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Takovite−Aluminosilicate Nanocomposite as Adsorbent for Removal of Cr(III) and Pb(II) from Aqueous Solutions[†]

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This work reports on the application of a takovite−aluminosilicate nanocomposite, synthesized by a coprecipitation procedure, as adsorbent for the removal of Cr(III) and Pb(II) from aqueous solutions. Experimental studies to determine the maximum fixation capacities, the adsorption isotherms, and the affinity order of the adsorption process were carried out. The sorption of Pb(II) ions is fast, and the equilibrium is reached within 20 min, while 180 min is necessary for the equilibrium to be reached in the case of Cr(III) ions. The adsorption kinetics of cations has been studied in terms of pseudofirst-order and pseudosecond-order kinetics. The Freundlich and Sips isotherm models have also been applied to the equilibrium adsorption data. The takovite−aluminosilicate nanocomposite material has excellent textural properties and can be used as an efficient adsorbent of Cr(III) and Pb(II) cations.

Introduction

In trace amounts, metallic elements are essential for cellular growth and maintenance of metabolic functions. In excessive amounts, however, they often exert an inhibitory influence on all living forms.[1] A natural disequilibrium can be observed when these elements are present above a certain level.[2] This is particularly important in aquatic environments, where toxic metals are known to cause several health problems to animals and human beings.[3]

The contamination of water by heavy metals is currently a matter of great concern. Heavy metals, especially Pb(II), Cr(VI), Hg(II), Cd(II), and Ni(II), can be found in the effluent of industries such as metal plating, mining plants, and tanneries, and they have become prominent pollutants. Their removal has considerable ecological and economic interest, and the selection of a removal method is based on the concentration of the metal ions, efficiency/cost ratio, and adsorption capacity of the adsorbent.[4] Some strategies have been proposed for the removal of heavy metals from these effluents or from soils, such as chemical precipitation, conventional coagulation, reverse osmosis, ion exchange, and adsorption on activated carbon. The most common methods are ion exchange and chemical precipitation,[5] but they generate secondary pollutants, have poor removal efficiency, and have low effectiveness for low metal concentration.[6] Thus, new methodologies have been developed, such as biosorption,[7,8] electrokinetics,[9] ultrafiltration,[10] membrane,[11] magnetic,[12] or the combination of several methods, such as osmosis/ultrafiltration/exchange.[13]

Metal sorption on substrate materials is considered to be the most suitable and economical method of removal, recovery, and recycling, both whether metals are present at low or high concentrations in the solution.[14] Various conventional and nonconventional adsorbents have been applied to remove metal ions from aqueous solutions. Natural adsorbents such as smectite clays and zeolites are some of the materials that have been most commonly employed for this goal, with great advantages. Clay minerals, important constituents of soils, are a group of microcrystalline secondary minerals consisting of hydrous aluminum silicates with sheetlike structures. They are highly valued for their adsorptive properties, which derive from their high surface area, hydrophilic character, and low cost.[2,15] Numerous approaches have been attempted for improving the adsorption properties of these materials with respect to heavy

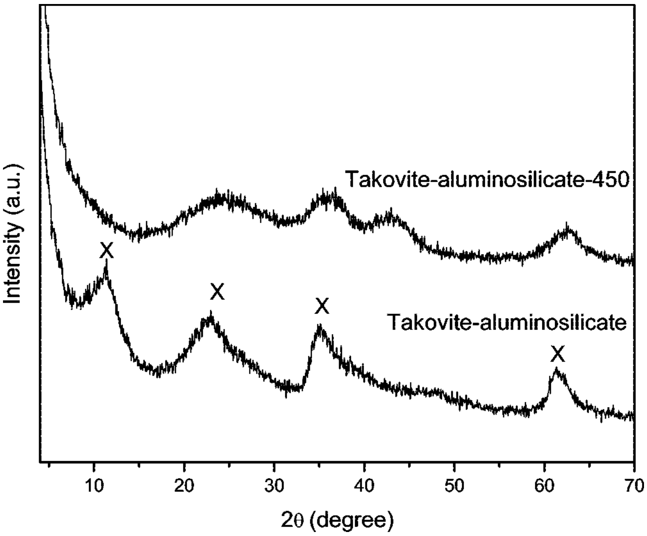

Figure 1. X-ray diffractograms of the adsorbents, takovite−aluminosilicate nanocomposite, and this same solid calcined at 450 °C. X = takovite peaks.

