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Ni(II) removal from aqueous effluents by silylated clays

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Abstract

Industrial effluents discharged in water bodies without proper treatment contribute to water pollution by potentially toxic metal ions. Considering that the legislation for discarding of such effluents is getting more and more rigorous, the development of efficient processes for the treatment of industrial effluents is of great interest. A study on the capacity of metal retention by silylated-modified clays was carried out with the aim to evaluate the efficiency of this application. K10 clay was modified with 3-mercaptopropyltrimethoxysilane (MPS) and tested in batch removal processes. We investigated the sorption process, obtaining isotherms and kinetics of adsorption and the influence of pH, the desorption process and the metal recovery. It was observed that the modified clay presents fast retention and good capacity of both adsorption and desorption. The use of K10/MPS as adsorbent shows to be more adequate in effluent final polishment, after a conventional treatment, or when Ni(II) initial concentration in the effluent is low enough to permit its adequate removal by conventional methods.
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1. Introduction

Industrial effluents have frequently been responsible for pollution caused in aquatic environments, especially those containing heavy metals, since these pollutants can easily be absorbed by aquatic organisms, bioaccumulated and spread along the food chain.

Nickel is one of the constituent of urban air, possibly as a result of the fossil fuel burning and it is not a natural constituent of the water. An important use of nickel is as electrodes of the reloadable batteries NiCad (nickel–cadmium) used in calculators and similar devices [1]. When incorporated in the organism, it accumulates in the lungs, kidneys, liver, intestine and heart. Moreover, it can cause cutaneous nauseas, injuries, liver and kidney diseases, infertility, apathy, chronic headaches, sleeplessness and diarrhea [2].

Methods commonly used in the removal of metallic ions are chemical precipitation, ultrafiltration, reverse osmosis, liquid–liquid extraction and ion exchange resins, amongst others. The most used is chemical precipitation; however this technique is not efficient when applied to effluents with low metallic concentrations. In this case, there are necessary subsequent treatments in order to reach the legal discarding specifications of these effluents [3]. Besides this limitation, precipitation processes are accompanied by the formation of large amounts of solids containing heavy metal species [4].

The use of natural adsorbents such as clays and zeolites has been studied due to their availability, low cost, simplicity of extraction and retention capacity [5,6]. The commercial clay Fluka K10 is a montmorillonite, which is formed by an octahedral central aluminum group between two tetrahedral silicon groups linked together by oxygen atoms. Silicate layers of this smectite have a slightly negative charge that is compensated by exchangeable ions in the intermediate layers. Due to their large specific surface area and cation exchange capacity, smectites are among clay minerals the more frequently used as adsorbents. The incorporation of an organic ligand can significantly increase both the retention capacity and the adsorption kinetics of the clay. This material combines the properties of ionic exchanger

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of the original material with the extraction properties of the chelant agent [7]. Published studies have shown that the process of clay impregnation with acid chelants is widely applicable and its original selectivity is kept [8]. However, chelant agent presents disadvantages in relation to the stability and regeneration of the modified material. This is related to the low stability of the electrostatic interactions between organic molecules and the clay surface, thus it is possible that losses of impregnated chelant may occur during regeneration and recycling processes. Organic units covalently bonded present advantages in opposition to the electrostatic interaction promoted by chelant agents [9,10]. The process of organofunctionalization of a surface consists in the use of a molecule that contains an organic group of interest and is covalently attached to the surface of the inorganic support, generally by interaction between alcoxi radicals and surface hydroxyls. The great advantage is the recycling possibility, besides to maintain the properties related to the thermal stability and accessibility of the reactive centers [11]. In the clay structure, most hydroxyl groups are located in the interlamelar surface, due to structural defects or irregularities, thus most of the induced functionalization will take place at the interlamelar space [9].

Reaction between clays and reagents containing thiol groups (−SH), particularly 3-mercaptopropyltrimethoxysilane (MPS), has been recently explored in order to prepare adsorbents with high adsorption capacity and selectivity for Pb(II), Hg(II), Cd(II), Zn(II), Ag(I), Co(II), Cu(II), Fe(III) and Ni(II) [12,13].

There are two methods used for the functionalization of surfaces with silylant agents. The first occurs by hydrolysis of silanes in the presence of water originated from clay moisture, atmosphere humidity or generated *in situ*. Another method involves the formation of covalent bonds through surface silanol condensation, or with hydroxyls in anhydrous conditions [14]. In this work, we used the latter method to chemically modify K10 clay. The success of the reaction in non-aqueous solvent depends on the availability of hydroxyl groups capable to form covalent bonds with the silylant agent in a tri-, bi- or monodentate way. Indeed, the linking forms most common are the mono- and bidentate types for reasons of sterical nature [12].

The aim of this work is to verify the behavior of the Fluka K10 montmorillonite modified with MPS in the retention of Ni(II) evaluating its adsorption kinetics and capacity, the influence of initial pH and the adsorbent stability and recycling possibility.

