Clays and Clay Minerals, Vol. 56, No. 1, 2–9, 2008.

NITRATE REMOVAL BY CALCINED HYDROTALCITE-TYPE COMPOUNDS

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Abstract—The sorption of nitrate ions on calcined hydrotalcite-type compounds at 550ºC (HT550), 650ºC (HT650), and 850ºC (HT850) from pure water solution at 25ºC has been studied. The influence of the temperature was also investigated for the sample calcined at 850ºC by studying the sorption process at 10 and 40ºC. The experimental sorption data points were fitted to the Langmuir equation in order to calculate the sorption capacities (X_m) of the samples; X_m values range from 61.7 g kg^{-1} (HT550 at 25ºC) to 147.0 g kg^{-1} (HT850 at 40ºC). The values for the removal efficiency (R) obtained ranged from 70.5% for HT550 at 25ºC to 99.5% for HT850 at 40ºC. The sorption experiments showed that the greater the calcination temperature (850ºC), the more effective the removal of nitrate. The increase in the temperature from 10 to 40ºC for sample HT850 also tends to increase the sorption of nitrate from 63.3 g kg^{-1} to 147 g kg^{-1} and the corresponding removal efficiency from 71.5 to 99.5%.

Key Words—Layered Double Hydroxides, Nitrate Fertilizers, Removal, Water Pollution.

INTRODUCTION

Nitrogenous compounds, including ammonia, nitrite, and nitrate, are frequently found in drinking water and various types of agricultural wastewater (Peavey *et al.*, 1985; Lin and Wu, 1996). Nitrate is a contaminant in drinking water (which is primarily from groundwater and wells) due to its harmful biological effects (Laigla *et al.*, 1990). High nitrate concentrations can cause methemoglobinemia and have been cited as a risk factor in developing gastric and intestinal cancer (Golden and Weinstein, 1998; Feleke and Sakakibara, 2002). Due to these health risks, a great deal of emphasis has been placed on finding a single method to reduce nitrate concentrations to safe levels in contaminated waters.

Reverse osmosis, ion exchange, and electrodialysis are considered the best available technologies to treat nitrate-contaminated water (Canter, 1997; Haugen *et al*., 2002). These traditional technologies do not solve the problem of excess nitrate in the environment, however, because they, in turn, produce nitrate concentrated in waste streams which pose a disposal problem due to the high saline content (Soares, 2000; Till *et al*., 1998). The best available technologies, as listed above, are relatively expensive (Haugen *et al*., 2002) and *in situ* application for decontamination of groundwater is complex (Hunter, 2001). Alternative nitrate-removal approaches that are applicable *in situ* are: chemical reduction, biological denitrification, and physical adsorption.

Adsorption is, in general, the process of collecting soluble substances in solution on a liquid/solid interface. Treatment processes, such as adsorption on solid substrates can have an immediate effect on reducing levels in drinking water. These processes do not remove all nitrate, but can help to decrease solution concentrations below the suggested level of 50 mg L^{-1} (Lin and Wu, 1996).

Materials which can be used for nitrate adsorption include ion-exchange resins, ester-type phosphonic acid, bamboo powder charcoal, *etc*. (Rocca *et al.*, 2007). All these materials (natural and synthetic) have large external surface areas in common. However, not all types of adsorbent can be used for *in situ* applications, particularly due to their high cost. Plastic materials and ion-exchange resins are inappropriate because they would cause impurities in the groundwater and in the soil. Other adsorbents must be investigated for the removal of the pollutant (Noll *et al.*, 1991; Ureña-Amate *et al*., 2003; González-Pradas *et al.*, 2005; Kameda *et al*., 2005).

Hydrotalcite-type compounds (HT), also known as layered double hydroxides (LDHs) or anionic clays, can be described as a CdI_2-type layered hydroxide (*e.g.* $Mg(OH)_2$, brucite-like) where a partial $Mg^{2+}/A1^{3+}$ substitution has taken place, with balancing of the electric charge being achieved by location of anions in the interlayer space (carbonate in most of the samples found in nature), where they co-exist with water molecules (Cavani *et al*., 1991; Rives and Ulibarri, 1999; Ulibarri and Hermosín, 2001). These types of compounds are not common in nature, unlike the well known smectites and other clays that have a net negative layer charge, but are easily and inexpensively prepared. What makes these materials interesting is the fact that by choosing the correct cation mixture, one can obtain HTs with different surface-chemical properties and therefore different affinities for different anions, depending on the physical chemistry of the anions.