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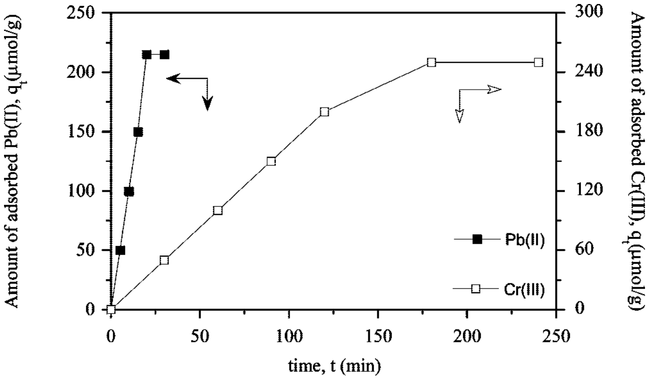

Figure 2. Kinetics of Cr(III) and Pb(II) adsorption on takovite−aluminosilicate. $T = 25$ °C; $C_0(\mathrm{Pb}) = 8\ \mu\mathrm{mol}\cdot\mathrm{mL}^{-1}$; $C_0(\mathrm{Cr}) = 6\ \mu\mathrm{mol}\cdot\mathrm{mL}^{-1}$.

Table 1. Adsorption Kinetics Parameters of Cr(III) and Pb(II) Adsorption on Takovite−Aluminosilicate Nanocomposite

	Cr(III)	Pb(II)
Pseudofirst-order		
k_1 ($\mathrm{L}\cdot\mathrm{min}^{-1}$)	0.016	0.086
R (regression factor)	0.995	0.89
χ^2 (average quadratic deviation)	122	1340
Pseudosecond-order		
k_2 ($\mathrm{g}\cdot\mu\mathrm{mol}^{-1}\cdot\mathrm{min}^{-1}$)	0.00010	0.00061
R (regression factor)	0.95	0.83
χ^2 (average quadratic deviation)	1106	2076

metals. The use of synthetic clays, both cationic clays and anionic clays, the last usually called layered double hydroxides, LDHs, or hydrotalcite-like compounds, may also become a potentially useful alternative to the sorption of these metals because the textural properties of these materials can be improved by tailoring some synthetic parameters.

In this work, we have studied the adsorptive capacity of a takovite−aluminosilicate nanocomposite material for Cr(III) and Pb(II) cations in aqueous solutions. The adsorbent was synthesized by a coprecipitation procedure, by reaction of $NiCl_2\cdot 6H_2O$, $AlCl_3$, Na_2CO_3, $Si(C_2H_5O)_4$, and concentrated ammonia in dichloromethane. We chose to study the removal of Pb(II) because it is largely present as a contaminant all over the world, while Cr(III) was chosen because it is largely present in the Brazilian State of São Paulo, particularly in the city of Franca, where there are numerous tanneries. Special attention was paid to the adsorption kinetics of the metallic cations on the takovite−aluminosilicate.

Experimental

Preparation of the Adsorbents. The synthesis and characterization of the adsorbents have been recently reported in a previous work,[16] but to make this paper understandable as a whole, a short summary is given here to facilitate the discussion of the adsorption results.

The takovite−aluminosilicate nanocomposite was synthesized by a coprecipitation method, by adding concentrated ammonia to a mixture of $NiCl_2\cdot 6H_2O$, $AlCl_3$, Na_2CO_3, and $Si(C_2H_5O)_4$ in dichloromethane. When pH 11 was reached, the mixture was maintained under reflux conditions at 60 °C for 20 h. The resulting solid was washed with several solvents, dried at 70 °C for 48 h, and calcined at various temperatures for 4 h. After preliminary tests, the dried solid and the one calcined at 450 °C were used for adsorption experiments, so we may refer to them as takovite or calcined takovite−aluminosilicate nanocomposites, respectively. Both solids were obtained in the form of very fine powders, and they were used as-synthesized.

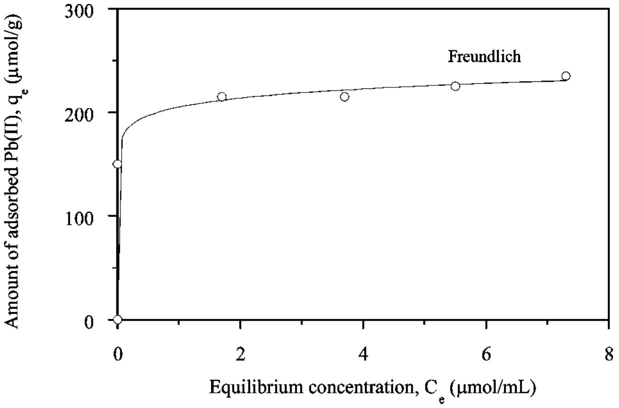

Figure 3. Equilibrium data of Pb(II) adsorption on takovite−aluminosilicate. $T = 25$ °C; time = 30 min.