2. Materials and methods

2.1. Starting material

Montmorillonite K10, identified as the parent clay, was obtained from Fluka and was tested without any previous treatment. This clay was previously characterized [15]: the B.E.T. surface area is $232 \, m^2 \, g^{-1}$; the formula of one half unit cell is $Na_{0.60}K_{0.12}Ca_{0.02}(Al_{1.78}Fe_{0.12}Mg_{0.10})_{VI}(Si_{3.89}Al_{0.11})_{IV}O_{10}(OH)_2$; experimental cation exchange capacity (CEC$_{exp}$) corresponds to $0.451 \, meq \, g^{-1}$.

2.2. Preparation of modified material

Modified clay (K10/MPS) was prepared as follows. A sample containing 7.0 g of commercial Fluka K10 montmorillonite clay was heated to 373 K under vacuum for 24 h, in order to remove moisture. Using a three-necked balloon, 175 mL of dry toluene and 7.0 mL of MPS (ACS grade, Aldrich) were added to the activated clay. An anhydrous atmosphere was maintained by a flux of dry nitrogen. The derivatization reaction was carried out under reflux for 24 h. The solid obtained was separated by filtration and washed first with toluene and then with ethanol. Residual silane was removed by a 24 h Soxhlet ethanol extraction.

Fourier transform infrared (FT-IR) spectra of parent and functionalized clays were recorded on KBr disks using a FTIR ABB BOMEM model FTLA 2000 spectrometer. Disks were dried at 373 K for 24 h prior to recording the FT-IR spectrum. The degree of MPS incorporated by the clay was determined by thermogravimetric (TG) analysis in a Thermal Analyser Netzsch TG 209 (detection limit of 0.01 mg), with 6 mg of sample submitted to a heating rate of $10 \, K \, min^{-1}$ in nitrogen atmosphere.

2.3. Sorption studies

Nickel(II) nitrate (analytical grade, Aldrich) was used as the source of metallic ions. A Perkin-Elmer model AA-300 atomic absorption spectrometer was used for nickel analysis. An analytical curve was prepared from $1000 \, mg \, L^{-1}$ stock solution (Titrisol, Merck). The limits of detection and quantification were 0.048 and $0.077 \, mg \, L^{-1}$, respectively, and the analytical curve is linear up to $2.0 \, mg \, L^{-1}$ Ni(II). The relative standard deviation for 12 replicates varies between 5% for $0.2 \, mg \, L^{-1}$ Ni(II) and 1.6% for $2.0 \, mg \, L^{-1}$ Ni(II).

Experimental solutions with different metal concentrations were prepared in stopped Pyrex glass flasks, at 298 K. The rate of metal sorption was investigated in bench-scale studies. It was mixed with 6.0 mL of a solution of the metal with an initial concentration (C_0) that varied from 10 to $2000 \, mg \, L^{-1}$ and 0.1 g of the clay, under magnetic stirring, at 298 K. After a time period of 15 min, the suspension was filtered through a $0.2 \, \mu m$ membrane filter (RC15) and the metal remaining in solution was quantified by atomic absorption spectrometry (AAS). The original pH values varied from 6.9 to 5.1, according to C_0. Kinetic adsorption studies using the silylated clay were carried out by the analysis of aliquots removed in time intervals that varied from 1 to 60 min, using 60 mL of the $100 \, mg \, L^{-1}$ solution and 1.0 g of solid.

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

Concentrated hydrochloric acid and sodium hydroxide (ACS grade, obtained from Merck and Aldrich, respectively) were used for pH adjustments. Studies on the effect of pH upon the sorption of Ni(II) were performed at the range 1.0–6.0 and a set concentration of $100 \, mg \, L^{-1}$ Ni(II). The pH was adjusted to desired values by the addition of hydrochloric acid or sodium hydroxide solutions and the sorption studies were performed as

described above. A digital pHmeter Analyser model 300 M was used for pH measurements.

2.4. Desorption and recycling studies

Desorption tests were conducted with solids previously submitted to the adsorption process, as described above. Three grams of clay were placed in contact with 180 mL of a 250 mg L^{-1} Ni(II) solution, during 30 min. The solid phase was filtered and dried, while the remaining metal in the liquid phase was quantified. To 2.5 g of dried clay, 75 mL of HCl 1 mol L^{-1} was added and the suspension was stirred for 180 min. After defined time intervals, aliquots of the aqueous phase were separated by filtration and the remaining concentration of metal was quantified by AAS.

Recycling tests were performed by adsorption–desorption steps. After each cycle, the concentration of metal remaining in solution was determined by AAS.