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DOI: 10.1346/CCMN.2008.0560101

On the other hand, calcined Mg-Al-CO_3-HT have been demonstrated to reconstruct their original layered structure after adsorption of various anions and are good ion exchangers/adsorbents for removal of toxic anions from contaminated water (Liang *et al.*, 2006). In light of this so-called 'memory effect', the removal of nitrate from aqueous solutions by calcined LDHs was studied in this work.

We studied the removal of nitrate anions from pure water at 25ºC on a series of adsorbents obtained from the calcination process (550ºC, 650ºC, and 850ºC) of a Mg-Al-CO_3 layered double hydroxide referred to as hydrotalcite. In addition, this study addresses the effect of temperature on post-calcination nitrate adsorption. Thus, the adsorption process at 10ºC, 25ºC, and 40ºC has also been investigated in order to obtain a better understanding of this variable on nitrate removal by using the sample calcined at 850ºC, *i.e*. that presenting the greatest adsorption capacity. The adsorption phenomena have been supported by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and thermogravimetric-mass spectrometry (TG-MS) results.

MATERIALS AND METHODS

Preparation of the adsorbents

Hydrotalcite was prepared by the co-precipitation method suggested by Reichle (1986), but with some modifications. A solution containing 1 mol of $MgCl_2.6H_2O$ and 0.5 mol of $AlCl_3.6H_2O$ in 700 mL of distilled water was added to a vigorously stirred solution (1000 mL) containing 3.5 mol of NaOH and 0.95 mol of anhydrous Na_2CO_3. The precipitate was washed with distilled water and then centrifuged. This operation was repeated until Cl^- was no longer detectable with $AgNO_3$. The washed precipitate was dried at 80ºC for 24 h (HT) and stored in a desiccator for subsequent calcination in air at 550ºC, 650ºC, and 850ºC for 12 h in order to obtain the corresponding mixed oxides (referred to here as HT550, HT650, and HT850, respectively). One portion of the calcined samples was added to 50 mL of distilled water, shaken at 25ºC for 24 h and desiccated at 110ºC until constant weight, in order to obtain and characterize the corresponding rehydrated samples, referred to here as HT550-RH, HT650-RH, and HT850-RH.

Characterization of the adsorbents

The material obtained was analyzed chemically by inductively coupled plasma-mass spectrometry (ICP-MS) using a Hewlett-Packard ICP-MS 4500 Series instrument (Technical Services, University of Almería). Specific surface area was determined from N_2-adsorption isotherms at 77.4 K, in a volumetric adsorption system (Micromeritics Gemini II-2375). The nitrogen used was 99.998% pure. The sample was degassed previously at 110ºC for 24 h.

Thermogravimetry (TGA and DTG) curves were obtained using a Mettler TA 3000 thermogravimetric analysis unit and Mettler TG 50 thermobalance. The FTIR spectrum of the sample was recorded using KBr pellets on an ATI Mattson spectrometer (ATI Instruments, Madison, Wisconsin) over a range of 4000−400 cm^{-1}. The XRD pattern was obtained on a Philips PW 1050/70 diffractometer (Philips, Eindhoven, The Netherlands) using graphite-monochromated CuKα radiation.

The reagents and salts used in the experiments were reagent-grade Panreac products (Barcelona, Spain).

Sorption experiments

Pure KNO_3 (99.9%) was obtained from Panreac (Barcelona, Spain) and used as the adsorbate in this study. Sorption isotherms were determined by batch equilibration of 0.1 g of the prepared solids with 50 mL of pure water solution of KNO_3 of varied initial concentration (12.7−236 mg L^{-1}). Experiments were carried out in a thermostatic shaker bath at 25ºC. Furthermore, in order to study the influence of the sorption temperature, the experiments were performed at 10ºC and 40ºC for the sample calcined at 850ºC (that with the greater sorption capacity, as will be seen below). Preliminary experiments were conducted for various time intervals to determine when sorption equilibrium was reached. The sorption equilibrium time required for KNO_3 was 24 h.