Table 2. Freundlich and Sips Equation Parameters for Cr(III) and Pb(II) Adsorption on the Takovite−Aluminosilicate Nanocomposite

	Cr(III)	Pb(II)
Freundlich		
k_F ($\mu\mathrm{mol}\cdot\mathrm{g}^{-1}$)	454	205
m_F	0.45	17
R (regression factor)	0.97	1
Sips		
q_S ($\mu\mathrm{mol}\cdot\mathrm{g}^{-1}$)	419	228
k_S ($\mathrm{mL}\cdot\mu\mathrm{mol}^{-1}$)	10	8
m_S	5.7	1.2
R (regression factor)	0.993	1

Characterization Techniques. Chemical analyses for Si, Al, Ni, and Na were carried out using atomic absorption in a Mark-II ELL-240 instrument in Servicio General de Análisis Químico Aplicado (University of Salamanca, Spain).

X-ray diffraction (XRD) patterns of the solids were obtained over nonoriented powder samples, between 2° and 70° of 2θ with a scanning velocity of $2°\cdot\mathrm{min}^{-1}$, by using a Siemens D-500 diffractometer, at 40 kV and 30 mA, and employing Cu Kα filtered radiation.

Textural analyses were carried out from the corresponding nitrogen (Air Liquide, 99.999 %) adsorption at −196 °C, obtained from a static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyzer). The samples, 0.2 g, were degassed at 200 °C for 24 h ($p < 0.133$ Pa). Specific surface area was obtained from the BET method; the external surface area was determined by means of the t method; and the total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.95.

Transmission electron microscopy (TEM) was accomplished on a 200 kV Philips CM 200 microscope. A drop of powder suspension was deposited on a copper grid, and the selected area diffraction (SAD) was recorded. Energy dispersive X-ray (EDX) analysis was accomplished on a Princeton Gamma Tech apparatus, model Prism, attached to the microscope.

Adsorption Procedure. The batch technique was selected in these studies because of its simplicity. A number of glass vials sealed with Teflon-coated silicone stoppers containing 5 mL of metal cation aqueous solutions were used. In the case of Cr(III), a $6\ \mu\mathrm{mol}\cdot\mathrm{mL}^{-1}$ solution, that is, $6\ \mathrm{mmol}\cdot\mathrm{L}^{-1}$ or 6 mM, obtained from $CrCl_3\cdot 6H_2O$ (Aldrich, 96.0 %) was employed, while in the case of Pb(II), a $8\ \mu\mathrm{mol}\cdot\mathrm{mL}^{-1}$ solution, obtained from $Pb(NO_3)_2$ (Sigma-Aldrich, 99.0 %), was used. In the case of Cr(III), the pH of the original solution was 3.2 but increased to 5.2 after contact with the adsorbent. As for Pb(II), the pH values were 4.5 and 4.8 before and after the adsorption process,