3. Results and discussion

3.1. Characterization of parent and modified clays

The infrared spectra of a functionalized sample revealed new peaks compared to the parent clay (Fig. 1), providing an evidence for the presence of the organic ligands in the modified clay. An aliphatic C−H vibration band of MPS organic chain at 2929 cm^{-1} was clearly identified in the FT-IR spectrum of K10/MPS. Both C−H deformation vibration and C−S stretching band of the MPS thiol group were also identified at 1402 and 682 cm^{-1}, respectively. At 465 cm^{-1}, we observed the band related to the Si−O deformation, while the Si−O−Si stretching is identified at 1026 cm^{-1}. It could be expected a decrease in the intensity of the O−H stretching band (3500 cm^{-1}) of the surface silanol groups in the modified clay. However, as pointed out by Celis et al. [16], the formation of new silanol groups from hydrolysis of the residual methoxy groups present in grafted MPS,
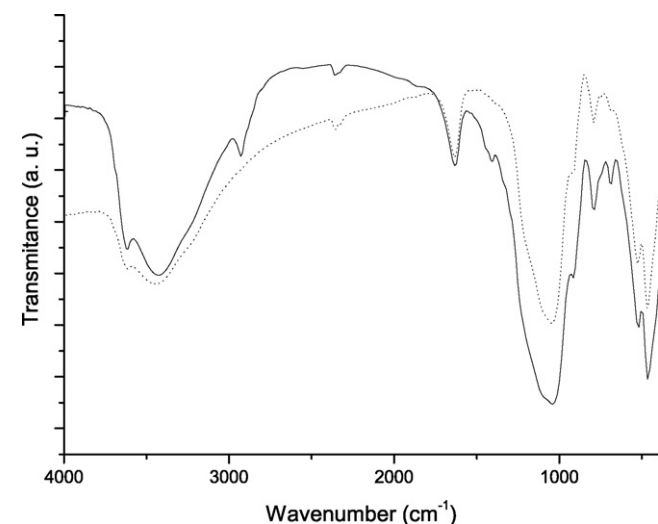

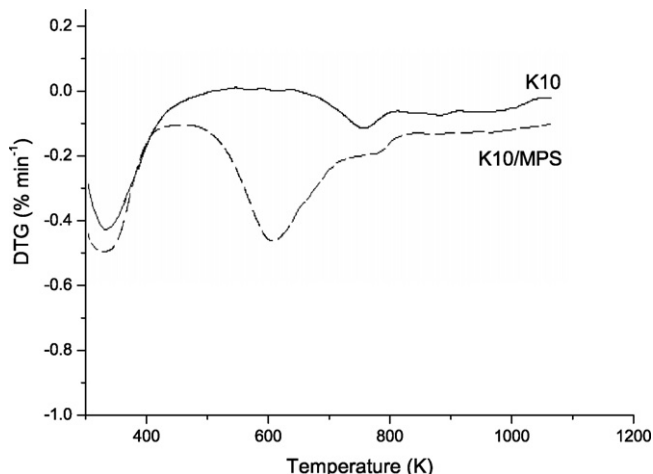Fig. 1. Infrared spectra of functionalized (solid) and parent (dotted) clays.

Fig. 2. DTG curves of K10 (solid) and K10/MPS (dashed) clays.

compensates the loss of silanol groups from original surface clay during the condensation reaction.

Thermogravimetric curves of parent and modified K10 are shown in Fig. 2. The curves exhibited a first mass loss centered at 340 K, which is related to the loss of moisture and to water molecules that are bound to interlayer cations. Moisture corresponds to 2.74% and 3.02%, respectively for K10 and K10/MPS. The second mass loss, centered at 763 K, is attributed to the dehydroxylation of the layer silicate and corresponds to 3.84% for K10 sample. There is not any noticeable weight loss process between water removal and dehydroxylation for K10 sample. Besides this dehydroxylation, K10/MPS presents a weight loss centered at 610 K that is related to the degradation of the chelating agent.

The amount of incorporated chelating agent obtained from thermogravimetric analysis corresponds to 11.66%. This value corresponds to a thiol group concentration in the modified clay of 0.9 mmol g^{-1} (based on the bidentate silane coordination to the solid surface [13,17]).

3.2. Sorption kinetic studies

Kinetic studies using K10/MPS as adsorbent were conducted in systems containing 100 mg L^{-1} of Ni(II). The results of such studies are shown in Fig. 3.

Metal removal is a rather fast process in which metal uptake by functionalized clay is attained within 15 min. In a similar way the system containing parent clay reaches equilibrium at the first 5 min of contact time between the phases [15]. These results indicate that all adsorption sites are located in a readily accessible region for heavy metal cations, either at external or expanded interlayer spaces. According to early studies [18,19], some mechanistic steps can be considered in these adsorption processes, as film or external mass transport, pore and surface diffusion and adsorption at sites located in the surface. The first step is not rate-limiting since the effect of transport in solution can be eliminated by efficient stirring. The second step must be deeply reduced in clay minerals because these materials undergo complete expansion in the presence of large amounts of water,
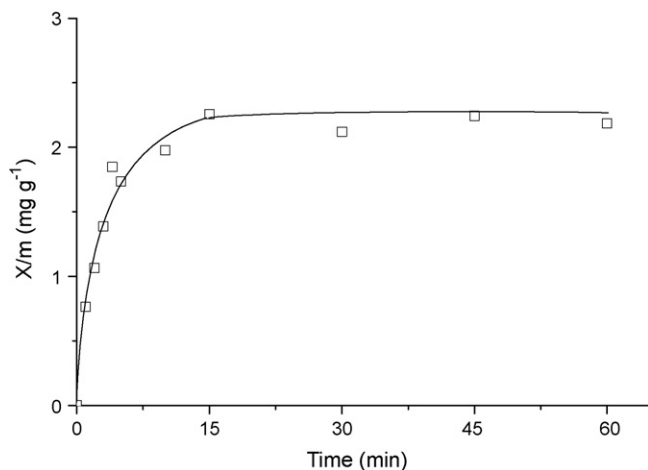
Fig. 3. Kinetic studies on the removal of Ni(II) by K10/MPS, where X/m is the mass of the solute (mg) adsorbed per gram of adsorbent.
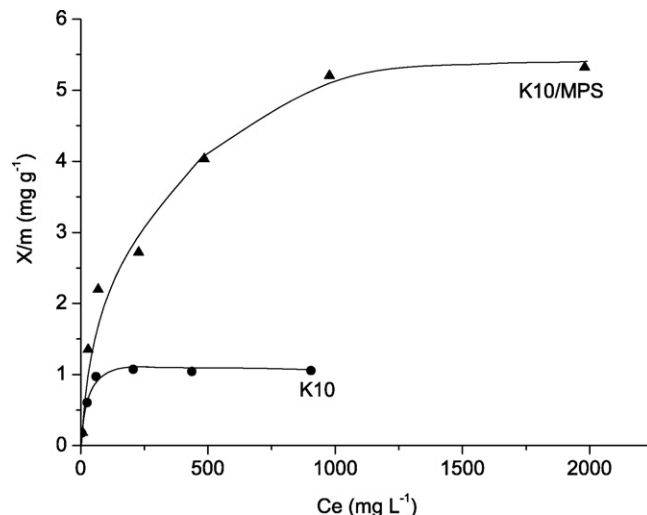