After equilibration, the suspensions were centrifuged, the supernatant solution filtered, and the nitrate concentration (C_e) measured in the supernatant solution by ion chromatography using a Vertex Technics S.L. DX 120 device (Barcelona, Spain). Separation was performed on an AS9-HC 4 × 250 mm Dionex IonPac column. The mobile phase was a 0.5 M solution of Na_2CO_3 and a Dionex ASRS ULTRA II-4mm was used as a suppressor column. The amount of nitrate adsorbed (X) was calculated from the difference in concentration between initial (C_i) and final (C_e) solutions. Blanks containing no KNO_3 and two replicates of each sorption point were used for each series of experiments.

RESULTS AND DISCUSSION

Characterization of the adsorbents

The Mg^{2+} and Al^{3+} contents of the synthesized (HT), calcined, and rehydrated samples are indicated in Table 1. The value of the molar ratio obtained (Al/(Mg+Al) = 0.31) confirms that the calcination process has no impact on the chemical composition, as expected. This value suggests pure hydrotalcite (Roy *et al*., 2001).

Figure 1 shows the XRD patterns corresponding to the synthesized and calcined hydrotalcite samples. The spacing sequences obtained in this study are similar to those reported for these types of compounds (Cavani *et*

Table 1. Chemical analyses (wt.%) of the hydrotalcite samples.

	HT	HT550	HT650	HT850	HT550-RH	HT650-RH	HT850-RH
Mg	11.0	18.7	19.2	20.6	13.2	13.2	14.4
Al	5.48	9.34	9.41	8.4	6.61	6.35	5.67

al., 1991; Drits and Bookin, 2001; Barriga *et al*., 2002). The original hydrotalcite sample shows 003 (0.76 nm), 006 (0.38 nm), 009 (0.26 nm), 110 (0.20 nm), and 113 (0.15 nm) reflections. As can be seen from the patterns of the calcined samples, the disappearance of the 003, 006, 009, 110, and 113 reflections clearly indicates the destruction of the layered structure of the hydrotalcite with the heat treatment. The appearance of the new 200 and 220 (0.21 nm and 0.15 nm, respectively) reflections for the 550ºC and 650ºC calcined samples is related to the formation of amorphous magnesium-aluminum mixed oxides (Labajos *et al*., 1992). The new 111 (0.25 nm) reflection for the 850ºC calcined sample is related to the formation of crystalline spinel-like oxides [$MgAl_2O_4$] (Labajos *et al*., 1992). The XRD patterns corresponding to the rehydrated samples indicated the general recovery of the original structure of the hydrotalcite.

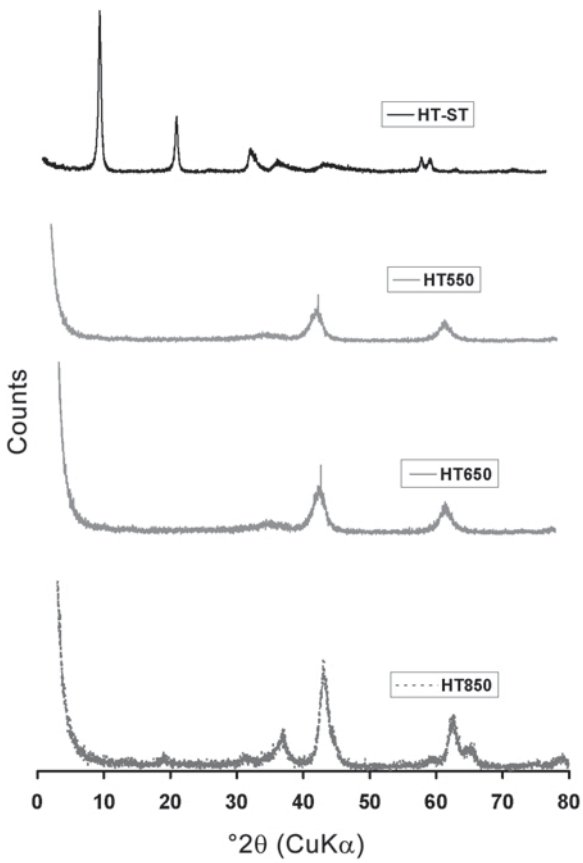

Figure 1. XRD patterns obtained for the synthesized and calcined hydrotalcite samples.

