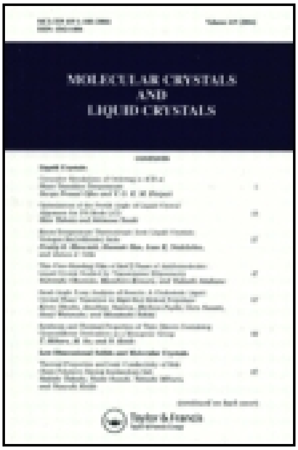

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Removal of Benzoate Anions from Aqueous Solution Using Mg-Al Layered Double Hydroxides

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REMOVAL OF BENZOATE ANIONS FROM AQUEOUS SOLUTION USING Mg-Al LAYERED DOUBLE HYDROXIDES

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The uptake of benzoate anions from aqueous solutions by calcined and uncalcined layered double hydroxides (LDHs) is reported. Adsorption (or sorption) isotherms have been determined at 25°C in the 0 to 100 mmol dm^{-3} *concentration range. The results showed that the calcined LDH sorbs 40 to 85% of the benzoate in solution in the concentration range usually found in industrial wastewater, and that the sorption capacity of this material is about 4 times greater than that observed for the parent LDH. The study of the sorption kinetics for the calcined material showed that it is a relatively slow process, which can be attributed to the fast regeneration of the calcined LDH with intercalated hydroxyl anions, followed by a slow process of anion exchange by benzoate. Collected solids after sorption present basal spacing close to 7.6 Å, characteristic of intercalated hydroxyl anions or carbonate, suggesting a horizontal arrangement of benzoate in the interlayer.*

Keywords: layered double hydroxides; hydrotalcite; benzoate; sorption; adsorption

INTRODUCTION

Layered double hydroxide (LDHs), the so-called anionic clays, are compounds with structure derived from that of brucite $Mg(OH)_2$, by the isomorphic substitution of divalent cations by trivalent ones. This exchange creates a net positive charge in the layers that must be neutralised by the

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intercalation of hydrated inorganic or organic anions [1]. These materials can be obtained in a wide range of composition by changing the nature of the metal cations and the M^{II}/M^{III} ratio, as well as the type of the intercaled anion A^{m-} in the general formula: $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]\,A^{m-}_{x/m}\cdot nH_2O$. A variety of anions may be intercaled and these materials can be applied as catalysts, adsorbents, anion exchangers and in medicines [1–3].

The layered double hydroxides can uptake anions from aqueous solution by three different mechanisms: (1) adsorption; (2) intercalation by anion exchange; and (3) intercalation by regeneration of the calcined material. The pure adsorption process can take place on the surface of LDHs containing interlayer anions that present strong electrostatic interaction with the layer, i.e., anions that cannot be exchanged by others, such as carbonate. The sorption by anion exchange process can occur when the anions intercalated in the layers of the precursor material, like chloride or nitrate, have electrostatic interactions that are weaker than those for other anions and hence substitution takes place, usually accompanied by adsorption.

The sorption of anions by the regeneration of calcined LDHs is based on the property so-called *memory effect*, characteristic of Mg-Al-LDHs [1, 3–5]. Owing to this property, a Mg-Al-LDH containing carbonate (or other anions that can be decomposed by the thermal treatment) heated to 723–823 K decomposes and yields mixed oxides, which can be regenerated into hydrotalcite-like structure when in contact with aqueous solutions.

The wide spread of organic contaminants in natural waters is a current subject that is impelling research for medicines [6]. The potential sorbent capacity of LDHs calcined products for organic anions makes these compounds attractive as possible filters for water containing anionic contaminants [7]. The oxidation process of p-xylene in the manufacture of polyester generates wastewater containing benzoic acid among others (a by-product derived from the oxidation of toluene) [8]. In this study we investigate the removal of benzoate anions (BA) from aqueous solution, by the regeneration of calcined products of LDHs containing carbonate, based on the *memory effect*.

EXPERIMENTAL

Preparation of Mg-Al-CO_3-LDH Sorbent and Calcination procedure

The preparation of Mg-Al-CO_3-LDH was carried out by the coprecipitation method described by Reichle [9]: a solution containing 1.00 mol of $Mg(NO_3)_2$ and 0.50 mol of $Al(NO_3)_3$ (Mg/Al ratio = 2) in 700 cm^3 of water was added dropwise and under vigorous stirring to a solution containing 3.50 mol of NaOH and 0.943 mol of Na_2CO_3 in 1000 cm^3 of water. The obtained slurry was aged for 18 hours at 338 K The resulting material was separated by vacuum filtration, washed with a great amount of water and vacuum dried at room temperature in the presence of silica gel.