Fig. 4. Metal sorption isotherms for the binding of Ni(II) at 298 K.

thus promoting complete separation of the unit layers. Thus, the third step seems to be the most relevant to induce the adsorption process. In spite of the presence of the surface functionalized groups in K10/MPS, we must consider that this clay presented a light hydrophobic character, probably due to the presence of carbon chains in the silylant agent [20]. This alteration in the surface properties of the solid was already identified by other authors, who demonstrated the possibility of application of these materials in the retention of organic pollutants via hydrophobic interactions [21,22]. This character could negatively influence the approach of metallic cations and consequently interferes in their retention.

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 by using the equations presented by Ho and McKay [23]. According to these models, linear plots of $\log(q_e - q_t)$ versus t indicate the applicability of the pseudo-first order Lagergren model (q_e and q_t are the amounts of sorbed metal ions on the clay surface, in mg g^{-1}, at equilibrium and at any time t, respectively). In a similar way, pseudo-second order model can be represented by a linear plot of t/q_t versus t.

Table 1 lists the kinetic parameters obtained for the sorption of Ni(II) on parent and modified clays.

Equations of pseudo-second order correspond to the model that best described the experimental data, since q_e values estimated by this model are in agreement with the experimental results ($q_{e,exp}$) and the values for the correlation coefficients were shown to be close to 1.

3.3. Sorption capacity

Nickel(II) sorption is strongly influenced by the initial concentration, as observed in the sorption isotherms presented in Fig. 4. The isotherms were plotted using a mass-based solid concentration, X/m (in mg of solute adsorbed per gram of adsorbent) as a function of concentration in solution, C_e (in mg of solute per litre of solution) in equilibrium conditions.

We can observe that the amount of adsorbed metal enhances according to C_0, until it reaches a maximum value. Each system stabilizes in a different quantity of solute adsorbed. Nickel(II) adsorption on K10 montmorillonite can be attributed to a cation exchange mechanism, while K10/MPS must retain these cations by a chelating process with −SH functionalities. K10/MPS presented the higher values of retention, revealing more efficient than the parent clay.

Despite these interesting results, Celis et al. [16] had demonstrated that a similar adsorbent (sepiolite/MPS) was able to retain amounts of Hg(II), Pb(II) and Zn(II) as high as 590, 70 and 35 mmol kg^{-1}, respectively. The latter results being explained in terms of metal affinity for the chelant. The authors employed a mass:volume ratio of 10 g L^{-1}. Taking these results into account, we tested the influence of adsorbent mass:solution volume ratio on the adsorption process. The results are presented in Table 2.

We observed that the amount of Ni(II) retained deeply enhances when the ratio mass/volume is low. Higher adsorptions were obtained when the volume of the solution is high compared to the mass of the clay, suggesting that this condition facilitates the access of Ni(II) cations to the adsorption sites. However, the percentage of retention is lower because the quan-

Table 1
Kinetic parameters related to the sorption of Ni(II) from a 100 mg L^{-1} solution, where r is the correlation coefficient

Adsorbent	$q_{e,exp}$ (mg g^{-1})	Pseudo-first order		Pseudo-second order		
		k_1 (min^{-1})	r	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	r
K10	1.21	0.0772	0.4214	6.8852	1.21	0.8252
K10/MPS	2.18	0.0409	0.6304	0.4453	2.24	0.9985

Table 2
Effect of adsorbent mass:solution volume ratio on the adsorption process

Mass/volume (g L^{-1})	Initial concentration (mg L^{-1})	Final concentration (mg L^{-1})	Retention	
			mg g^{-1}	mmol kg^{-1}
0.05	10.84	9.98	17.12	291.7
0.316	10.84	10.16	2.14	36.46
2.01	10.84	8.18	1.32	22.49
2.65	10.84	8.82	0.77	13.12
17.0	10.46	7.38	0.18	3.06

tity of adsorbent sites is small. We presented in this work sorption and desorption processes related to a ratio mass/volume equal to 17, thus these results can be compared to the literature cited below.