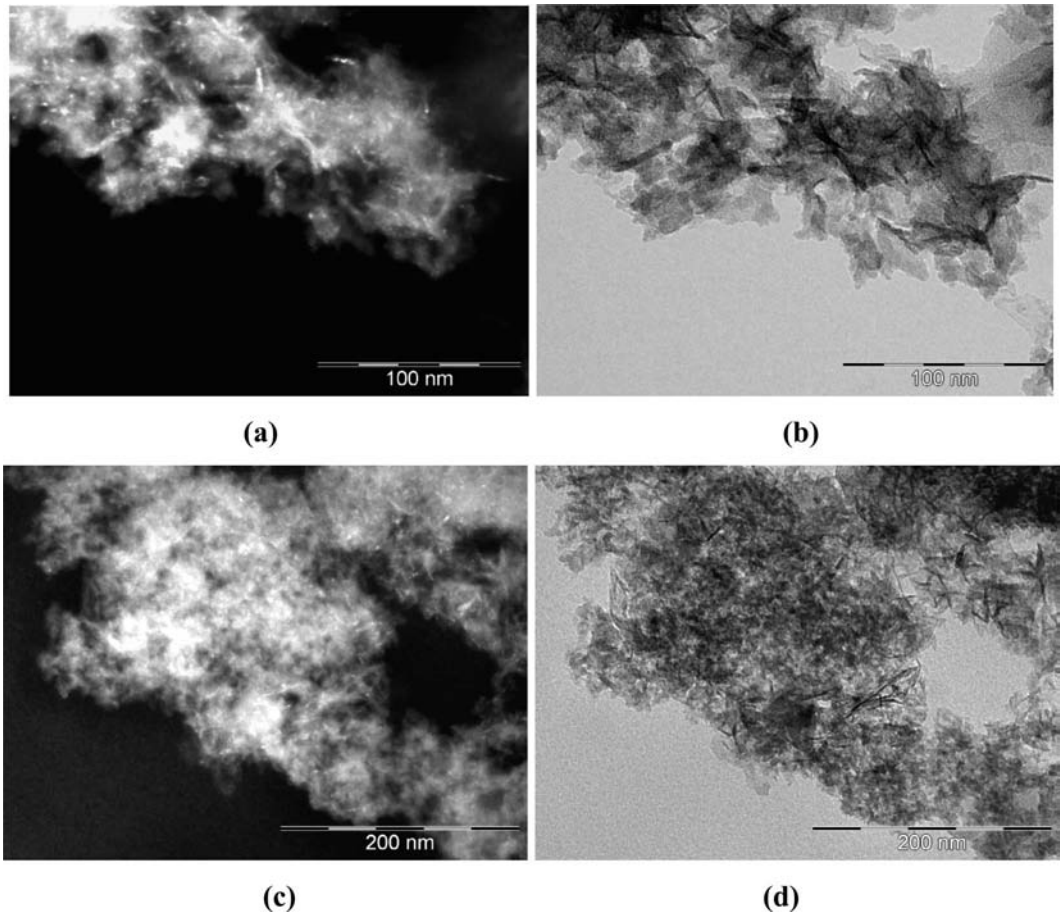

Figure 4. TEM micrographs of the takovite−aluminosilicate adsorbent before (a and b) and after (c and d) adsorption of Cr(III). Micrographs were obtained by the dark-field (a and c) and bright-field (b and d) techniques.

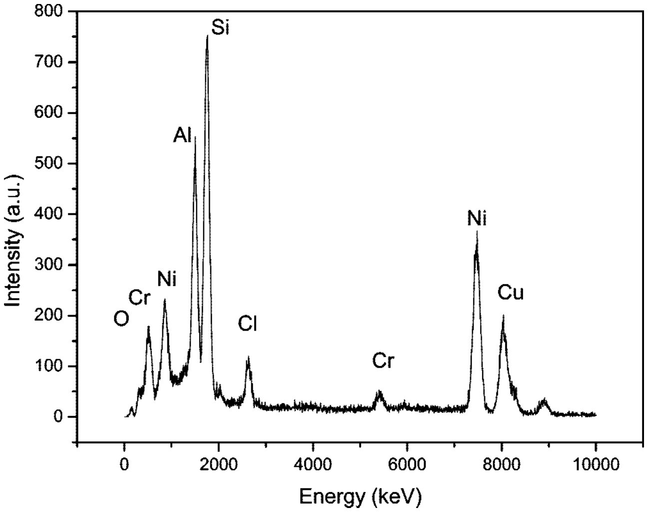

Figure 5. EDX spectrum of the takovite−aluminosilicate adsorbent after Cr(III) adsorption, corresponding to a selected region from Figure 4. The Cu signal is due to the grid used for sample preparation.

respectively. Typically, 0.1 g of the adsorbent was poured into each vial, and the solutions were kept under constant magnetic stirring. After previous tests, the solutions were separated from the adsorbent by centrifugation and analyzed for determination of the adsorbate uptake at predicted time intervals: (0, 15, 30, 60, 90, 180, and 240) min in the case of Cr(III) and (0, 5, 10, 15, 20, and 30) min in the case of Pb(II). Metal cation concentrations were determined by UV spectroscopy at the following optimal wavelengths: 453 nm for Cr(III) and 300 nm for Pb(II). A Hewlett-Packard 8453, Diode Array UV−vis spectrophotometer was used for these analyses. The amount of metal cation adsorbed on takovite was calculated as the change in the aqueous-phase concentration from the initial value, according to the following equation

$$q_t = V \cdot (C_0 - C_t)/m \tag{1}$$

where C_0 is the initial concentration (μmol·mL^{-1}); C_t is the concentration (μmol·mL^{-1}) at a certain contact time t (min); V is the solution volume (mL); and m is the amount of takovite (g).

The effect of the initial concentration of Pb(II) and Cr(III) on the adsorption process was also studied by varying the initial concentration of the metal cations but maintaining the amount of adsorbent set at 0.1 g. In the case of Pb(II), the initial cation concentrations were (3, 6, 8, 10, and 12) μmol·mL^{-1}, while for Cr(III), they were (2, 3, 6, and 8) μmol·mL^{-1}. After 30 min of reaction in the case of Pb(II) and 180 min in the case of Cr(III), the solutions were centrifuged, and the concentration of the metal cation in the aqueous solutions was determined. The amount of metal cation adsorbed on takovite was calculated as the change in the aqueous-phase concentration from the initial value, according to the following equation

$$q_e = V \cdot (C_0 - C_{\mathrm{eq}})/m \tag{2}$$

where C_0 is the initial concentration (μmol·mL^{-1}); C_{eq} is the equilibrium concentration (μmol·mL^{-1}); V is the solution volume (mL); and m is the amount of takovite (g). The equilibrium results were fitted to the Freundlich ($q_e = k_{\mathrm{F}} \cdot C_{\mathrm{eq}}^{1/n}$) and Sips ($q_e = q_{\mathrm{S}} \cdot k_{\mathrm{S}} \cdot C_{\mathrm{eq}}^{ms}/(1 + (k_{\mathrm{S}} \cdot C_{\mathrm{eq}}^{ms}))$) equations,

