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Temperature effect on the sorption of cholate anions on calcined LDH

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Layered Double Hydroxides are a class of materials that can be described as positively charged layers of divalent and trivalent cations in the centre of edge-sharing octahedra. Cholesterol derivatives such as cholic acid are substances that play an important role in the digestion of fat components by the organism. This work presents a study on the intercalation of cholate anions in calcined MgAl-CO_3–HDL. Isotherm experiments were performed at three different temperatures to evaluate the capacity of anion removal by sorption in the calcined LDH. The plateau was reached in all conditions. Increasing temperature results in decreasing cholate sorption. Characteristic peaks of LDH regenerated with OH^- anions were observed at lower cholate concentrations. A peak in 2θ equals to 7.5° and peaks between 15° and 20° are observed. Those peaks are the same as the ones observed in the pure sodium cholate PXRD. At higher cholate concentrations the sorbed solids present PXRD related to an additional layered phase, which is related to intercalation of cholate anions with basal spacing equal to 34.3 Å. Thus, the cholate anions are also intercalated with a bilayer molecular arrangement at equilibrium concentrations at the isotherms plateau.

1. Introduction

Layered Double Hydroxides (LDH) are a class of materials originated from the isomorphous substitution of divalent cations, such as Mg^{2+}, by trivalent ones, like Al^{3+}, in a planar brucite-like structure. Such substitution gives rise to a positive residual charge in the layers that should be balanced by intercalation of anionic species together with water molecules. This leads to the stacking of the layers and results in the hydrotalcite-like structure. These materials can present different properties, depending on the kind of di- and trivalent cations and their ratio, as well as the interlamellar anion.

One important potential application of this class of materials comes from their ability to remove anionic species from aqueous solution by three different processes: (i) adsorption (surface interaction); (ii) anion exchange (intercalation); and iii) sorption, a combination of intercalation and adsorption that is more likely to occur in the regeneration of a calcined precursor ("memory effect") mainly from an LDH of magnesium aluminum or zinc aluminum pairs [1–4]. The regeneration of a calcined precursor requires the preparation of an LDH containing carbonate that has to be treated thermally (calcination) at an adequate temperature (determined by thermogravimetric analysis), forming a double oxide–hydroxide.

The obtained calcined material, when in contact with a solution containing an anion of interest, can regenerate the LDH structure with intercalation of the anion. This method is specially useful for the preparation of LDH intercalated with hydroxyl anions, which are difficult to obtain in their pure form by other methods [5].

Cholic acid (CA) is one of the main products of bile, that helps to promote the transport of lipids through aqueous systems and play an important role in the digestion of all fat-soluble components of food by the organism. Whenever cholic acid is overproduced, it is sequestered by adsorbents in the gastrointestinal tract, therefore reducing cholesterol levels in the blood, as well as the risk of such diseases as bradycardia, hypertonia, and hemolysis [6].

LDH have been used as adsorbents/sorbents in several processes, such as the removal of different anionic species from aqueous solutions. Among their uses, we can outline the removal of anions from water used in refrigeration of nuclear reactors, sulphur oxide removal from gaseous mixtures, and the removal of pigments in beetroot juice in sugar manufacturing.

In this work, we have studied the sorption of cholate anions on calcined MgAl-CO_3–LDH, investigating the effect of temperature on the sorption process and the cholate concentration on the LDH regeneration.

2. Experimental

The MgAl-CO_3–LDH was prepared according to the coprecipitation method proposed by Reichle [7]; all reactants were acquired from Merck (> 99% assay).

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The sorbate sodium cholate was also acquired from Merck (99% assay) and used without previous purification. All solutions used in the experiments were prepared with deionized water (MilliQ®), and the initial pH was adjusted by addition of NaOH when necessary.

The MgAl-CO_3–LDH was thermally treated (calcined) in a ceramic oven "EDGCON-5P" under oxygen atmosphere at 773 K for 6 h. This resulted into a mixed Mg and Al oxide–hydroxide, which was employed as the sorbent. The calcined material was then cooled to room temperature under vacuum, in the presence of activated silica gel. The resulting calcined material and the solids after sorption were characterized by techniques such as Powder X-ray Diffraction (PXRD) and Fourier-Transform Infrared Spectroscopy (FT-IR).

The isotherms were achieved by the addition of a constant mass (200 mg) of the sorbent (calcined material) in 16 different erlenmeyers in each one it was added 25 cm^3 of cholate solutions at different concentrations. The mixtures were kept at constant temperature, in a thermostatic orbital shaking bath, for 72 h, for the chemical equilibrium to be reached. After that, each sample was divided into two parts: one was centrifuged. The solid material was separated from the supernatant solution and dried. The final solutions were then analyzed for quantification of cholate anions. The second part was kept in suspension for electrokinetic potential analysis. These experiments were carried out at three different temperatures (288, 298 and 323 K).

Quantification of cholate anions in the solutions, before and after the sorption, was performed by high performance liquid chromatography (HPLC), by adapting a method from the literature [8]. The chromatographic column was C18 RP-ODS (250 mm $\times$ 4.6 mm $\times$ 5 mm) connected with a refractive index detector (RID). The mobile phase consisted of (% v/v) 69.6% methanol, 17.4% acetonitrile, 12.99% water, and 0.01% formic acid. The elution flow through the column was 1.4 mL min^{-1}.

