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A comparative study between chloride and calcined carbonate hydrotalcites as adsorbents for Cr(VI)

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Abstract

Hydrotalcite-type solids with different metal ions within the layers (M^{II} = Mg or Zn and M^{III} = Al and/or Fe) and carbonate or chloride between them have been synthesized. Chloride-LDHs and the solids obtained upon carbonate-LDHs calcination have been evaluated in the adsorptive removal of Cr(VI) from aqueous solutions. All the adsorption tests were carried out at 30 °C following two different stirring conditions: a) using a thermostatic bath with mechanical stirring at a speed of 52 rpm or b) in a sonicator bath under ultrasound waves. It was observed that no significant difference in the amount of adsorbed chromate is produced in both cases but the time spent to reach the equilibrium is much lower when the adsorbent/adsorbate mixture is submitted to ultrasounds. In all experiments L-type adsorption isotherms were obtained. The results show that chloride hydrotalcites are better adsorbents than calcined CO_3-hydrotalcites and in these last ones their adsorption capacity increases with increasing the surface area: MgAlFe > MgAl > MgFe > ZnAl.

Keywords: Layered Double Hydroxides; Chromate; Adsorption; Kinetics; Wastewater

1. Introduction

Humankind daily life activities as well as industry or agriculture processes are responsible for the important increasing pollution that soils, sediments and waters have experimented in recent decades. Its treatment and elimination is generally expensive and difficult to attain in some cases.

As some other essential elements, chromium is necessary in small amounts in the human and animal diet but an excess can be extremely toxic. Chromium (VI), with a proved toxicity, is one of the elements with more industrial applications due to its acidic and oxidant properties and its ability to form insoluble colourful salts. Currently the amount of Cr (VI) in wastewaters that chemical, textile or metallurgy industries spill is larger than that allowed by the United States Environmental Protection Agency (USEPA, 2002).

One of the possible ways for pollutants elimination from water and soils involves their adsorption on an adequate solid; although nowadays active carbon is the best well known and proved most efficient adsorbent, there is currently a huge interest in the research of new solids with similar efficiency, price and easier regeneration than carbons. Different solids such as zeolites, clay minerals, metal oxides, organic polymers, etc., have been tested as insoluble adsorbents (Schulthess and Huang, 1991; Johns et al., 1993; Zhao et al., 1998; Tenorio and Espinosa, 2001; Mier et al., 2001). Among

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these the Layered Double Hydroxides (LDHs), also known as hydrotalcites (Hts) or anionic clays, have also deserved interest, due to their large ionic exchange capacities (3.3 meq/g in comparison to 1 meq/g in cationic clays). The adsorption capacity of carbonate-containing LDHs is low if compared to other adsorbents, but this capacity is increased 10 times in their calcined-derived systems. Lazaridis et al. (2004) reported that the largest adsorption capacity is achieved with samples calcined at 450 °C. In addition, there is an important advantage when using hydrotalcites instead of other adsorbents, since the first ones can be used at pH values close to that at which pollutants are usually found in the environment, while for other adsorbents the maximum adsorption capacity is achieved at extremely low pH values (Kovanda et al., 1999).

Hydrotalcites can be described by the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}\cdot mH_2O]^{x-}$ where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively. The structure consists of brucite-like layers with a positive charge owing to the replacement of Mg^{2+} by Al^{3+}, this charge being balanced by interlayer anions (A^{n-}). The synthesis conditions have been widely studied (Miyata, 1983; Reichle, 1986; Drits et al., 1987; Sato et al., 1988; De Roy et al., 2001) and the interlayer anions can be incorporated to the structure during the synthesis process as well as in a later ionic exchange step; environmental technologists have taken advantage of this property in water purification by using them as anion scavengers (Parker et al., 1995; Shin et al., 1996; Houri et al., 1998, 1999). The reconstruction method, based in the so-called “memory effect” of hydrotalcites, can also be used to remove toxic anions from water. Moreover, the calcined samples behave as good adsorbents not only because of their ability to incorporate anions in the interlayer space, but also because they usually exhibit high specific surface areas, so they can act as adsorbing oxides (Goswamee et al., 1998; Lazaridis et al., 2001; Lazaridis and Asouhidou, 2003; Lazaridis et al., 2004).