It is possible to find extensive literature about the evaluation of natural adsorbents (*in natura* and modified) as, for example, quitosan, zeolites and agricultural residues. Huang et al. [24] tested the retention capacity of quitosan, obtaining an adsorption of 2.4 mg g^{-1} of Ni(II). Natural zeolites as clinoptilolite, whose cost is considerably lower than quitosan, also was used but the results were quite worse. Zamzow and Eichbaum [25] were able to retain 0.48 mg g^{-1} of Ni(II) on clinoptilolite. The silylated clay tested by us demonstrated high capacities of metal removal from aqueous solutions, reaching values as high as 5.3 mg g^{-1}. On the other hand, if we calculate the ratio between thiol groups and the maximum amount of metal retained in K10/MPS (respectively, 0.9 and 0.09 mmol g^{-1}), we observe that the concentration of thiol groups is 10 times higher than metal adsorbed. This result is similar to that obtained by Mercier and Detellier [9], which proved that it was related to the metal retention by more than one −SH group. Thereafter, only those surface regions with high concentration of chelant agent could effectively bind Ni(II).

Equilibrium uptake data found at room temperature were processed according to linear Langmuir and Freundlich isotherms [26]. For the traditional Langmuir isotherm, Eq. (1) was used.

$$\frac{C_e}{x/m} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \qquad (1)$$

where C_e is the equilibrium concentration of solute, x the mass of adsorbed solute, m the mass of adsorbent, b and Q_0 are Langmuir constants. The Langmuir adsorption model is based on the assumption that the maximum adsorption corresponds to the formation of a saturated monolayer of solute molecules on the adsorbent surface. Additionally, 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 $R_L > 1$) [27]. This parameter can be calculated as indicated in the following equation:

$$R_L = \frac{1}{1 + bC_0} \qquad (2)$$

where C_0 is considered as the highest initial solute concentration.

For the Freundlich isotherm, Eq. (3) was used.

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n} \log C_e \qquad (3)$$

where K_f and n are Freundlich constants, x, m and C_e are defined as mentioned above. The Freundlich isotherm describes equilibrium on heterogeneous surfaces and hence does not assume a monolayer capacity.

The analysis of equilibrium data according to Langmuir and Freundlich-type equations allowed us to obtain the parameters presented in Table 3.

Data in Table 3 confirms that the equilibrium related to modified and parent K10 is best described by a Langmuir-type isotherm, with high correlation coefficients. The Q_0 parameters are related to the sorption capacity with respect to a specific solute, being closed to the experimental data (Q_{exp}) presented in Table 3. The R_L values obtained in this study ranged between 0 and 1 in all studied systems. Most of the values are close to the lower limit, indicating the tendency to an irreversible character probably due to the strong interaction between heavy metal cations and surface adsorption sites.

We must stand out that most of the original assumptions regarding the Langmuir model (adsorption at planar surfaces with a fixed number of identical sites, in which reversibility and adsorption energy is the same for all sites) are not valid for the heterogeneous surface found in these clays. Thus, Langmuir equation should be used only for qualitative and descriptive purposes, while for quantitative analysis one must be careful. However, even considering the restrictions, many authors have demonstrated that the Langmuir model described equilibrium behaviors of many materials (including polyfunctional adsorbents) in a suitable manner [28,29]. This fact can be traduced as a homogeneous distribution of surface functional groups.

3.4. pH influence

The effect of pH on the removal of Ni(II) from solution was evaluated at room temperature, varying the pH of a 100 mg L^{-1} Ni(II) solution-clay suspension from 1.0 to 6.0. Results are shown in Fig. 5.

Nickel(II) removal is influenced by the pH. The maximum value of metal retention occurred approximately at pH 6.0. However, even at pH 6.0, Ni(II) precipitation is negligible [30]. It can be observed that there is a decrease in the capacity of retention in solutions with reduced pH. Such fact can be related to an increase in the concentration of H$^+$ ions according to a reduction in pH. Under this condition, two facts can be considered. On the parent clay, a competition by the surface sorption sites occurred between protons and heavy metal ions, while thiol groups present in silylated clay are converted to a protonated
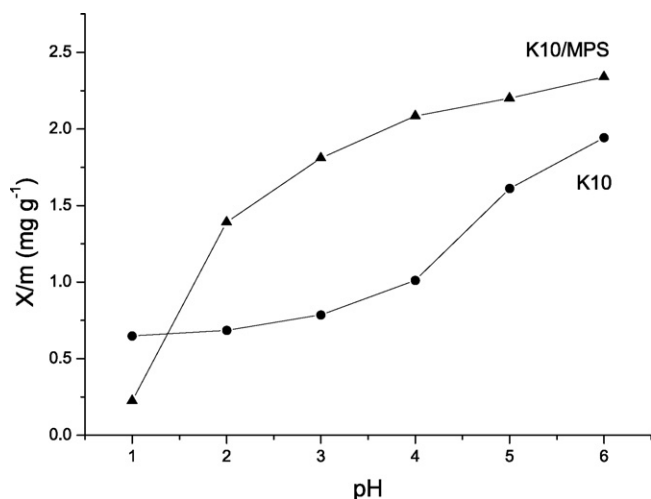
Fig. 5. Uptake values for the removal of Ni(II) as a function of the pH media ($C_0 = 100 \, mg \, L^{-1}$).