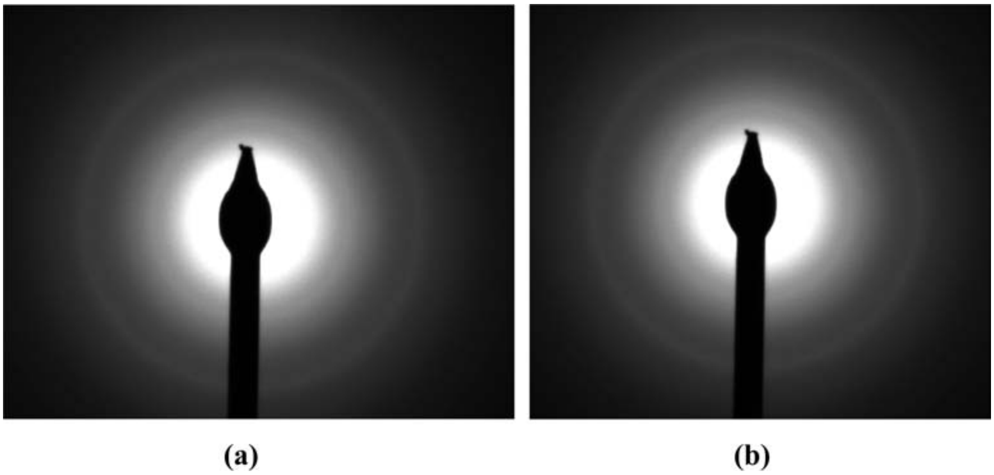

Figure 6. Electron diffraction pattern of the takovite−aluminosilicate adsorbent before (a) and after (b) Cr(III) adsorption, corresponding to selected regions from Figure 4.