So far, most of the adsorption tests in which hydrotalcite-like solids are involved have been performed using the oxides obtained upon MgAl-carbonate calcination, although NiAl and ZnCr LDHs have also been tested (Goswamee et al., 1998). Recently, suspicion of the risk of aluminium has been attracting much attention because aluminium exposure is hypothesized as a risk factor for accelerated onset of Alzheimer disease in humans (Guidelines for Drinking Water Quality, 1998). For this reason, it is important to develop different systems with similar structure and low aluminium content which can act as adsorbents. Pyroaurite (a MgFe-carbonate LDH) has been tested as an adsorbent for Pb and humic acids, and a MgFe-chloride LDH has also been tested in the adsorption of different organic compounds (Seida and Nakano, 2000, 2001; Seida et al., 2001). The oxides formed upon calcination of a MgFeAl-carbonate LDH were tested for As(V) adsorption, and it was found that the Fe^{2+}/Mg^{2+} substitution increases their specific surface areas, while microporosity is simultaneously developed, these facts being related to their enhanced adsorption capacity (Carja et al., 2005).

In this work, hydrotalcite-like solids with $M^{II}=Mg$ or Zn and $M^{III}=Al$ and/or Fe and carbonate or chloride in the interlayers have been prepared. The effect that a partial or complete Fe to Al substitution has on some physicochemical properties of the uncalcined and calcined solids was analyzed. The LDH-chloride and the oxides obtained upon LDH-carbonate calcination have been used to study the chromate adsorption mechanism, and the effect of various factors like (i) layer composition of the LDH precursor, (ii) initial concentration, and (iii) stirring conditions (mechanical stirring or ultrasound), have been studied.

2. Experimental

2.1. Sample preparation

The MgAl, ZnAl and MgAlFe LDHs samples with carbonate as the interlayer anion were prepared following a standard coprecipitation method from the metal chlorides (Reichle, 1980; Hashi et al., 1983; Fernández et al., 1998). A solution containing the corresponding metal chlorides was dropwise added over a dissolution at pH = 10 containing Na_2CO_3 (1 M) and NaOH (2 M); pH (10) and temperature (40 °C) were kept constant under continuous stirring during the addition process. Once the addition was completed the suspension was maintained with constant stirring at 70 °C for 24 h, to be finally washed, centrifuged and dried in air.

The MgAl- and ZnAl-Cl LDHs were prepared by coprecipitation in a N_2 atmosphere (to avoid incorporation of carbonate from atmospheric carbon dioxide) from aqueous solution of $MgCl_2\cdot 6H_2O$ at pH = 9 (or $ZnCl_2\cdot 6H_2O$ at pH = 8) and $AlCl_3\cdot 6H_2O$ at pH = 9 using 2 M NaOH. The suspensions were aged for 24 h at room temperature without stirring or at 70 °C and simultaneous stirring for samples with Zn, Al and Mg, Al, respectively.

In all cases the M^{II}/M^{III} molar ratio in the starting solution was 2.

The samples are labelled using the chemical symbol of the metals present in the brucite-like layers followed by a C (carbonate) or Cl (chloride), in reference to the specific interlayer anion. In the case of samples containing Mg, Al and Fe, the amount of iron is indicated by a number after the element symbol which represents the atomic percentage of this element in the starting solution with respect to the total amount of trivalent cations.

Carbonate containing samples have been calcined at the temperature at which the layered structure is completely collapsed, 450 °C (Fe-free samples) or 500 °C. The calcined solids are labelled with the symbols of the metals they contain followed by the calcination temperature (i. e., $M^{2+}M^{3+}/T$).

2.2. Characterization techniques

Element chemical analyses for Mg, Al and Fe were carried out in Servicio General de Análisis Químico Aplicado (University of Salamanca, Spain) in a plasma emission spectrophotometer ICP-OES from Jovin Yvon Ultima-2 model, after dissolving the samples in nitric acid.

Powder X-ray diffraction patterns (PXRD) were collected on a Siemens D-500 diffractometer using CuKα radiation ($\lambda = 1.54050$ Å).

Specific surface area measurements were carried out in a Micromeritics Flowsorb II 2300 instrument after degassing the samples in situ for 2 h at 150 °C in a Micromeritics FlowPrep 060 apparatus.

The chromate amount in solution was determined by UV–V spectroscopy in a UV–V Hewlett Packard 8452 spectrophotometer, using a quartz cell of 1 cm in width.