The calcination of the materials was done in an oven in synthetic air (flow rate of 150 cm^3 min^{-1}) at 773 K for 4 hours. This temperature was determined by the TG/DTA analysis with a heating rate of 1 K min^{-1} up to 1273 K.

Determination of the Adsorption (Sorption) Isotherms

The sorption isotherms were obtained by the batch method. A constant mass of 200 mg of LDH (original or calcined) was added to aliquots of 50 cm^3 of benzoate solution ($pH_i = 7.3$) in a concentration range from zero to 75 mmol dm^{-3}. The suspensions were kept in an orbital shaking Dubnoff type bath during 72 hours at 298 ± 0.5 K After this period the solid material was separated by centrifugation. The concentration of benzoate in the supernatant was determined by UV-Vis spectrophotometry using a calibration curve ($\lambda = 223$ nm).

Kinetics of Adsorption (Sorption)

A suspension with the same mass/volume ratio described above was prepared by the addition of 800 mg of the calcined Mg-Al-CO_3-LDH to 200 cm^3 of 12 mmol dm^{-3} benzoate solution in a 300 cm^3 closed flask to avoid evaporation of water. Aliquots were taken in selected times (from 15 minutes to 72 hours). The analysis of benzoate concentration and pH at the supernatant was done as described above.

Characterisation of the Solids

A Siemens D5005 X-ray diffractometer using the Cu-Kα radiation was used to obtain the powder X-ray patterns in steps of $0.02^\circ s^{-1}$.

RESULTS AND DISCUSSION

The PXRD pattern for Mg-Al-CO_3-LDH (Fig. 1a) is typical of a well-ordered LDH, and the basal spacing of 7.60 Å is in agreement with the intercalation of carbonate [9]. The PXRD diffraction pattern obtained for the calcined Mg-Al-CO_3-LDH at 773 K (temperature which material eliminate most of the carbonate ions, determined by TG/DTA analysis) is shown in Figure 1b. The broad diffraction peaks indicated low structural order of a material with structure similar to that of MgO (JCPDS card no. 45–0946).

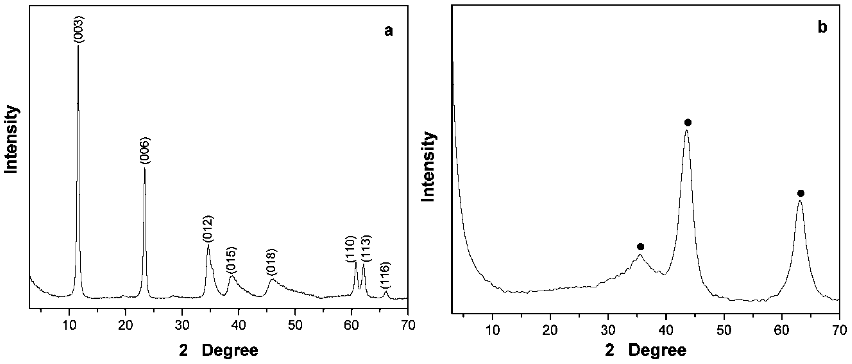

FIGURE 1 PXRD patterns for (a) Mg-Al-CO_3-LDH, (b) Mg-Al-CO_3-LDH calcined at 773 K, ($\star$) = MgO.

The adsorption isotherm (at 298 K obtained for the calcined material is shown in Figure 2a. The shape of the isotherm can be classified as L-type (sub-group 2) according to the classification of Giles *et al.* [10], indicating a system where ions adsorb on specific sites of the sorbent, mostly by electrostatic interaction reaching a saturation value given by the plateau of the adsorption isotherm. This plateau corresponds to a monolayer of sorbate on the surface, which gives the maximum value that can be used as a measure of the sorption capacity [2,7].