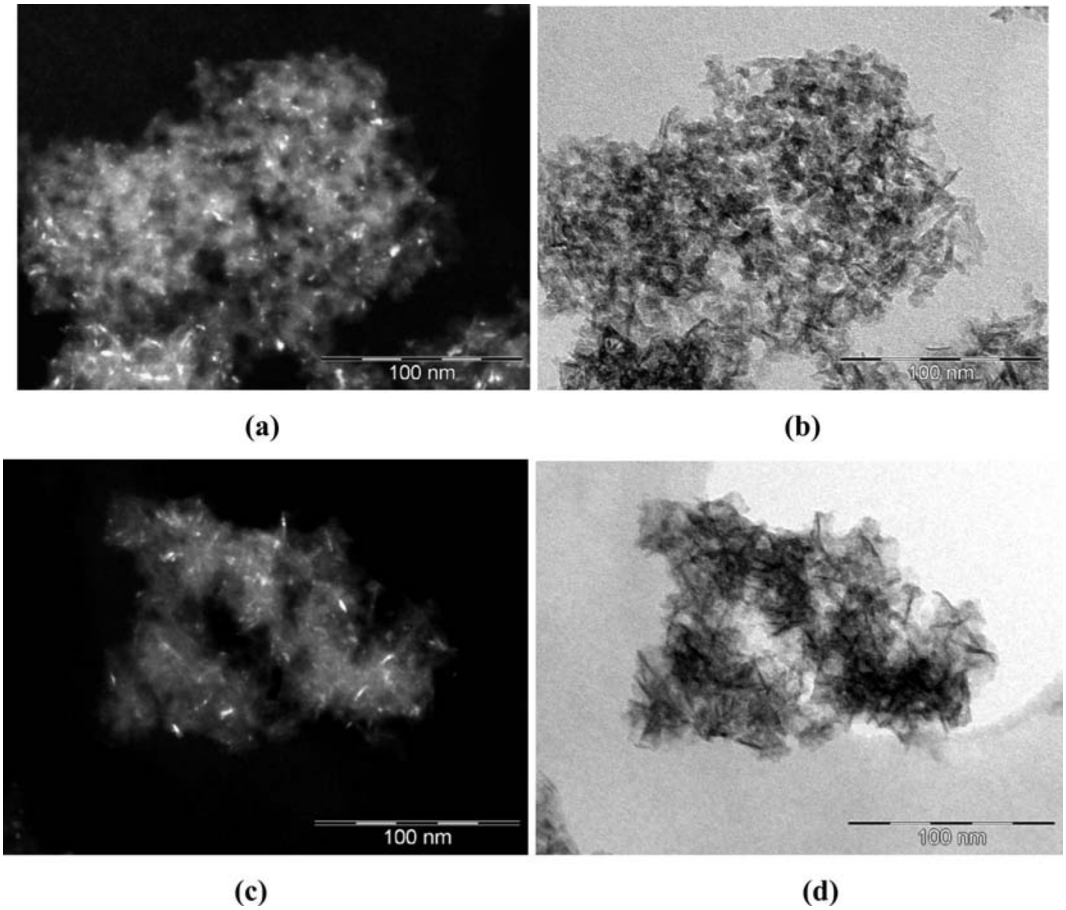

Figure 7. TEM micrographs of the calcined takovite−aluminosilicate adsorbent before (a and b) and after (c and d) Pb(II) adsorption. Micrographs were obtained by the dark-field (a and c) and bright-field (b and d) techniques.

where k_F and q_S are constants related to the adsorption capacity; k_S is the Sips equilibrium constant; and n and m_S are empirical parameters representative of the magnitude of the adsorption force.[17]

Results and Discussion

Characterization of the Adsorbents. As indicated before, a dried solid and several solids calcined at various temperatures were synthesized. However, preliminary adsorption tests showed that the dried solid has an excellent adsorption capacity for Cr(III), and the solid calcined at 450 °C has an excellent adsorption capacity for Pb(II). So, the dried solid was selected for studying the adsorption of Cr(III), while the solid calcined at 450 °C was employed in the studies with Pb(II). The adsorption capacity of the solids calcined at other temperatures was low, and they were not considered for further experiments. As indicated before, we may refer to these solids as dried and calcined takovite−aluminosilicate nanocomposite solids, respectively.

The dried solid is composed of Ni−Al hydrotalcite, takovite, and an amorphous phase (see Figure 1). Takovite displays a basal spacing of 7.76 Å and low crystallinity, and carbonate and chloride are the interlayer anions. Chemical analyses reveal

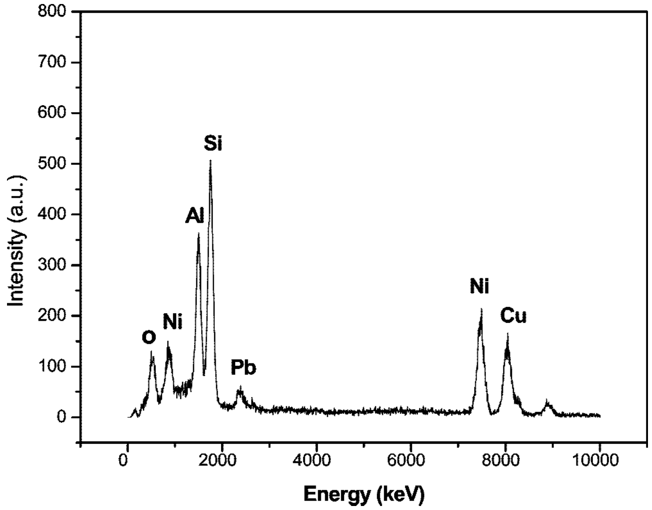

Figure 8. EDX spectrum of the calcined takovite−aluminosilicate adsorbent after Pb(II) adsorption, corresponding to a selected region from Figure 7. The Cu signal is due to the grid used for sample preparation.

a Ni/Al atomic ratio very close to 1:1, while this same ratio is 3:1 in takovite. Therefore, there is an excess of Al, which may be taking part in the amorphous phase together with Si. The total absence of Na in the final solid is also remarkable.

The surface area of the solid is rather high, 302 $m^2 \cdot g^{-1}$, higher than the values usually found for hydrotalcite compounds. This value can be justified by the low crystallinity of the hydrotalcite phase and mainly by the contribution of the amorphous phase. It is noteworthy that almost all the surface, 297 $m^2 \cdot g^{-1}$, corresponds to the external surface. The total pore volume is also rather high, 0.608 $cm^3 \cdot g^{-1}$.

The solid calcined at 450 °C shows the effects due to the maintenance of the hydrotalcite structure, although the first band disappears, and the others are less intense than in the case of the dried solid, showing the collapse of the layers. The formation of crystalline species, NiO and $NiAl_2O_4$, observed at higher temperatures, does not take place at this temperature. The surface area of the solid is also rather high, 256 $m^2 \cdot g^{-1}$, showing that there is a slight decrease in this parameter during calcination. The total pore volume is 0.786 $cm^3 \cdot g^{-1}$, thus a certain development of the porosity occurs during calcination, probably related to the removal of carbonate exchange anions.