2.3. Experimental procedure for adsorption

The adsorption tests were carried out in a 50 mL flask plunging a constant amount of sample (≈ 0.2 g) into 25 mL of a solution containing potassium chromate at different concentrations and pH = 9 (in some cases some drops of a KOH 1 M solution were added to reach this pH), keeping the mixture at a constant temperature of 30 ± 1 °C.

In order to insight in the influence that the stirring conditions have on the adsorption process, some of the experiments were performed placing the flask containing the mixture in a thermostated bath at a constant stirring speed of 52 rpm, while others were stirred in a Sonicator (from Selecta) for 5 min.

The time needed to reach the adsorbent/adsorbate equilibrium under both stirring conditions was determined beforehand; once it was reached, the mixtures were centrifuged at 400 rpm and the supernatant liquid was extracted with a syringe equipped with a 0.4 μm pore diameter Millex HV filter (Millipore, Bedford, MA, USA).

The chromate concentration in solution was determined by UV–V spectroscopy, by applying the Lambert–Beer law for the absorption at $\lambda = 372$ nm. All tests were performed twice and blank tests (hydrotalcite/water) under the same adsorption conditions were also carried out.

The amount of chromate adsorbed on the solids (Cs) was determined from the difference between the initial (Ci) and final (or equilibrium) chromate concentrations (Ce) per gram of solid adsorbent: $Cs = (Ci - Ce) \cdot V/m$. The adsorption isotherms were obtained by plotting Cs *vs.* Ce.

3. Results and discussion

The adsorption properties of the solids studied are in close relation to their morphology, composition and physicochemical properties; moreover, the coprecipitation method yield solids with different morphologies owing to the wide range of preparation variables (temperature, reagent concentration, pH, ageing time, etc.). Consequently, the solids prepared have been characterized by different techniques prior to be tested in the chromate adsorption experiments.

3.1. Samples characterization

Element Chemical Analysis results show that the M^{II}/M^{III} molar ratios in the solids are similar to that in the starting solutions, except for the ZnAlC and ZnAlCl

Table 1
Formulae and characteristics of the prepared samples

Sample	Formula or crystallographic phase (PXRD)	S_{BET} ($m^2\ g^{-1}$)	AEC (meq g^{-1})
MgAlC	$[Mg_{0.63}Al_{0.36}(OH)_2](CO_3)_{0.18}\ .0.66H_2O$	72	4.4
ZnAlC	$[Zn_{0.63}Al_{0.37}(OH)_2](CO_3)_{0.19}\ .0.60H_2O$	32	3.6
MgFeC	$[Mg_{0.67}Fe_{0.33}(OH)_2](CO_3)_{0.165}\ .0.98H_2O$	84	3.4
MgAlFe50C	$[Mg_{0.65}Fe_{0.16}Al_{0.16}(OH)_2](CO_3)_{0.162}\ .0.81H_2O$	86	3.7
MgAlFe25C	$[Mg_{0.64}Fe_{0.08}Al_{0.245}(OH)_2](CO_3)_{0.162}\ .0.85H_2O$	69	3.8
MgAlCl	$[Mg_{0.67}Al_{0.33}(OH)_2]Cl_{0.30}(CO_3)_{0.02}\ .0.66H_2O$	42	4.0
ZnAlCl	$[Zn_{0.61}Al_{0.39}(OH)_2]Cl_{0.33}(CO_3)_{0.03}\ .0.58H_2O$	13	3.1
MgAl/450	MgO (and disperse Al^{3+})	117	4.4
ZnAl/450	ZnO (and disperse Al^{3+})	51	3.6
MgFe/500	MgO (and disperse Al^{3+} and Fe^{3+})	102	3.4
MgAlFe50/500	MgO (and disperse Al^{3+} and Fe^{3+})	197	3.7
MgAlFe25/500	MgO (and disperse Al^{3+} and Fe^{3+})	144	3.8

AEC: anionic exchange capacity.

