$$

Table 2 lists the kinetic parameters obtained for the sorption of metals on K-10.

The correlation coefficients indicated that a pseudo-first order model failed to describe the sorption mechanism. A Lagergren pseudo-second order model best described these kinetic parameters, since q_e values estimated by this model are in agreement with the experimental results and the values for the correlation coefficients were shown to be close to 1.

3.2 Influence of temperature

Single-metal sorption studies were performed at temperatures of 278, 288 and 298 K, for solutions with $C_0 = 50$ mg L^{-1} and original pH values. Temperature influenced the time required to reach saturation, as observed in Figs. 9 and 10, respectively for Mn(II) and Cd(II). The results have been analyzed by using the pseudo-second order model.

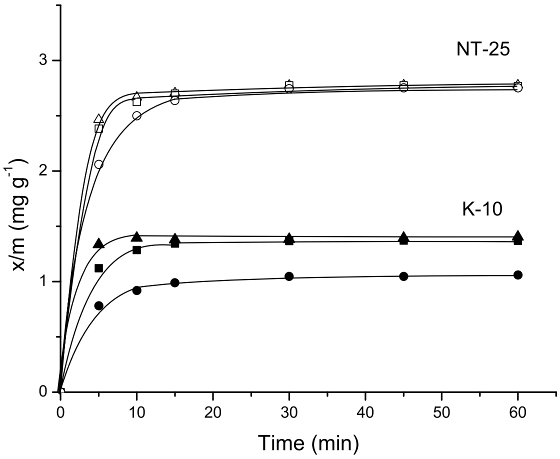


Fig. 9 Manganese(II) sorption isotherms in K-10 and NT-25 ($C_0 = 50$ mg L^{-1}): 278 K (circles), 288 K (squares) and 298 K (triangles)

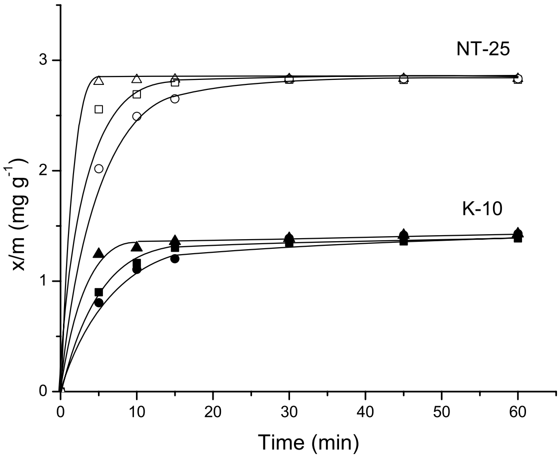


Fig. 10 Cadmium(II) sorption isotherms in K-10 and NT-25 ($C_0 = 50$ mg L^{-1}): 278 K (circles), 288 K (squares) and 298 K (triangles)

As shown in Table 3, the initial sorption rate in the system K-10/Mn(II) varied from 0.52 to 4.97 mg g^{-1} min^{-1} when the temperature increased from 278 to 298 K. In a similarly way, values of rate constants were found to increase from 0.41 to 2.51 g mg^{-1}min^{-1}. Rate constants and initial sorption rates correlate positively

Table 3 Influence of temperature according pseudo-second order rate constant

Clay/Metal	Temperature (K)	q_e (mg g^{-1})	k_2 (g mg^{-1}min^{-1})	h_0 (mg g^{-1} min^{-1})	r
K-10/Mn	278	1.12	0.41	0.52	0.9999
	288	1.39	0.87	1.68	0.9998
	298	1.41	2.51	4.97	0.9999
K-10/Cd	278	1.61	0.13	0.33	0.9996
	288	1.43	0.37	0.76	0.9998
	298	1.44	2.01	1.38	0.9999
NT-25/Mn	278	2.93	0.18	1.57	0.9996
	288	2.81	0.53	4.17	0.9999
	298	2.81	0.64	10.1	0.9999
NT-25/Cd	278	3.07	0.13	1.26	0.9998
	288	2.85	0.78	6.34	1.0000
	298	2.84	6.75	54.4	1.0000

with temperature in all systems studied, while the equilibrium sorption capacity was little affected. These results can be correlated to a physisorption process, in which a rise in temperature increases the rate to approach equilibrium.