Fig. 6. Ni(II) desorption from samples previously submitted to the adsorption process.

form (mainly at pH values below 2) that limits their complexation capacity, as previously observed for the uptake of heavy metal ions by aminopropyl- and mercaptopropyl-grafted smectites [31]. Thus the increase in nickel(II) removal with pH may be explained by an increase in electrostatic repulsion between cations and the positively charged surface of K10/MPS at low pH values. This is the major limitation in the use of K10/MPS as an adsorbent. On the other hand, this pH dependence can be applicable in desorption processes.

3.5. Desorption and recycling studies

Conventional methods for heavy metal removal, as chemical precipitation, may be ineffective or extremely expensive when metallic ions are present at relatively low concentrations in large volumes of effluent [32]. On the other hand, methods based on adsorption are frequently concentration processes. After desorption, they produce aqueous solutions more concentrated in heavy metals than original effluent, which can be satisfactorily treated by a conventional method.

K10/MPS shows a high efficiency in the retention of Ni(II) at low concentrations. This allows the treatment of large volumes of effluent, reducing its heavy metal concentration to levels that let an adequate discharge. However, a new toxic solid waste is produced, and methods of desorption and recycling must be estimated. Two alternatives can be evaluated concerning this solid waste. Low cost sorbents contaminated with heavy metals can be stabilized through their encapsulation in concrete blocks, allowing their safe disposal in industrial landfills [33]. When
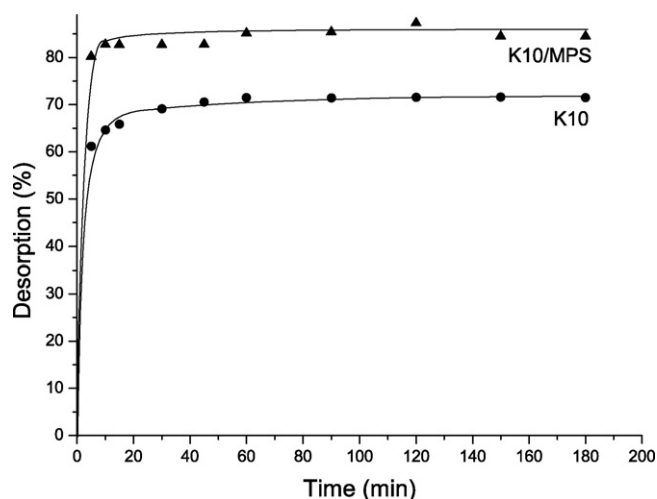
low cost adsorbents are modified, as in this work, the aim is to promote the sorptive properties and recycling studies.

In order to test the reusable capacity of the modified clay, desorption and recycling tests were performed. We have tested the possibility of metal desorption in systems treated with HCl. The results are presented in Fig. 6.

It could be observed that functionalized clay presents a good desorption capacity, reaching 85% at the first 10 min. Parent clay desorbs a maximum of 71% and its equilibrium is attained only after 30 min of contact with HCl solution. Based on these results, we tested the use of K10/MPS in adsorption/desorption cycles, respectively promoted by Ni(II) and HCl solutions. The results are presented in Fig. 7.

The functionalized clay presented good results in the regeneration process. It is possible to observe that no reduction in the adsorption capacity was observed throughout the cycles. In contrast, the retention increased after the first stage. This fact can be related to a reduction in the hydrophobic character after hydrochloric acid washing, which presented better dispersion of the clay in the aqueous phase. Thus, the acid washing favored the contact of the solid phase with metallic cations. In fact, after a washing with HCl solution in the newly modified clay, it produced a more appropriated dispersion in the aqueous phase inducing a retention capacity that reached 2.9 mg g^{-1} against 2.2 mg g^{-1} obtained with the as-synthesized sample.

The mass of silylated agent present on used K10/MPS was measured by thermogravimetric analysis. As can be seen in Fig. 8, MPS-modified sample was stable, since no leakage of chelating agent was observed. Thus, this functionalization

Table 3
Characteristic parameters obtained from Langmuir and Freundlich equations, where Q_{exp} is the maximum adsorbed quantity obtained from experimental isotherms

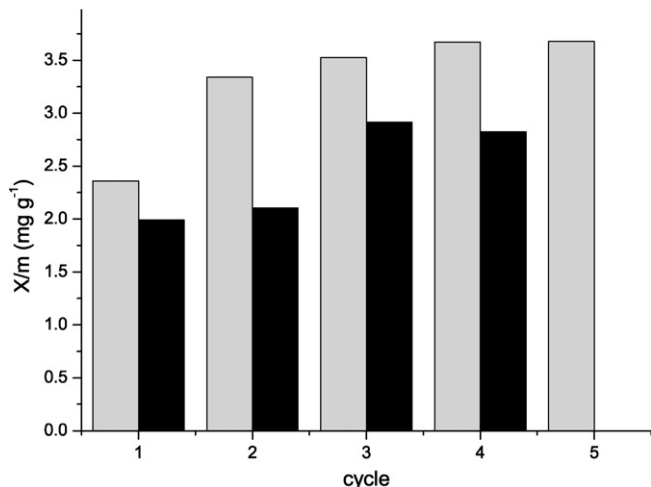| System	Q_{exp} (mg g^{-1})	Langmuir isotherm				Freundlich isotherm		
		Q_0 (mg g^{-1})	b (L mg^{-1})	R_L	r	K_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	n	r
K10	2.07	2.10	0.15682	0.0123	0.9987	1.000	2.198	0.8180
K10/MPS	5.32	4.73	0.0101	0.0131	0.9822	0.410	3.531	0.8149