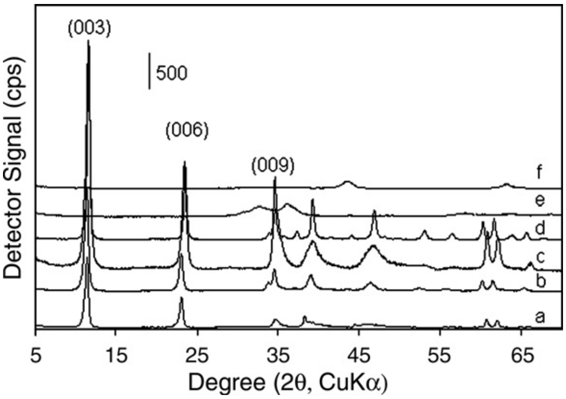

Fig. 1. XRD patterns of the samples: (a) MgAlCl, (b) ZnAlCl, (c) MgAlC, (d) ZnAlC, (e) ZnAl/450 and (f) MgAl/450.

samples, for which the Zn/Al ratios are 1.7 and 1.6, respectively; this fact is probably due to an incomplete precipitation of Zn because of the high pH used. The formulae determined for the different samples are given in Table 1; the water content was calculated from the weight loss measured by TG (not shown).

The PXRD patterns of representative samples and of the oxides obtained upon their calcination at different temperatures are shown in Figs. 1 and 2. PXRD pattern characteristics of well-crystallised hydrotalcite-type solids are obtained for the uncalcined samples in all cases. The spacings measured for the (003) diffraction are included in Table 2, together with lattice parameters *a* and *c*; these values are similar to those previously reported by other authors (Suzuki and Ono, 1988; Kooli et al., 1997; Seida et al., 2001; Rives, 2001).

Calcination of samples MgAlC and ZnAlC at 450 °C, Fig. 1, produces the complete collapse of the layered structure. Only weak, broad peaks reflections at 2.43, 2.1 y 1.49 Å are observed in the PXRD pattern of sample MgAl/450; these peaks reflections correspond to diffraction by planes (111), (200) and (220), respectively, of MgO (periclase). Also weak peak reflections characteristic of ZnO at 2.62 and 2.46 Å are recorded for the ZnAl/450 sample. The aluminium compounds should be well dispersed or forming an amorphous phase.

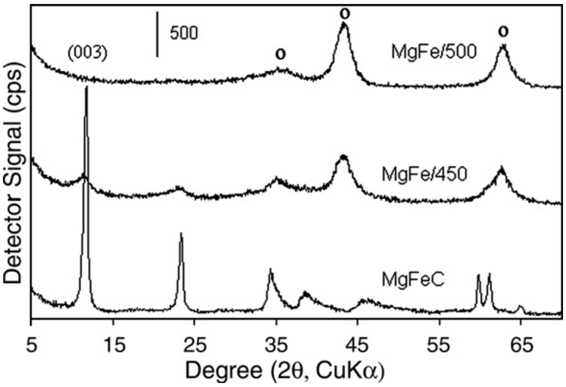

Fig. 2. XRD patterns of sample MgFeC and its calcination products; (o) MgO.

Table 2
Basal spacings (Å) and lattice parameters (Å) of the samples

Sample	d_{003}	*a*	*c*
MgAlC	7.61	3.04	22.83
MgAlCl	7.78	3.04	23.34
ZnAlC	7.58	3.07	22.74
ZnAlCl	7.74	3.07	23.22
MgFeC	7.53	3.10	23.16
MgAlFe50C	7.61	3.07	22.83
MgAlFe25C	7.59	3.06	22.72

The samples containing Fe^{3+}, with or without aluminium, show similar diffraction patterns; that corresponding to sample MgFeC is shown in Fig. 2. They are thermally more stable than non-iron containing samples, since at 450 °C their layered structure still remains and calcination at 500 °C is required to produce its total collapse, rendering MgO as the only crystalline phase. The iron and/or aluminium-containing phases are well dispersed and are not detected by PXRD.

The specific surface areas measured for the uncalcined and calcined samples are summarized in Table 1. In samples with Mg and carbonate between the brucite-like layers the specific surface values range between 69 and 86 $m^2\ g^{-1}$, being not significantly affected by iron incorporation. The specific surface area values for the Cl-LDHs are about one half of that measured for the carbonate ones. Calcination of samples with interlayer carbonate produces, in all cases, a large enhancement of their specific surface areas, because when the layered structure collapses the evolved gases (CO_2 and H_2O) escape forming craters through the brucite-like layers and developing new tiny pores in the materials (Kagunya and Jones, 1995). The increase in the specific surface areas observed upon calcination is higher in samples which contain both Fe and Al, reaching values of 144 and 197 $m^2\ g^{-1}$ for the MgAlFe25/500 and MgAlFe50/500 samples, respectively, which are twice larger than that observed for the uncalcined samples; this fact is probably due to the presence of amorphous or highly dispersed species of Fe and/or Al in these samples.