The activation energy of sorption can be obtained using the equation of Dubinin-Radushkevich (Eq. (9)).

$$\ln X = \ln X_m - K\varepsilon^2 \tag{9}$$

Where X is the amount of solute adsorbed per unit mass of adsorbent (mol g^{-1}), X_m is the sorption of adsorbent per unit mass (mol g^{-1}), K is a constant related to the sorption energy (mol^2 kJ^{-2}) and ε is the Polanyi potential (kJ mol^{-1}). The latter parameter was obtained as a function of temperature and the concentration of solute in aqueous phase at equilibrium (Eq. (10)). The activation energy of sorption can be calculated by Eq. (11).

$$\varepsilon = RT\ln(1 + 1/Ce) \tag{10}$$

$$E = (-2K)^{-1/2} \tag{11}$$

Values of ln$X$ were plotted against ε^2, so that the activation energy values can be obtained from K values (the slope of the linear plots) were (in kJ mol^{-1}) K-10/Mn(II) = 10.21 K-10/Cd(II) = 23.57, NT-25/Mn (II) = 18.26, and NT-25/Cd(II) = 28.87. Ion-exchange processes have activation energies in the range 8–16 kJ mol^{-1} (Helferrich, 1962). The obtained values are within or slightly higher than the range of ion-exchange processes, and are in agreement with the mechanism previously presented. Therefore, at low ionic strength the cation exchange mechanism is predominant, being the formation of surface complexes more pronounced for systems containing cadmium(II). Kraepiel et al. (1999) demonstrated that the mechanism of complex formation at the surface can be represented by a model that takes into account both the intrinsic affinity of surface sites for solutes and the coulombic interactions between the surface charge and dissolved ions.

3.3 Influence of pH

The effect of pH on metal removal was evaluated at room temperature, by varying the pH of a 50 mg L^{-1} metal solution-clay suspension from 1.0 to 6.0. The results are shown in Fig. 11.

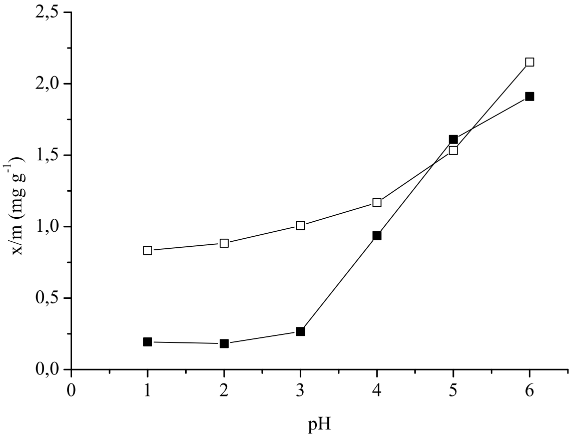


Fig. 11 Uptake values (mg g^{-1}) in function of pH media ($C_0 =$ 50 mg L^{-1}): cadmium (■) and manganese (□)

The effect of pH must be considered from a combination of effects that occur on the solute molecules and on the surface of each clay. The removal of metals from solution is a function to the pH of the solution. The maximum uptake of metals occurs at a pH value of about 6.0. It is assumed from the results that, at low initial concentrations, the predominant metal retention mechanism is due to ion exchange, since at pH values lower than 6.0 the precipitation of metals is greatly reduced (Baes and Mesmer, 1976). According to MINEQL predictions, the main species present in solution at pH 4 and 6 are showed in Table 4. The results confirm a predominance of metals in their free forms.