The sorption isotherms were plotted as cholate concentration in the equilibrium versus quantity sorbed (mmol of cholate per gram of LDH).

3. Results and discussion

The obtained isotherms are showed in Fig. 1. The curves present similar profiles at all conditions, as seen from the graphs. All the curves indicate a trend toward the sorbent saturation in the last points. The experimental condition that resulted in the highest sorption efficiency was the one at temperature 288 K.

A comparison of the curves reveals that an increase in temperature from 288 to 323 K causes a decrease in the amount of cholate sorbed. A higher temperature causes a reduction in sorption, because it results in the enhancement of the entropic factor in the variation of the system's free energy (given by: $\Delta G = \Delta H - T\Delta S$). Considering that the sorption of Cholic acid anions on the surface of the LDH results in higher system organization, or a reduction in entropy ($\Delta S < 0$), this causes a reduction in the negative value of the free energy, ruled by the negative enthalpic factor (ΔH).

The electrokinetic potential curves, shown on Fig. 2, also present very similar profiles. Initially, they present a positive potential values next to 14 mV which decreases quickly until null values. This null results confirm the proposition of saturation of the sorbent.

Comparing the PXRD patterns shown on Fig. 3, many differences are noticed. In the material regenerated only in water (Fig. 3a), a lamellar phase with basal spacing of 7.56 Å was observed, indicating intercalation of hydroxyl anions. This material presents a high structural organization. Fig. 3b, c and d shows the material after sorption at different temperatures. In these cases, the peaks due to intercalation of hydroxyl anions are also observed. In addition, a high intensity peak in 2θ equal to 7.5º and several peaks in the region between 15° and 20° are noticed, which are related to the pure sodium cholate. It can be said that as the amount of sorbed cholate anions increases, crystals of the salt may have been formed into the LDH surface, and detected by X-ray diffraction.

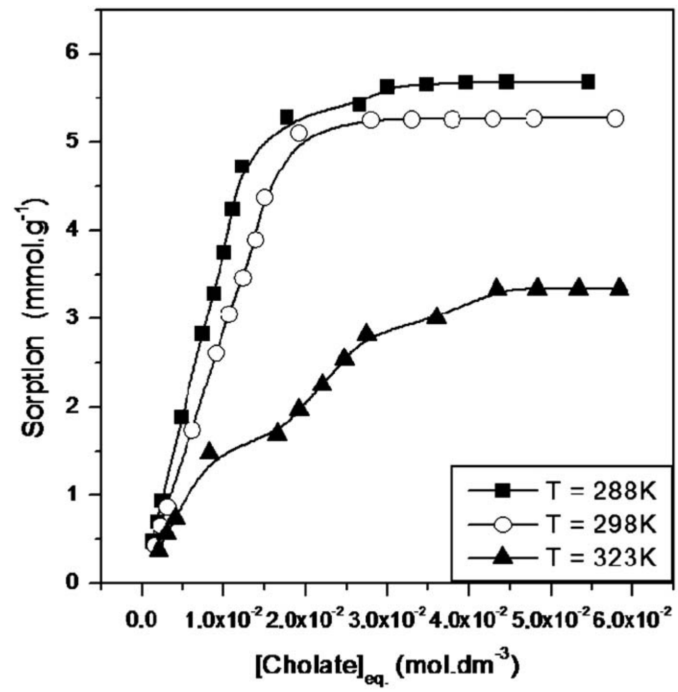

Fig. 1. Isotherms of Cholate sorption in calcined LDH at three different temperatures (288, 298 and 323 K).

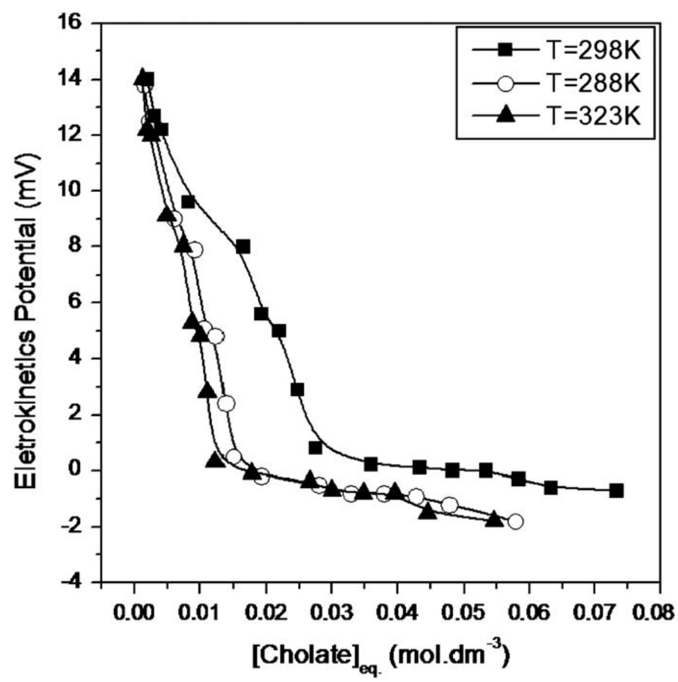

Fig. 2. Electrokinetic Potential Measurements following Cholate sorption Isotherms in calcined LDH at three different temperatures (288, 298 and 323 K).