3.2. Chromate adsorption studies

3.2.1. Kinetic studies

Representative results of the kinetic studies carried out with the different samples, submitted to mechanical stirring at 52 rpm or under ultrasounds, and pH = 9, are shown in Figs. 3 and 4. To determine the equilibrium time needed for the samples submitted to ultrasounds, the mixtures (Cl-LDHs or calcined samples and the potassium chromate solution) were maintained in the sonicator bath for 5 min, and then were taken off, left for a few seconds and the amount of chromate in the supernatant liquid was measured after different periods of time.

3.2.1.1. Calcined carbonate hydrotalcites. A plot of the amount of chromate adsorbed vs. time at different initial concentration values for MgAl/450 sample is included in Fig. 3. It can be observed that the time needed to reach the equilibrium and the amount of chromate adsorbed increase when increasing the initial concentration; this behaviour is shown by all samples studied whatever their composition. In all experiments performed involving calcined hydrotalcites submitted to mechanical stirring, whatever the concentration tested (7.7×10^{-4}–1.5×10^{-2} M) the time to reach the equilibrium was shorter or close to 24 h. The shortest times were measured for samples ZnAl/450 and FeMg/500 (~ 10 h) which are also the solids with the lowest adsorption capacities.

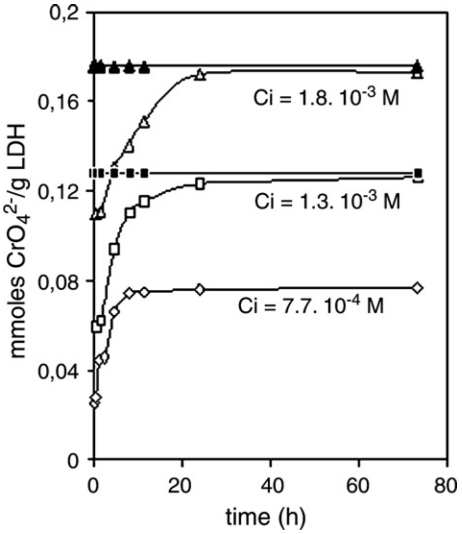

Fig. 3. Kinetics study of adsorption of chromate on sample MgAl/450, at given (Ci) initial concentrations; performed under mechanical stirring at 52 rpm (open symbols) or after being submitted to 5 min under ultrasounds (filled symbols).

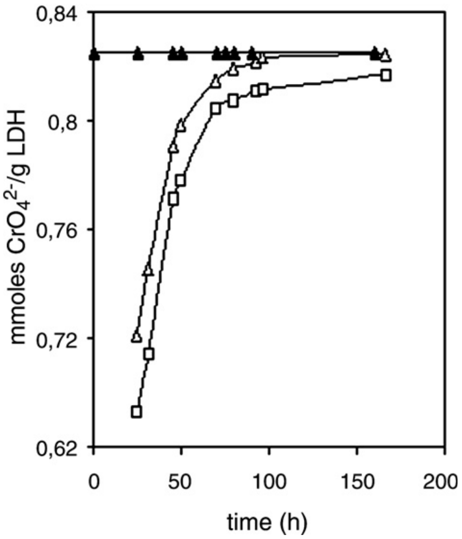

Fig. 4. Kinetics study of adsorption of chromate on samples MgAlCl (□) and ZnAlCl (△,▲); performed under mechanical stirring at 52 rpm (open symbols) or after being submitted to 5 min under ultrasounds (filled symbols).

When ultrasound is applied, Fig. 3, the amount adsorbed was constant whichever the time elapsed after removing ultrasounds. Moreover, the amounts adsorbed for different initial concentrations are similar to those recorded for the same samples mechanically stirred for 24 h. These results indicate that ultrasounds treatment is enough, even for a few minutes, to reach the adsorbate/adsorbent equilibrium, shortening drastically the time for adsorption.