The thermogravimetric curves (TG and DTG) obtained for the original hydrotalcite sample (HT) are shown in Figure 2a, these curves being similar to those described in the literature for analogous samples (Cavani *et al*., 1991; Miyata, 1980; Ferreira *et al*., 2004). Thus, a continuous weight loss can be seen between 200ºC and 800ºC, the differential thermogravimetric (DTG) curves showing two endothermic effects. The first of these appears in two steps as a consequence of the gradual loss of (1) the physically adsorbed water molecules (centered at ~171ºC), and (2) the interlayer water molecules (centered at ~226ºC). The second effect also takes place in two steps as a consequence of (1) the removal of the hydroxyl groups linked to the Al^{3+} of the type brucite sheet (centered at ~350ºC), and (2) the breakdown of the $Mg(OH)_2$ octahedra and the removal of interlayer CO_3^{2-} (centered at ~444ºC). The continuous analysis of the bands corresponding to H_2O and CO_2 in the FTIR obtained on-line from the combined TGA-FTIR instrument confirmed these gaseous losses. The thermogravimetric curves corresponding to the calcined hydrotalcite samples (Figure 2b) are less defined than those obtained for the original hydrotalcite, with, in all cases, a gradual weight loss from 25ºC to ~700ºC taking place. The curves obtained for the rehydrated samples were similar to those corresponding to the original hydrotalcite. This indicates the general recovery of the initial layered structure due to the 'memory effect' of these compounds. Table 2 shows the total weight loss, the weight loss up to 255ºC, and the weight loss from 255ºC to 700ºC. The total weight loss decreases, as expected, with the heat treatment applied to the hydrotalcite sample, *i.e.* from HT (44.3%) to HT850 (6.99%). For the rehydrated samples HT550-RH and HT650-RH, the total weight losses are similar to that obtained for the original sample (HT), confirming the complete recovery of the original layered structure. The small difference obtained for

Table 2. Wt.% loss of the hydrotalcite samples.

Sample	Weight loss 35−255ºC	Weight loss 255−700ºC	Total weight loss
HT	16.6	27.7	44.3
HT550	–	–	12.1
HT650	–	–	10.7
HT850	–	–	6.99
HT550-RH	14.2	29.6	43.8
HT650-RH	13.8	28.3	42.0
HT850-RH	10.9	23.6	34.6