The maximum amount of BA adsorbed for Mg-Al-CO_3-LDH was 0,81 mmol g^{-1}. For trichlorophenol (TCP) [7] and sodium dodecylsulfate (SDS) [6], an adsorption of 0,75 and 0,60 mmol g^{-1} was respectively

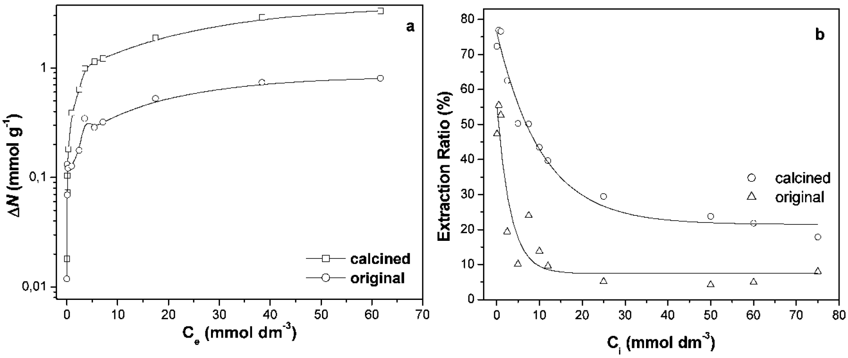

FIGURE 2 Sorption isotherm of BA anions (a); extraction ratio of BA anions from aqueous solution (b).

reported. For the uncalcined LDH, the affinity of the hydrotalcite layers for the carbonate ions exceeds that for other monovalent anions [11], due to the better fit of the layer surface/charge distribution with the interlayer conformation of the carbonic ions, and thus their displacement by monovalent anions is difficult [2,7]. For the calcined product, the maximum amount BA sorbed was 3,28 mmol g^{-1}, about 4 times the maximum amount adsorbed in the original material. In the case of calcined material the process may not be described as a pure adsorption, but as a conjugation of adsorption and intercalation. This material in presence of water can rehydrate and, with anions present in the solution, reconstitute the hydrotalcite layered structure [7]. The adsorption capacity of BA by calcined product is higher than the maximum amount adsorbed for SDS and TNP, which presents a value of 2,26 mmol $g^{-1}$and 2,89 mmol g^{-1} respectively [7,12]. On the other hand, the adsorption of dodecylbenzylsulfonate (DBS) is close to that of BA on the same material, showed a maximum of 3,45 mmol g^{-1} [7]. Therefore, it is possible to conclude that the intercalation process is much more important than the adsorption process to uptake anions from the solution.

Figure 2b shows the extraction ratio (the ratio between the sorbed quantity of BA and the total amount of BA anions in the system) for calcined and original LDHs. The calcined material is a efficient sorbent for BA anions presenting an extraction ratio between 40 and 85% in the BA concentration range of 0.4 and 12 mmol dm^{-3} usually found in wastewater [8]. The kinetic study of the sorption process is shown in Figure 3.

The sorption of BA anions is a quite slow process and the equilibrium state is reached after 10 hours of contact time. The variation of the BA concentration is accompanied by an increase of the solution pH. The PXRD patterns for solid samples after different periods of sorption (in Fig. 4) showed a basal spacing of 7.64 Å for all materials. This value is in agreement with the intercalation of hydroxyl anions [12] and no evidences for the intercalation of benzoate can be observed from those patterns [13].

The whole of these results showed that the reconstitution of the LDH with hydroxyl anions intercalated is a fast process (occurring in less than 15 minutes) and the sorption probably takes place by the anion exchange between the interlayer hydroxyl anions and BA, a statement supported by the increase in pH, but not by the PXRD results. Indeed, if BA anions are intercalated, these anions should be in a horizontal orientation in the interlayer. BA-containing LDH can also be low crystalline, and so not detectable by PXRD analysis.

An alternative explanation for the higher adsorption capacity of the calcined material is that the regeneration process conduct to a LDH that present a “clean” surface, formed *in-situ*, and so presenting more active and/or a higher number of adsorption sites. However, the high difference

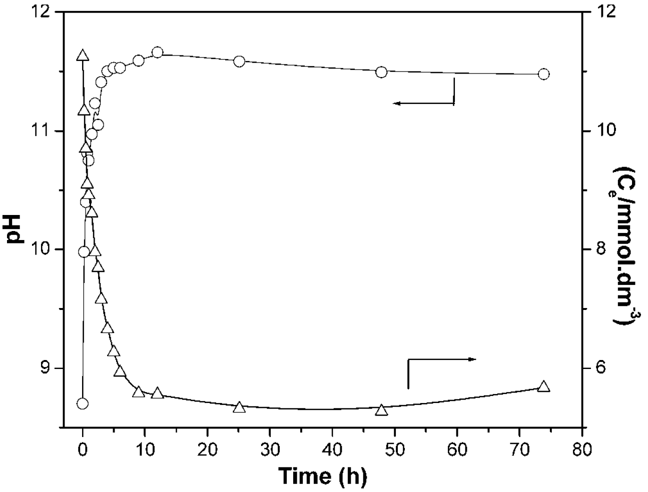

FIGURE 3 Kinetic study of sorption of BA ($C_i = 12\,\text{mmol}\,\text{dm}^{-3}$) on the calcined LDH.