The origin of cation exchange capacity (CEC) is attributed to two processes. The isomorphic substitution of Al(III) by Mg(II) or Fe(II) and of Si(IV) by Al(III) leads to a negative net charge. This could be considered the constant contribution for CEC, since it is almost not sensitive to the pH of the system. The dissociation of aluminol groups on the edges of the structure is the second process. Since these groups are weakly acids, the surface-edge charges are pH-dependent and thus the CEC depends on pH. At pH 7, about 20% of the CEC of smectites is located at the surface edges (Lagaly, 1981). At low pH values, where the concentration of H_3O^+ is high, we expected that the interlayer sites must be proton-saturated and therefore the clay surface is positively charged. At higher pH values, the clay particles become less positive (or even negative) and the retention on the permanent charge sites increases accordingly. The retention on the surface hydroxyl edge sites is already favored under these conditions, so the high metal concentration in the solid surface may lead to the formation of complexes or precipitates on these sites. This would explain the increase in metal removal that corresponds to 2.5 times for manganese and 10 times for cadmium, which is observed when the pH is increased. Considering that cadmium(II) have an ionic radius that is larger than that of manganese(II) and, consequently, lower charge density, its retention is therefore more affected by the deprotonation of the surface groups.

Table 4 Species (%) of cadmium and manganese predicted by MINEQL at pH 4 and 6

Metal	Species	pH 4 (%)	pH 6 (%)
Cd	Cd^{2+}	99.8	99.8
	$Cd(OH)^+$	<0.1	<0.1
	$Cd(OH)_2$	<0.1	<0.1
Mn	Mn^{2+}	99.9	99.9
	$Mn(OH)^+$	<0.1	<0.1
	$Mn(OH)_2$	<0.1	<0.1

3.4 Modified clay

Complexing agents were incorporated on the surface of K-10 as described above. The thermogravimetric analyses indicate that these agents decompose, with peaks centered at 486 K (APDC), 564 K (EDTA) and 505 K and 628 K (DTPA). Figure 12 illustrates the thermogravimetric curves obtained for original and DTPA modified clays. The amount of complexing agent incorporated in the samples was determined, giving the values of 3.74% (0.228 mmol g^{-1}) for APDC, 1.95% (0.052 mmol g^{-1}) for EDTA and 14.84% (0.377 mmol g^{-1}) for DTPA.

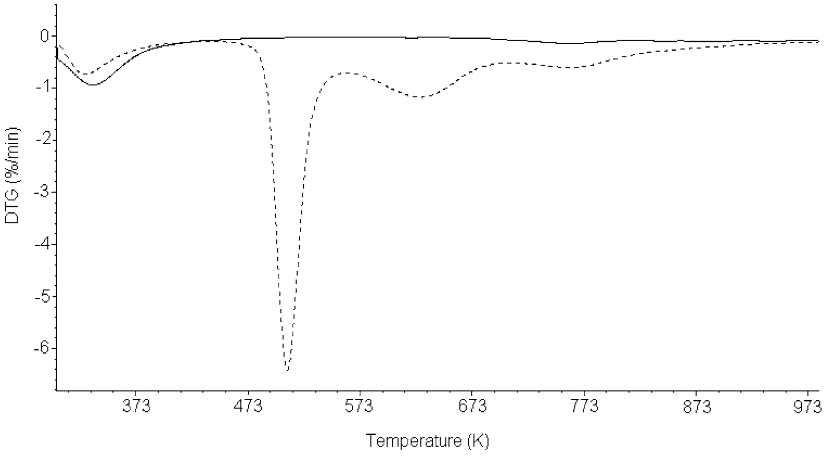


Fig. 12 DTG curves of K-10 (solid) and K-10/DTPA (dashed) clays

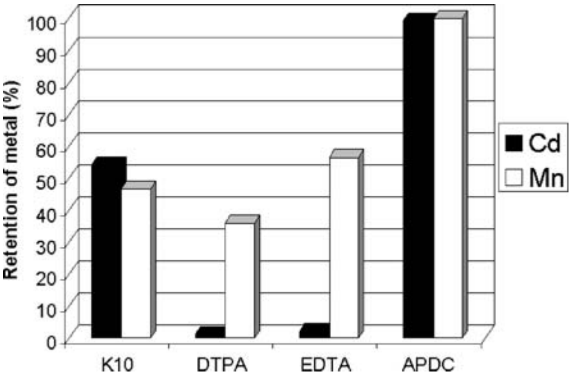


Fig. 13 Uptake values for the retention of metal (%) in function of complexing agents ($C_0 = 50$ mg L^{-1})