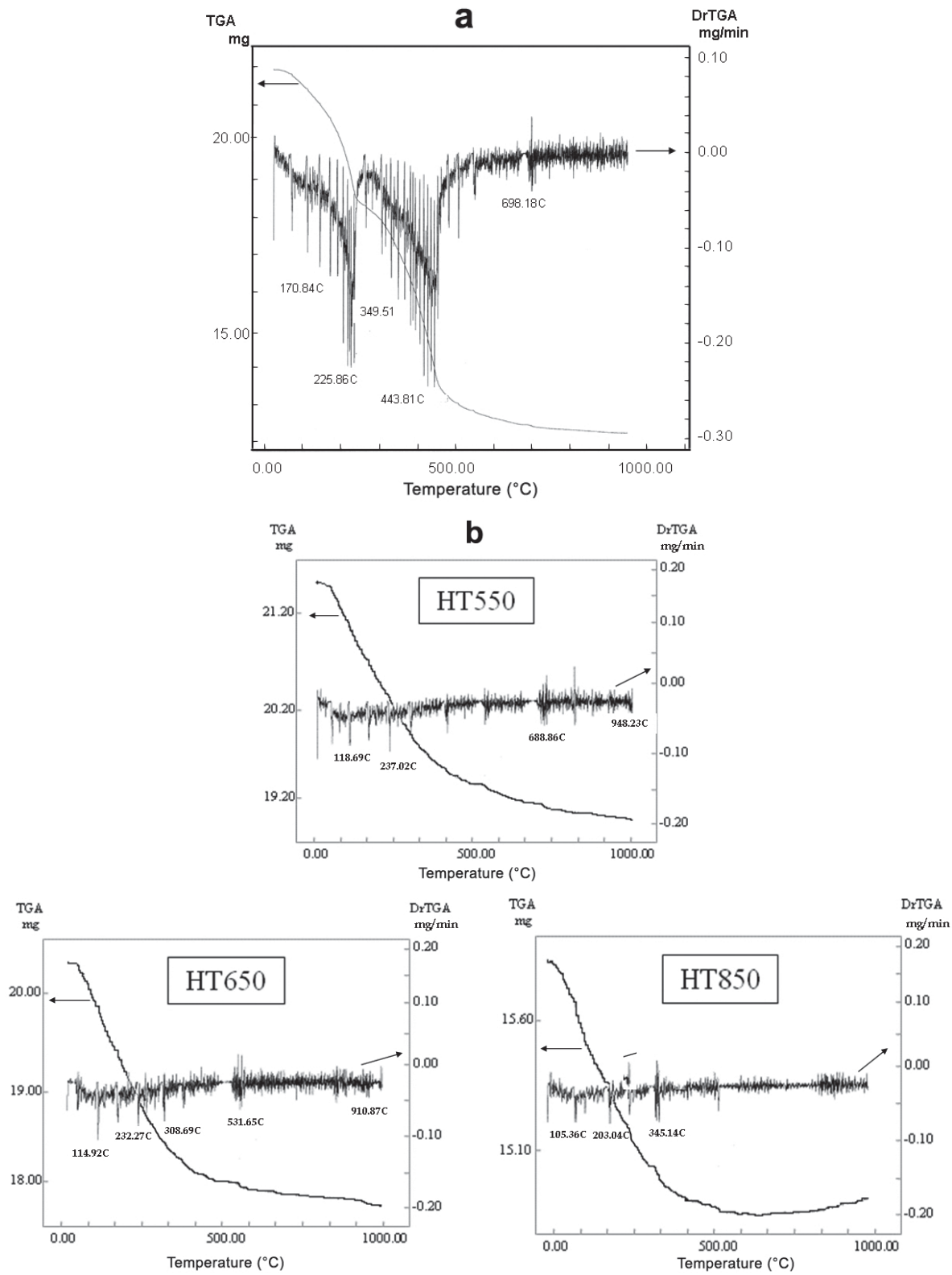

Figure 2. TG and DTG curves obtained for the (a) synthesized and (b) calcined hydrotalcite samples.

HT850-RH also indicates that the 850ºC heat-treated sample fails to completely recover its initial structure. The formation of spinel-like crystalline oxides is irreversible and thus removes some LDH from further reaction.

Figure 3 shows the experimental N_2 adsorption-desorption isotherms at 77.4 K on the synthesized and calcined hydrotalcite samples. As can be seen from the shape of the isotherms, they can be classified as type IV of the Brunauer, Deming, Deming, and Teller classification (BDDT) (Sing *et al*., 1985), which are characteristic of mesoporous solids. Also noted is an hysteresis cycle similar to H-3 type which is usual in aggregates of lamellar particles with poor cohesion and with open pores in fissure form (Parida and Das, 2000). The surface area (*S*) of the samples available to the N_2 molecules was calculated by applying the Brunauer, Emmett, and Teller equation (BET) to the experimental data points obtained in the N_2-adsorption process. The values of the specific surface area obtained appear in Table 3. In all cases, the correlation coefficients were >0.999. As can be seen from Table 3, the heat treatment at 550ºC and 650ºC produces an increase in the surface area values (from 63.5 $m^2\ g^{-1}$ to 80.9 $m^2\ g^{-1}$ and 189 $m^2\ g^{-1}$, respectively) which may be due to: (1) the elimination of CO_2 molecules as a consequence of the presence of the interlayer carbonate anion; and (2) the elimination of the interlayer and structural H_2O molecules. The removal of carbon dioxide and water molecules, which together results in the formation of amorphous Mg-Al mixed oxides, produces an increase in the surface area of the hydrotalcite which is accessible to the N_2 molecules (Rives, 2002). On the other hand, the heat treatment at 850ºC produces a decrease in the surface area in relation to the sample heated at 650ºC (from 189 $m^2\ g^{-1}$ to 134 $m^2\ g^{-1}$). This decrease could be explained by taking into account the formation of spinel-like crystalline oxides which takes place at temperatures of >800ºC (Labajos *et al*., 1992). In relation to the rehydrated samples, those heat treated at 550ºC and 650ºC seem to recover their initial layered structure, as can be seen from the similar *S* values obtained relative to the natural sample (63.0 $m^2\ g^{-1}$ and 64.6 $m^2\ g^{-1}$, respectively). The 850ºC heat-treated sample, which has a smaller *S* value (24.6 $m^2\ g^{-1}$), apparently only partially recovers its initial structure, probably due to the irreversible formation of spinel-like crystalline oxides.

Table 3. Specific surface area of the hydrotalcite samples.