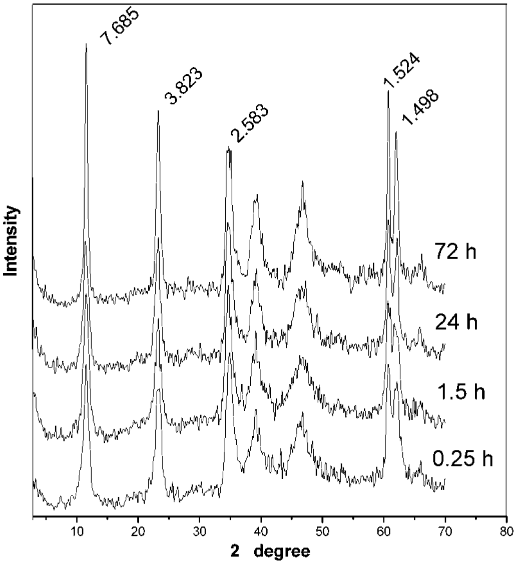

FIGURE 4 PXRD patterns for the calcined LDH after regeneration process in the kinetic study.

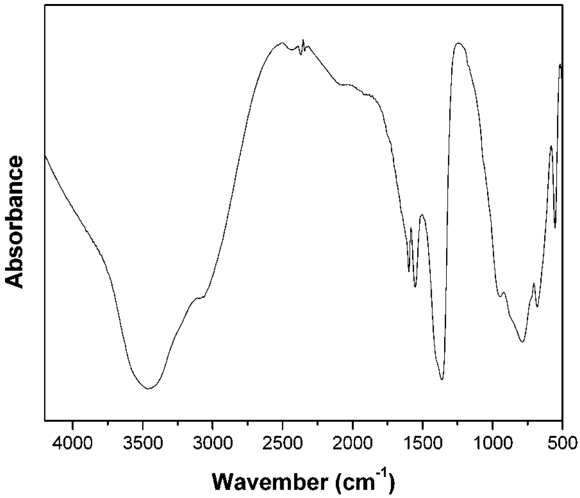

FIGURE 5 FTIR spectra of LDH after regeneration in kinetic study samples at 72 hours.

found (from 0.81 mmol g^{-1} for the original material to more than 3 mmol g^{-1} for the calcined material) is not likely to be due to only a difference in the surface area.

The high pH reached in the regeneration process can favour the intercalation of hydroxyl anions instead of benzoate. We conducted the present study starting from neutral pH (to allow the dissolution of the BA and so the construction of the adsorption isotherm). On the other hand, the pH usually found in the wastewater containing benzoic acid is around 4.4 [8]. Thus, in a lower pH the competition between hydroxyl anions for the interlayer sites should be much smaller, allowing the intercalation of higher quantities of BA, and in this case the calcined LDH can play a double hole, as adsorbent of BA and pH neutraliser.

The presence of benzoate in the regenerated materials can be confirmed by FTIR. In the Figure 5 one can observe the presence of intense bands characteristic of the carboxyl and phenyl groups at 1596, 1540 and 1364 cm^{-1}, associated with benzoate anions.

CONCLUSIONS

It has been shown that calcined products of hydrotalcite-like compounds exhibit interesting sorption properties, which can be used to remove benzoate anions from water. The calcined product is much more effective than the original LDH in removing anions from solution. The extraction ratio of BA for calcined LDH was between 40 and 85% in the concentration range usually found in wastewater produced by polyester industry. The regenerated material presented an interlayer spacing characteristic of intercalated hydroxyl anions. The high amount of benzoate anions removed by sorption cannot be explained only by the adsorption process, so a part of the anions should be located between the layers. These results suggest that LDH calcined products may be useful as sorbents for the removal of benzoate anions from aqueous solution.

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