Single-metal sorption for solutions with $C_0 = 50$ mg L^{-1} is presented in Fig. 13.

The unmodified montmorillonite has two different cation-exchange groups. After the addition of APDC, a third kind of exchange reaction must be considered, as the complexing molecules promote modifications in some of the interlayer permanent charge sites. The difference in the amount of adsorbed metals is dependent of the equilibrium constants of the exchange reactions. The results denote a strong interaction between the cations and the APDC complexing molecules. EDTA and DTPA molecules bonded to interlayer exchange sites turn them inaccessible to metal cations, since these complex molecules are bulky and thus fill up the interlayer spaces.

4 Conclusions

The sorption removal of cadmium(II) and manganese(II) from single aqueous solutions using commercial and Brazilian natural clays was investigated. Sorption was rapid during the first 5 min and equilibrium was attained within 60 min. A Lagergren pseudo-second order model best described the kinetics of sorption. The rate constants and the initial sorption rates correlate positively with temperature in all systems studied, while the equilibrium sorption capacity was little affected. Two mechanisms could be inferred from these results: (i) a cation exchange process occurring at the permanent charge interlayer sites and (ii) formation of inner-sphere complexes on the hydroxyl edge sites.

The sorption isotherms could be fitted in the Langmuir model and represents favourable processes. The amount of metal that is sorbed increases with increasing pH values.

The APDC-modified clay showed higher affinity for cadmium(II) and manganese(II), promoting total retention when the initial concentration was 50 mg L^{-1}.

The acceptably high capacity and fast kinetics for metal sorption indicates their potential application for treatment of industrial wastewaters with low concentrations of cadmium(II) and manganese(II). In such cases, this selective cation-exchanger may provide an economical way of removing heavy metals from effluents.

Nomenclature

AAS	atomic absorption spectrometry
APDC	Ammonium pyrrolidinedithiocarbamate
b	Langmuir constant, L mg^{-1}
B.E.T.	Brunauer, Emmett and Teller
C_0	initial metal concentration, mg L^{-1}
Ce	equilibrium concentration of the solute, mg L^{-1}'
CEC	cation exchange capacity, meq g^{-1}
CEC_{exp}	experimental cation exchange capacity
DTG	differential thermogram
DTPA	diethylenetriaminepentaacetic acid
E	activation energy of sorption, kJ mol^{-1}
EDTA	disodium salt dihydrate of ethylenediaminetraacetic acid
h_0	initial sorption rate, mg $g^{-1}min^{-1}$
K	Dubinin-Radushkevich constant, mol^2 kJ^2
k_1	Lagergren first order rate constant, min^{-1}
k_2	Lagergren second order rate constant, g $mg^{-1}min^{-1}$
K_f	Freundlich constant, mg g^{-1}
LOI	loss on ignition
m	mass of the adsorbent, g
n	Freundlich constant
Q_0	Langmuir constant, mg g^{-1}
q_e	amount of sorbed metal ions on the clay surface at equilibrium, mg g^{-1}
q_t	amount of sorbed metal ions on the clay surface at any time t, mg g^{-1}
r	correlation coefficient

R	universal gas constant, 8.31451 J mol^{-1} K^{-1}
R_L	Langmuir equilibrium parameter
t	time (h)
x	mass of the solute adsorbed, mg
X	concentration of the solute adsorbed, mg g^{-1}
X_m	sorption of adsorbent per unit mass, mol g^{-1}
ε	Polanyi potential, kJ mol^{-1}

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