Sample	S_{BET}* ($m^2\ g^{-1}$)
HT	63.5
HT550	80.9
HT650	189.0
HT850	134.0
HT550-RH	63.0
HT650-RH	64.6
HT850-RH	24.6

* Correlation coefficients (r) were 0.999 in all cases and significant at 0.001 probability level

The FTIR spectra of the original and calcined hydrotalcite samples are shown in Figure 4, where the characteristic bands of this type of compound are observed, as noted in the literature (Kustrowski *et al*.,

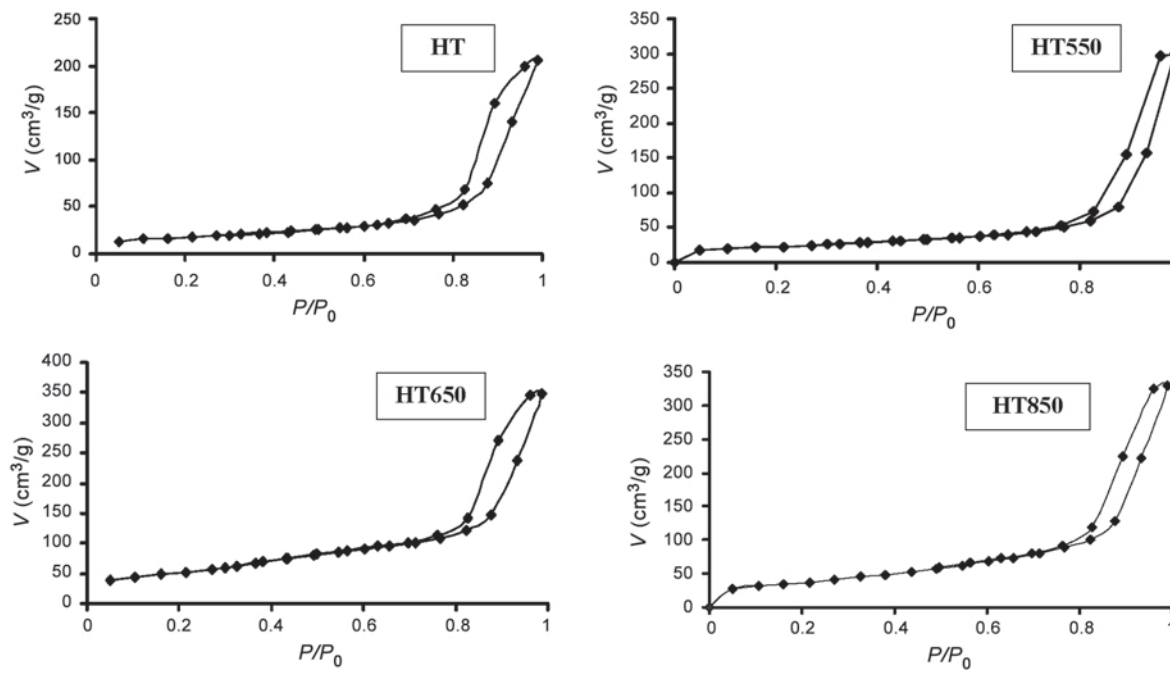

Figure 3. N_2 adsorption and desorption isotherms obtained for the synthesized and calcined hydrotalcite samples.

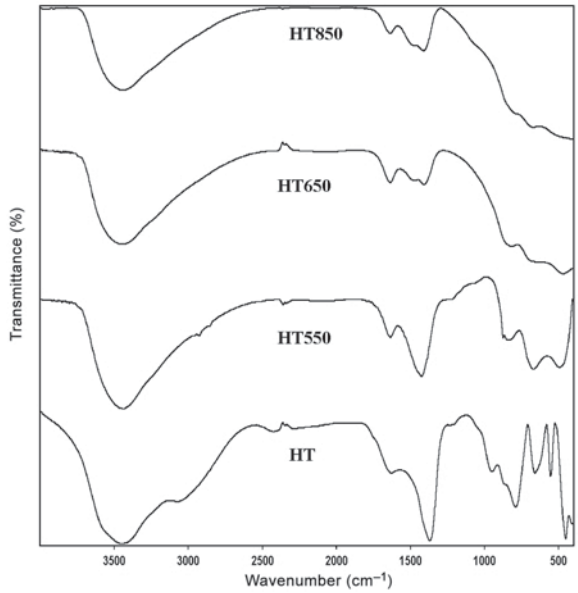

Figure 4. FTIR spectra of the synthesized and calcined hydrotalcite samples.