3.2.1.2. Chloride hydrotalcites. The behaviour observed for the chloride-samples, Fig. 4, is quite similar to that shown on other systems above described; in both cases the amount of chromate adsorbed and the time needed to reach the equilibrium increase as the initial concentration does; for the largest Ci studied, saturation is reached very slowly after 7 days, this time is larger than that observed when using calcined hydrotalcites; probably in the uncalcined systems the adsorption mainly proceeds by an exchange process Cl$^-$/CrO$_4^{2-}$, which is slowly achieved under the mechanical stirring conditions.

After being submitted to ultrasounds, the samples behave in the same way as the calcined hydrotalcites, the amount adsorbed was constant whichever the time elapsed after removing ultrasounds. Moreover, the amounts adsorbed for different initial concentrations are similar to those recorded for the same samples mechanically stirred for 7 day, Fig. 4.

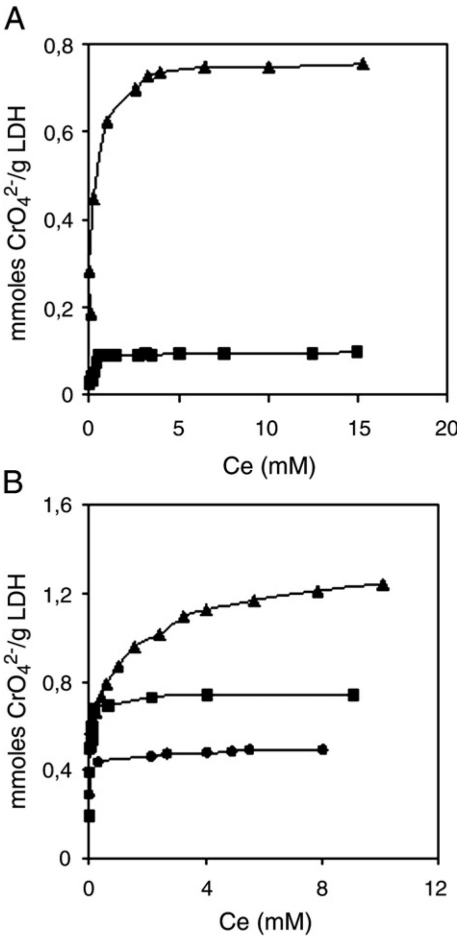

Fig. 5. Chromate adsorption isotherms on: A) MgAl/450 (▲) and ZnAl/450 (■) samples and B) different calcined Fe-containing samples, (▲) MgAlFe50/500, (■) MgAlFe25/500 and MgFe/500 (●). (Conditions: 5 min ultrasounds).

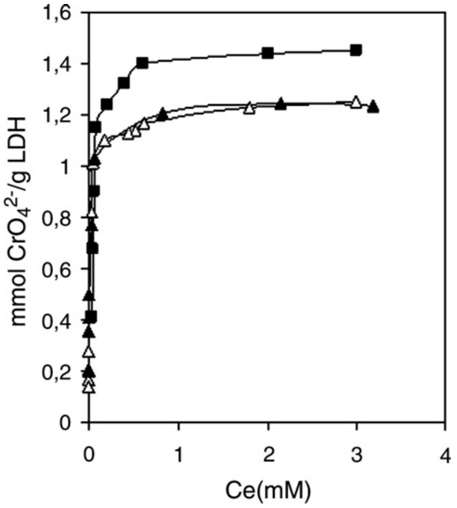

Fig. 6. Chromate adsorption isotherms for MgAlCl (■) and ZnAlCl (▲,△) samples, under ultrasound (filled symbols) or under mechanical stirring at 52 rpm (open symbols) conditions.

3.2.2. *Adsorption isotherms*

The chromate adsorption isotherms have been determined for both stirring conditions (24 h or 7 days at a stirring speed of 52 rpm or 5 min under ultrasounds), but owing to their similarities only the plots for the ultrasounds-treated samples are shown.

3.2.2.1. Calcined carbonate hydrotalcites. The adsorption isotherms for MgAl/450 and ZnAl/450 samples are included in Fig. 5A. According to their shape they correspond to L-type in the Giles classification (Giles et al., 1960). These sorts of isotherms are recorded for solids where chromate is preferentially adsorbed, but the adsorption decreases as the adsorbate concentration is increased due to the decreasing surface concentration of free adsorption sites, suggesting that adsorption takes place on specific centres of the adsorbent surface. Due to its low specific surface area, the adsorption capacity of sample ZnAl/450 is very low if compared to that for sample MgAl/450. However, the adsorption capacity for sample MgAl/450 is four times that for sample ZnAl/450, while the ratio between their specific surface areas is only 2. Consequently, the lower adsorption capacity measured should be due too to the total recovering of the layered structure of calcined MgAl hydrotalcites (Rocha et al., 1999), while the ZnAl system is only partially reconstructed (Kooli et al., 1997) due to crystallisation of ZnO, detected by PXRD in our samples.