Fig. 7. Adsorption/desorption cycles: total amount of Ni(II) adsorbed on the clay (gray) and Ni(II) released after desorption process (black).
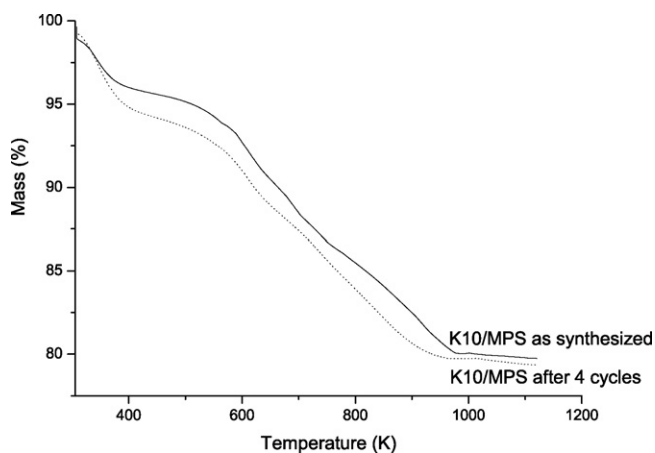

Fig. 8. TG curves of as-synthesized (solid) and used (dotted) K10/MPS clays.

enables the formation of a stable organic–inorganic hybrid, preventing the leaching process.

After four adsorption/desorption cycles the quantity of incorporated chelant agent decreased only from 11.66% to 10.93%. This reduction was observed after the first desorption process (not shown in Fig. 8), after that the sample remained stable. One could infer that this is due to the loss of some MPS molecules weakly bound to the solid surface, probably attached to the solid by van der Waals' interactions.

The liquid waste obtained after desorption process, with reduced volume and high heavy metal concentration, can be efficiently treated by a conventional method. Alternatively, metal ions present at high concentrations can be recovered in their metallic form by electrochemical treatment.

4. Conclusions

MPS/K10 was prepared by functionalization of K10 montmorillonite clay with 3-mercaptopropyltrimethoxysilane. Its adsorption performance was evaluated using Ni(II) in aqueous phase. The results demonstrated that the adsorption is a

rather fast process. A Lagergren pseudo-second order model best described the kinetic parameters. MPS/K10 also shows high capacity for metal removal, reaching values as high as 5.3 mg g^{-1}. The equilibrium related to both parent and modified clay is best described by a Langmuir-type isotherm. The influence of pH is related to competition between H$^+$ and heavy metal ions by the adsorption sites, thus high concentration of H$^+$ ions limits the complexation capacity. Desorption process can be promoted by HCl washing solution, which recycles the solid without reduction on its adsorption capacity.

Silylated clay was shown to be a potential alternative as an adsorbent for Ni(II). High adsorption capacities concur for this purpose, mainly in low metal concentrations. Thus, the use of silylated clays shows to be more appropriate in effluent final polishing, after conventional treatment, or when Ni(II) initial concentration in the effluent is low enough to permit its adequate removal by conventional methods.

References

[1] C. Baird, M. Cann, Environmental Chemistry, 3rd ed., W.H. Freeman, New York, 2004.

[2] R.P. Beliles, The lesser metals, in: F.W. Oehme (Ed.), Toxicity of Heavy Metals in the Environment, Part 2, Marcel Dekker, New York, 1978.

[3] T.A. Kurniawan, G.Y.S. Chan, W.-H. Lo, S.B.A.T. Leon, Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals, Sci. Total Environ. 366 (2006) 409–426.

[4] C. Fabiani, Metal removal from aqueous wastes by means of membrane hybrid processes, in: P. Aimar, P. Apt'el (Eds.), Recent Progress an Genie des Proceeds, Membrane Processes Water Treatment—Pervaporation, Lavoisier Press, Paris, 1992.

[5] H. Ceylan, T. Sahan, R. Gurkan, R. Kubilay, Removal of some heavy metal cations from aqueous solution by adsorption onto natural kaolin, Adsorpt. Sci. Technol. 23 (2005) 519–534.

[6] M.L. Schlegel, L. Charlet, A. Manceau, Sorption of metal ions on clay minerals. II. Mechanism of co sorption on hectorite at high and low ionic strength and impact on the sorbent stability, J. Colloid Interface Sci. 220 (1999) 392–405.

[7] A. Kaya, A.H. Ören, Adsorption of zinc from aqueous solutions to bentonite, J. Hazard. Mater. 125 (2005) 183–189.