2005). Thus, the following characteristic bands can be seen for the HT sample, centered at: (1) 3439 cm^{-1}, corresponding to the $\nu_{O\text{-}H}$ mode of free and hydrogen-bonded hydroxyl groups and water molecules; (2) 1631 cm^{-1}, corresponding to the bending mode of the interlayer and adsorbed water molecules; (3) 1369 cm^{-1}, corresponding to the vibration mode of the carbonate ion; (4) 451, 554, 787, and 944 cm^{-1}, which can be assigned to the tension mode of the Al–O bond; and (5) 664 cm^{-1}, corresponding to the vibration of the Mg–O bond. The small shoulder appearing at 3071 cm^{-1} could be interpreted as being a consequence of the interaction between the OH groups and the interlayer carbonate ions (Rives, 2001). Figure 4 also shows that the calcined samples do not, in general, display well defined bands, and this is more evident as the heat treatment increases from 550ºC to 850ºC (Klimova *et al.*, 1998; Voll and Beran, 2002). The heat treatments at 550ºC, 650ºC, and 850ºC lead to the progressive disappearance of the bands centered at 3071 cm^{-1} and 1369 cm^{-1}. These results can be interpreted to mean the gradual elimination of the carbonate ions. The FTIR spectra of the rehydrated hydrotalcite samples showed that these rehydrated samples, in general, recover their original structure.

Sorption experiments

Figure 5 shows the sorption isotherms of nitrate ions on the calcined hydrotalcite samples at 25ºC. In addition, Figure 6 shows the corresponding sorption isotherms on the sample calcined at 850ºC at temperatures of 10ºC, 25ºC, and 40ºC. According to the slope of the initial portion of the curves, these isotherms may be classified as changing from L-type (HT550) to H-type (HT850) using the Giles classification (Giles *et al.*, 1960). This suggests that the 550ºC-treated sample has a medium affinity for nitrate ions whereas the 850ºC-treated sample has high affinity, while the 650ºC-treated sample has an intermediate affinity. For a given equilibrium concentration, the amount of nitrate ions adsorbed, therefore, increases as the heat treatment increases from 550ºC to 850ºC.

In relation to the effect of the experimental sorption temperature, the amount of nitrate ions adsorbed (X) (Figure 6) is greater – for a given equilibrium concentration (C_e) – as temperature increases from 10ºC to 40ºC.

To discover the sorption capacities of the hydrotalcite samples, the experimental data points were fitted to several equations applicable to adsorption from solution processes such as Langmuir (Kipling, 1980), BET (Tiren Gu, 1982), Freundlich (Adamson, 1990), and Henry (Voice *et al.*, 1983). According to the shape of the isotherms, the best results were obtained using the Langmuir equation 1:

$$\frac{C_e}{X} = \frac{1}{b \cdot X_m} + \frac{C_e}{X_m} \quad (1)$$

where: X = nitrate adsorbed per kg of adsorbent (g kg^{-1}); C_e = equilibrium solution concentration (g L^{-1}); X_m = the

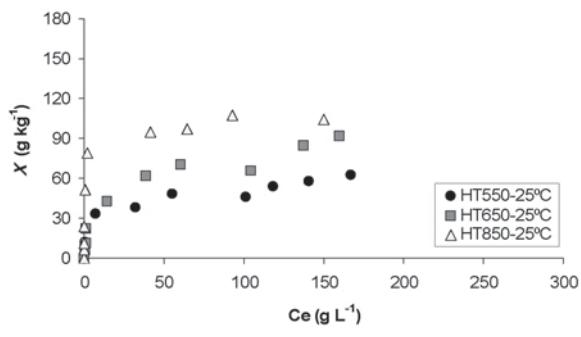

Figure 5. Sorption isotherms of nitrate ions on the calcined hydrotalcite samples at 25ºC.

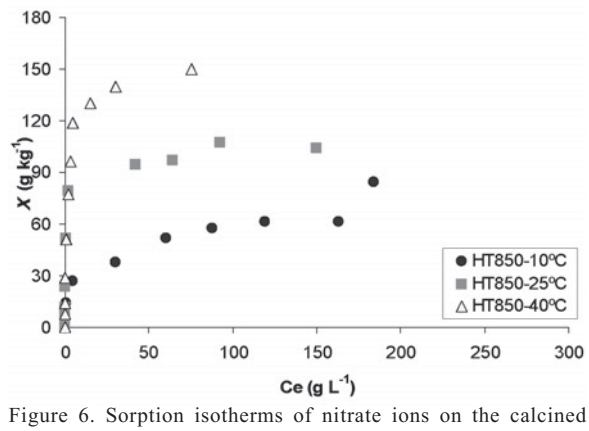

Figure 6. Sorption isotherms of nitrate ions on the calcined HT850 hydrotalcite sample at 10, 25, and 40ºC.