Adsorption Results. Studies on adsorption kinetics are necessary for the evaluation of the effectiveness of an adsorbent. The evolution of the amount of adsorbed metal cations, q_t, as a function of the adsorption time is presented in Figure 2. The equilibrium capacity under the conditions used in the kinetic experiments was evaluated as 250 $\mu mol \cdot g^{-1}$, in the case of Cr(III), and 215 $\mu mol \cdot g^{-1}$, in the case of Pb(II). Saturation values were only reached for the most concentrated metal solutions. The adsorption kinetics for both cations is clearly different. Adsorption increases with time for both cations, but while in the case of Pb(II) the equilibrium is reached after 20 min of contact, 180 min is necessary for the equilibrium to be reached in the case of Cr(III).

Various models are available for evaluating the controlling mechanism of the adsorption process and the experimental data. The rate constant of Cr(III) and Pb(II) removal from the solution by takovite−aluminosilicates was determined by using pseudofirst-order and pseudosecond-order equations. The Lagergren[18] pseudofirst-order equation was employed for fitting of the experimental results.

$$\frac{dq}{dt} = k_1 \cdot (q_e - q) \tag{3}$$

Integrating eq 3 for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$ gives

$$q_t = q_e \cdot [1 - \exp(-k_1 \cdot t)] \tag{4}$$

where k_1 ($L \cdot min^{-1}$) is the first-order rate constant; q_t ($\mu mol \cdot g^{-1}$) is the amount of metallic cation adsorbed at time t (min); and q_e ($\mu mol \cdot g^{-1}$) is the equilibrium sorption capacity. The adsorption kinetic parameters are included in Table 1. The adsorption data were also analyzed in terms of a pseudosecond-order mechanism.[18]

$$\frac{dq}{dt} = k_2 \cdot (q_e - q)^2 \tag{5}$$

Integrating eq 5 for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$ gives

$$q_t = \frac{k_2 \cdot q_e^2 \cdot t}{1 + k_2 \cdot q_e \cdot t} \tag{6}$$

where q_e ($\mu mol \cdot g^{-1}$) is the equilibrium adsorption capacity and k_2 ($g \cdot \mu mol^{-1} \cdot min^{-1}$) is the rate constant of the pseudosecond-order adsorption.

The adsorption kinetics parameters are listed in Table 1. From these results and the equilibrium sorption capacity and compared with the experimental results, the first-order model is more reasonable than the second-order one.

Variation of adsorption capacity for Pb(II) as a function of the initial concentration of the solutions is shown in Figure 3. A maximum adsorption capacity of 235 $\mu mol \cdot g^{-1}$ was found, and the curve shows a trend to reach this plateau when the initial concentration was higher than 6 $\mu mol \cdot mL^{-1}$.

The adsorption equilibrium data were mathematically modeled by means of the Freundlich and Sips isotherm models. The parameters of the isotherm model equation can give information on the influence of the adsorption sites and the competition between various ions for adsorption on available sites. The equation parameters for the Cr(III) and Pb(II) adsorptions are summarized in Table 2.

The adsorption capacity of takovite−aluminosilicate nanocomposites may be classified as intermediate compared with other adsorbents reported in the literature. Low adsorption capacities have been reported when natural clay minerals are used as adsorbents.[2,4,15,19] Using an aniline−silica hybrid material prepared by a sol−gel procedure as adsorbent, Pavan et al.[20] found an adsorption capacity of 600 $\mu mol \cdot g^{-1}$ for Cr(III) and reported that the equilibrium was reached after 30 min. Combining the intermediate adsorption capacity of takovite−aluminosilicate nanocomposite with the short time needed for the equilibrium to be reached, this nanocomposite may be considered an efficient adsorbent, mainly for chromium removal.

The adsorption behaviors of Cr(III) and Pb(II) are rather different. In general, the adsorption of a cation can be influenced by a large number of factors, such as the cation/adsorbent ratio, the pH of the solution, the ionic strength of the solution, or the presence of soluble ligands that could complex with the free metal.[21] We did not control the pH of the solutions, and a value between 4.8 and 5.2 was measured after the adsorption processes. This value results from the interaction between the solid suspension and the cations. Thus, an aqueous suspension of takovite−aluminosilicate has a pH of 7.4, while the suspension of calcined takovite−aluminosilicate has a pH of 4.8. Pb(II) has a smaller hydrated radius, higher electronegativity, and lower