[8] J.-H. Chen, W.-R. Chen, Y.-Y. Gau, C.-H. Lin, The preparation of di(2-ethylhexyl)phosphoric acid modified Amberlite 200 and its application in the separation of metal ions from sulfuric acid solution, React. Funct. Polym. 56 (2003) 175–188.

[9] L. Mercier, C. Detellier, Preparation, characterization, and applications as heavy metals sorbents of covalently grafted thiol functionalities on the interlamellar surface of montmorillonite, Environ. Sci. Technol. 29 (1995) 1318–1323.

[10] F. An, B. Gao, Chelating adsorption properties of PEI/SiO$_2$ for plumbum ion, J. Hazard. Mater. 145 (2007) 495–500.

[11] M.G. Fonseca, C. Airoldi, New amino-inorganic hybrids from talc silylation and copper adsorption properties, Mater. Res. Bull. 36 (2001) 277–287.

[12] C. Airoldi, R.F. Farias, O uso de sílica gel organofuncionalizada como agente sequestrante para metais, Quim. Nova 23 (1999) 496–503.

[13] L. Mercier, T.J. Pinnavaia, A functionalized porous clay heterostructure for heavy metal ion (Hg^{2+}) trapping, Micropor. Mesopor. Mater. 20 (1998) 101–106.

[14] E. Ruckenstein, Z.F. Li, Surface modification and functionalization through the self-assembled monolayer and graft polymerization, Adv. Colloid Interface Sci. 113 (2005) 43–63.

[15] W.A. Carvalho, S.M. Dal Bosco, R.S. Jimenez, C. Vignado, J. Fontana, B. Geraldo, F.C.A. Figueiredo, D. Mandelli, Removal of Mn(II) and Cd(II) from wastewaters by natural and modified clays, Adsorption 12 (2006) 133–146.

[16] R. Celis, M.C. Hermosín, J. Cornejo, Heavy metal adsorption by functionalized clays, Environ. Sci. Technol. 34 (2000) 4593–4599.

[17] R.K. Iler, The Chemistry of Silica, John Wiley & Sons, New York, 1979.

[18] S.V. Mohan, N.C. Rao, J. Karthikeyan, Adsorptive removal of direct azo dye from aqueous phase onto coal based sorbents: a kinetic and mechanistic study, J. Hazard. Mater. 90 (2002) 189–204.

[19] F. Pagnanelli, F. Beolchini, A. Esposito, L. Toro, F. Vegliò, Mechanistic modeling of heavy metal biosorption in batch and membrane reactor systems, Hydrometallurgy 71 (2003) 201–208.

[20] N.N. Herrera, J.-M. Letoffe, J.-P. Reymond, E. Bourgeat-Lami, Silylation of laponite clay particles with monofunctional and trifunctional vinyl alkoxysilanes, J. Mater. Chem. 15 (2005) 863–871.

[21] R. Prost, B. Yaron, Use of modified clays for controlling soil environmental quality, Soil Sci. 166 (2001) 880–895.

[22] G.R. Alther, Organically modified clay removes oil from water, Waste Manage. 15 (1995) 623–628.

[23] Y.S. Ho, G. McKay, Comparison of chemisorption kinetic models applied to pollutant removal on various sorbents, Chem. Eng. Res. Des. 76B (1998) 332–340.

[24] C.-P. Huang, Y.-C. Chung, M.-R. Liou, Adsorption of Cu(II) and Ni(II) by pelletized biopolymer, J. Hazard. Mater. 45 (1996) 265–277.

[25] M.J. Zamzow, B.R. Eichbaum, Removal of heavy metals and other cations from wastewater using zeolites, Sep. Sci. Technol. 25 (1990) 1555–1569.

[26] C. Hinz, Description of sorption data with isotherm equations, Geoderma 99 (2001) 225–243.

[27] S.H. Lin, R.S. Huang, Heavy metal removal from water by sorption using surfactant-modified montmorillonite, J. Hazard. Mater. 92 (2002) 315–326.

[28] E. Álvarez-Ayuso, A. García-Sánchez, Palygorskite as a feasible amendment to stabilize heavy metal polluted soils, Environ. Pollut. 125 (2003) 337–344.

[29] G.D. Matos, M.A.Z. Arruda, Vermicompost as natural adsorbent for removing metal ions from laboratory effluents, Process Biochem. 39 (2003) 81–88.

[30] C.F. Baes, R.E. Mesmer, The Hydrolysis of Cations, Wiley, New York, 1976.

[31] I.K. Tonle, E. Ngameni, D. Njopwouo, C. Carteret, A. Walcarius, Functionalization of natural smectite-type clays by grafting with organosilanes: physico-chemical characterization and application to mercury(II) uptake, Phys. Chem. Chem. Phys. 5 (2003) 4951–4961.

[32] A.B. Pérez-Marín, V.M. Zapata, J.F. Ortuño, M. Aguilar, J. Sáez, M. Lloréns, Removal of cadmium from aqueous solutions by adsorption onto orange waste, J. Hazard. Mater. 139 (2007) 122–131.

[33] C.-K. Park, Hydration and solidification of hazardous wastes containing heavy metals using modified cementitious materials, Cem. Concr. Res. 30 (2000) 429–435.