The chromate adsorption isotherms recorded for samples MgFeC and MgAlFeC calcined at 500 °C are included in Fig. 5B; all show similar shapes, but with some differences in their adsorption capacities. They can also be considered as L-type according with the Giles classification (Giles et al., 1960) although, taken into account the vertical profile of its first part, they can also be included among the H-type; this is a special case of L-type isotherms in which adsorbate molecules have an extremely high affinity with the solid and at low Ci

Table 3
Langmuir parameters for chromate adsorption

Sample	C_m (mmol/g)	L	r^2
MgAl/450	0.78	2.7	0.9999
ZnAl/450	0.097	7.1	0.9999
MgFe/500	0.49	15.4	0.9999
MgAlFe25/500	0.74	16.8	0.9999
MgAlFe50/500	1.23	4.5	0.9999
MgAlCl	1.43	21	0.9999
ZnAlCl	1.25	41	0.9999

values it is completely removed from solution, leaving a negligible, undetectable concentration in solution. This effect is clearly observed in the samples without Al or with a low, for which the *plateau* is reached very quickly. However, for sample MgAlFe50/500 this effect is less intense, the adsorbed amount slowly increases with increasing the concentration in equilibrium, reaching the *plateau* at larger Ce values.

3.2.2.2. Chloride hydrotalcites. L-type isotherms are also recorded on adsorbing chromate on samples MgAlCl and ZnAlCl, Fig. 6; for comparison, the adsorption isotherms recorded under mechanical stirring are also plotted; both sets of isotherms are completely coincident whichever the stirring conditions used.

The isotherms data have been fitted to the Langmuir model, which provides the best results for these sorts of curves. The determination coefficient r^2 (r=Pearson correlation coefficient) and the parameters calculated for the different samples are included in Table 3. As it can be noticed, the r^2 values are in all cases larger than 0.99 supporting the validity of the model chosen. The C_m values, which represent the amount (mol) of chromate adsorbed per unit mass (gram) of adsorbent once a monolayer is completed, are similar to those experimentally obtained from the *plateau* in all the isotherms and are in agreement with those previously reported by other authors for adsorption tests on this type of solids (Clearfield et al., 1991; Hansen, 1995; Goswamee et al., 1998; You et al., 2001), but they are lower than the anionic exchange capacity (AEC) determined from the samples formulae, Table 1. The adsorbed amounts for the best adsorbents for samples MgAlCl, ZnAlCl and MgAlFe50/500 correspond to 69, 65 and 67%, respectively, of the calculated AECs. The values obtained for the calcined MgAlC and MgFeC samples are much lower, ranging between 35 and the 28% of their AECs.

It should be mentioned that the maximum AEC is not achieved whatever the system tested. This result can be related to a competitive intercalation of chromate, carbonate and hydroxyl anions, as the experiments were carried out with non-decarbonated water at rather high pH values; moreover, Cl^- anions also exist for samples MgAlCl and ZnAlCl. Consequently chromate adsorption should be rather difficult, especially in competition with carbonate, for which these solids have a high affinity.

In order to check if chromate is actually located in the interlayer space after the adsorption tests, PXRD patterns of the solids used in the experiments were recorded; they show only diffraction lines corresponding to a hydrotalcite–carbonate phase or meixnerite (the solid with intercalated hydroxyl groups), for which the basal spacing due to planes (003) is close to 7.6 Å, none of the samples showing peaks corresponding to a hydrotalcite–chromate phase, for which a value of 8.6 Å is expected.

Houri et al. (1999) have proposed that chromate adsorption takes place exclusively on the external surface of the crystallites through electrostatic interaction between the oxoanion and the positively charged brucite-like layers. However, this situation does not hold for our samples, as in such a case, the chloride-LDHs would show the lowest adsorption capacities because of their low specific surface areas. It can be tentatively assumed that a partial intercalation of chromate, via anionic exchange, actually takes place, leading to samples with different anions (chromate, carbonate, probably chloride and hydroxyl) in the interlayer (Ulibarri et al., 1995; Goswamee et al., 1998), giving rise to an heteroanionic sample; alternatively, following Bookin et al. (1993) and Schollhorn and Otto (1986), if stereochemical factors would not permit the co-existence of these anions in the *same* interlayer, different elemental layers (with an homogeneous anion interlayer composition) could be formed and stack together, resulting in a solid with mixed layers. Both models would account for the lack of a single hydrotalcite–chromate phase observed by PXRD.