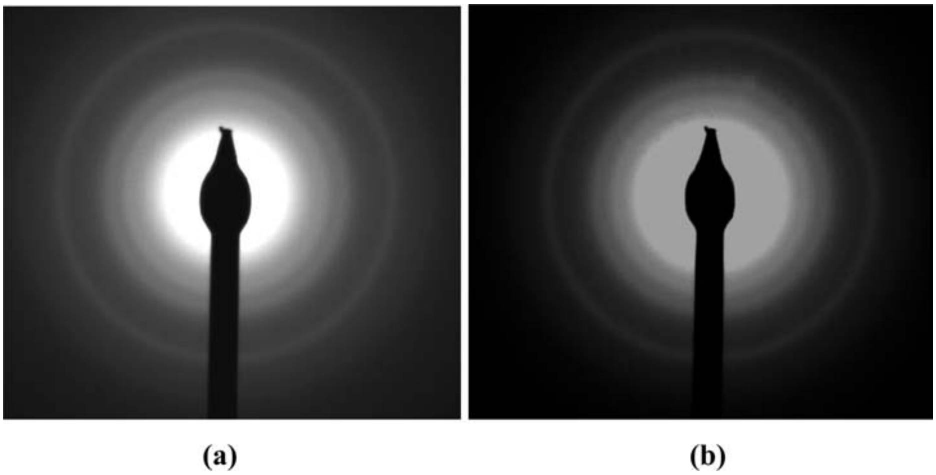

Figure 9. Electron diffraction pattern of the calcined takovite−aluminosilicate adsorbent before (a) and after (b) adsorption of Pb(II), corresponding to selected regions from Figure 7.

charge density than Cr(III), and therefore the electrostatic attraction between the surface charge and the cations is more favorable for Pb(II).[15] This interaction may also be related to the Al−O−Si framework in the adsorbents. In this sense, it is remarkable that the as-synthesized takovite−aluminosilicate has great affinity for Cr(III) and low affinity for Pb(II), whereas just the opposite behavior is found for the solid calcined at 450 °C. Thus, the observed adsorption accords with the acid−base properties of the solid: the slightly basic takovite−aluminosilicate has high affinity for a hard acid cation such as Cr(III), while the calcined solid, with a much lower concentration of hydroxyl surface groups, has high affinity for a soft acidic cation such as Pb(II). Therefore, calcination allows for the tailoring of the adsorptive properties of the solid, facilitating modification of the solid's affinity for cations.

Desorption experiments were also carried out, and Cr(III) can be more easily removed than Pb(II). It was possible to remove 90 % of the adsorbed Cr(III) by using a nitric acid aqueous solution, 0.2 $\text{mmol} \cdot \text{mL}^{-1}$. However, various nitric acid, hydrochloric acid, and ethylenediaminetetraacetic acid aqueous solutions did not remove Pb(II). This could confirm that Pb(II) interacts more strongly with the adsorbent compared with Cr(III).

The changes that occurred in the solids during cation adsorption were studied by TEM. In Figure 4, the takovite−aluminosilicate solid is shown before and after Cr(III) adsorption. The as-synthesized solid (Figure 4a and b) is amorphous and has a layered structure. Small crystalline particles can also be observed in the material agglomerates, giving evidence of the onset of crystallization. After Cr(III) adsorption (Figure 4c and d), small bright points, not observed before the adsorption, become clearly visible, which suggests that they are related to the adsorption of the cation on the surface of the takovite solid. Chromium adsorption was confirmed by EDX of this solid (Figure 5). The changes in the solid due to the adsorption process were also confirmed by electron diffraction (Figure 6a and b). Before adsorption, two rings can be seen at (2.52 and 1.57) Å, which also suggest the beginning of crystallization. After adsorption, however, no new rings are observed, which confirms the absence of morphological changes in the material and evidences cation adsorption on the surface of the solid.

The calcined takovite−aluminosilicate used for adsorption of Pb(II) has a more crystalline character than the dried material, as shown by TEM (Figure 7a and b). This contrasts with the XRD results, which do not show the formation of crystalline phases. This indicates that the formation of NiO and $NiAl_2O_4$ crystallites may be just beginning under calcination at this temperature, which is observed by TEM but not detected by XRD. Again, after metal adsorption, small points are observed over the agglomerate of the material (Figure 7c and d), showing that Pb(II) is adsorbed over the surface of the solid. Pb adsorption is also confirmed by EDX (Figure 8). Indeed, electron diffraction of the adsorbent (Figure 9) reveals the presence of four rings, at (5.31, 2.46, 2.15, and 1.53) Å, which confirms crystallization of the takovite−aluminosilicate under calcination at 450 °C. Adsorption of Pb(II) does not yield new rings, confirming its adsorption on the surface of the solid.

Conclusions

Takovite−aluminosilicate nanocomposite materials are efficient adsorbents of Cr(III) and Pb(II) cations from aqueous solutions, reaching adsorption capacities of 250 $\mu\text{mol} \cdot \text{g}^{-1}$ in the case of Cr(III) and 215 $\mu\text{mol} \cdot \text{g}^{-1}$ in the case of Pb(II). It is interesting that the as-synthesized takovite−aluminosilicate has high affinity for Cr(III) and low affinity for Pb(II), while just the opposite behavior is found for the solid calcined at 450 °C. This is tentatively explained on the basis of the nature of the solids and the acid−base interaction with the cations. Thus, modification of the adsorbent by means of calcination modifies its affinity for different cations.

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