Table 4. Parameters of the Langmuir equation and removal efficiencies for adsorption of nitrate on the hydrotalcite samples.

Sample	HT550	HT650	HT850		
Temperature	25ºC	25ºC	10ºC	25ºC	40ºC
X_m (g kg^{-1})	61.7	82	63.3	105	147
b (L g^{-1})	0.109	0.100	0.130	0.430	0.739
r	0.988	0.985	0.994	0.999	0.999
R (% nitrate removed)	70.5	85.3	71.5	99.2	99.5

maximum amount of nitrate that can be adsorbed in a monolayer (sorption capacity) (g kg^{-1}); b = constant related to the energy of sorption (L g^{-1}); Langmuir parameters (X_m, b) are summarized, together with the correlation coefficients, in Table 4. The correlation coefficients were, in all cases, >0.99 (all correlations were significant at the 0.001 probability level). The X_m values range from 61.7 g kg^{-1} for the HT550 sample to 147.0 g kg^{-1} for the HT850 sample (Table 4). Thus, the heat treatment of the hydrotalcite (from 550ºC to 850ºC) increases its sorption capacity for the nitrate ions. In relation to temperature (HT850 sample), an increase in the amount of nitrate adsorbed of 63.3 g kg^{-1} to 147.0 g kg^{-1} occurs as temperature increases from 10 to 40ºC, this behavior showing the endothermic nature of the sorption process.

The average value of X_m is about three times greater than that obtained for the sorption of nitrate ions on acid-activated sepiolite (Öztürk and Bektas, 2004).

The removal efficiency, R, is defined as:

$$R = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \quad (2)$$

where C_0 (105.2 g L^{-1}) is the initial concentration of an aqueous solution of nitrate (0.05 L) placed in a stoppered conical flask and shaken for 24 h with 0.1 g of the samples, and C_e is the equilibrium solution concentration; R is expressed in terms of percentages, as in Table 4. The removal efficiency values (R) range from 70.5% (HT550 at 25ºC) to 99.5% (HT850 at 40ºC).

The variation of X_m and R with the heat treatment applied to the hydrotalcite seems to be related to the sorption mechanisms of the nitrate ions; *i.e.* related to the access by the nitrate anions to the recovered layered structure of the calcined hydrotalcite once rehydrated, by occupying the locations of the carbonate anions initially present in the synthesized sample (HT). It is interesting to note that for the calcined samples, and according to the characterization data discussed above, a change in the hydrotalcite structure is observed, mainly due to the loss of CO_2 and the formation of amorphous $Mg_{1-x}Al_xO_{1+x/2}$ mixed oxide. The re-hydration of this mixed oxide leads to the incorporation of nitrate in the interlayer space, so the sample recovers its original structure. As the calcination temperature increases to 850ºC, a greater loss of CO_2 occurs, thus increasing the amount of nitrate adsorbed. This is in agreement with the results obtained by Hibino *et al*. (1995) which indicated that hydrotalcites with a high charge density – like that used here – still lose CO_2 even at 850ºC.

CONCLUSIONS

These experiments indicate that the greater the calcination temperatures of hydrotalcite, the more effective is the removal of nitrate from pure water. The increase in temperature at which the sorption was carried out also tends to increase the degree of removal of nitrate in the range of experimental conditions used. The results obtained from this work are of interest because they offer a better set of experimental conditions for the use of a synthetic hydrotalcite for sorption of nitrate. In general, hydrotalcites calcined at 850ºC apparently were most effective at retention of nitrate when sorption conditions of 40ºC were used. Lower calcination (550–650ºC) and sorption temperatures still provide acceptable nitrate removal, and might prove to be more cost effective under industrial-scale applications. Since hydrotalcite materials are easily and inexpensively manufactured, they may usefully replace the more expensive activated carbon typically used.

Thus, our interest in the results obtained here lies not only in the determination of nitrate-ion sorption potential for heat-treated hydrotalcite samples but also in the potential application of this type of hydrotalcite as a test- and ultimately industrial-scale water decontaminant.

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(*Received 14 December 2006; revised 2 July 2007; Ms. 1243; A.E. Will P. Gates*)