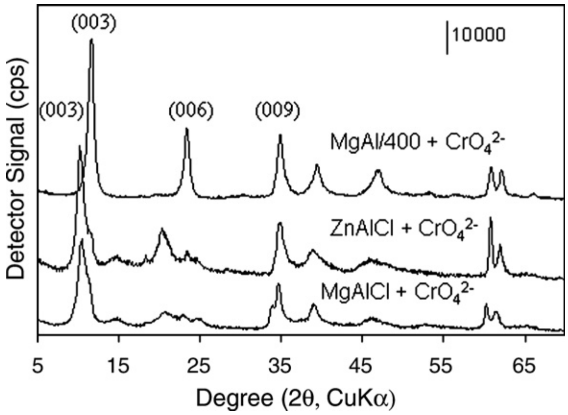

Fig. 7. XRD patterns of the solids obtained after the chromate adsorption tests using ultrasounds.

In order to avoid such a competitive adsorption, the tests were repeated under the same stirring conditions, but using carbon dioxide-free water to prepare the chromate solutions; under these conditions, the MgAlCl and ZnAlCl solids recovered after ultrasound treatment show PXRD patterns with maxima at 8.6 and 4.3 Å, Fig. 7, corresponding to the diffraction by (003) and (006) planes, respectively, of chromate-LDHs (Chibwe and

Jones, 1989; Malherbe and Besse, 2000; Del Arco et al., 2005). However, the patterns recorded for the solids recovered after adsorption under mechanical stirring did not show these chromate-LDH diffraction patterns, probably because the long time required to carry out the adsorption (7 days) leads to contamination by atmospheric CO_2 and the above mentioned competitive adsorption, resulting in solids with a basal spacing of 7.6 Å.

No intercalation of chromate is concluded from the PXRD patterns of the solids recovered after adsorption on the calcined solids, even when decarbonated water is used, whichever the stirring conditions used. Insertion of chromate in these samples is only possible via reconstruction of the layered structure and the pH of the suspensions of these solids is more basic (pH = 11.5) than that of the suspensions of the Cl-LDHs (pH = 10), so the suspensions become easily carbonated, even when using ultrasounds for a period of time as short of 5 min. So, it seems that chromate adsorption on these samples, at pH values larger than 10, mainly takes place on the surface of the crystallites through electrostatic interactions, and consequently the adsorption capacity increases as the specific surface areas of the samples. These results are in agreement with previous studies on LDH-chromate preparation (Del Arco et al., 2005) which claim that insertion of chromate is not possible at a so high pH value, the exchange being only achieved at pH values lower than 9. Other authors (Lazaridis et al., 2004) have demonstrated that the adsorption capacity of these sorts of solids is increased under low pH values conditions, as the chromate–carbonate competition for adsorption decreases.

4. Conclusions

The results here reported support the advantages of using ultrasound instead of the traditional thermostatic baths, since: (i) it decreases the time needed to reach the equilibrium to 5 min, and (ii) it permits an easy and fast synthesis of chromate–hydrotalcites at low temperatures, contrary to other methods generally applied (Chibwe and Jones, 1989; Malherbe and Besse, 2000; Del Arco et al., 2005).

L-type adsorption isotherms were obtained in all cases. The calcined MgAl sample is a better adsorbent than the ZnAl or MgFe ones. The simultaneous presence of Al^{3+} and Fe^{3+} in the layers increases the adsorption capacity in the calcined samples, due to their high specific surface areas probably due to the existence of amorphous or highly dispersed Fe and/or Al species; the largest adsorption was observed for samples with equimolecular amounts of Fe and Al, MgAlFe50/500, whose adsorption capacity is similar to that measured for chloride hydrotalcites. Summarizing, the adsorption capacity of the different samples here studied change in the following way: MgAlCl > ZnAlCl ≈ MgAlFe > MgAl > MgFe > ZnAl.

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