J Mater Sci (2008) 43:6986–6991
DOI 10.1007/s10853-008-2952-z

Adsorption of cholate anions on layered double hydroxides: effects of temperature, ionic strength and pH

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Received: 15 December 2007 / Accepted: 14 August 2008 / Published online: 17 September 2008

Abstract Layered Double Hydroxides are a class of materials that can be described as positively charged planar layers consisting of divalent and trivalent cations in the center of edge-sharing octahedra. The positive charge in the LDH layers must be compensated by anion intercalation. These materials have applications that include adsorption and/or sorption of anionic species. Cholic acid is one of the main acids produced by the liver. It promotes transport of lipids through aqueous systems. This work reports on the adsorption of Cholic acid anions in MgAl–CO_3–LDH taking ionic strength, pH, and temperature effects into account. The adsorbent was characterized by different techniques. Cholate anion adsorption was performed at two different temperatures (298 and 323 K), two different ionic strength conditions (0.0 and 0.1 M of NaCl), and two different pH values (7.0 and 10.0). The results show that the sorption of Cholate anions in calcined LDH can remove a considerable amount of these anions from the medium. Cholate anion adsorption in the LDH with no calcining also occurs, but at a lower amount.

Introduction

Cholic acid (CA) is one of the main products of bile. It is a white, crystalline substance with surfactant properties similar to those of organic salts derived from long-chain organic acids. Cholic acid promotes the transport of lipids through aqueous systems.

Cholesterol derivatives such as Cholic acid are amphiphiles that 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, thereby reducing cholesterol levels in the blood, as well as the risk of such diseases as bradycardia, hypertonia, and hemolysis [1, 2].

Layered Double Hydroxides (LDHs) are a class of materials originated from the isomorphous substitution of divalent cations, such as Mg^{2+}, by trivalent ones, such as 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. Layered double hydroxides can be represented by the general formula $\left[M_{1-x}^{2+}M_x^{3+}(OH)_2\right]^{x+}A_{x/m}^{m-}\cdot nH_2O$, in which M^{2+} and M^{3+} are the divalent and trivalent cations, respectively, and A^{m-} is the intercalated anion with an m^- charge. 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 a LDH of magnesium aluminum or zinc aluminum pairs [3–13]. When the LDH is intercalated with an anion for which undergoing anion exchange is very difficult (like $CO_3{}^{2-}$ anions), only the adsorption process is expected to

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occur. In this case, the most important adsorbent/adsorbate interaction occurs on the external surface of the LDH.

LDHs have been used as adsorbents in several processes, such as the removal of different anionic species from aqueous solutions. The removal of anions from water used in refrigeration of nuclear reactors, the removal of sulfur oxide from gaseous mixtures, and the removal of pigments in beetroot juice in sugar manufacturing [14] are same of the uses of LDH.

In this work, we have studied the removal of Cholate anions from aqueous solutions by adsorption on MgAl–CO_3–LDH, and we have investigated the effects of variables such as temperature, ionic strength, and pH of the medium on the process.

Experimental

The adsorbent MgAl–CO_3–LDH was prepared according to the coprecipitation method proposed by Reichle [15]; all reactants were acquired from Merck (>99% assay). The prepared LDH and the adsorbed solids were characterized by techniques such as Powder X-Ray Diffraction (PXRD) and Fourier-Transform Infrared Spectroscopy (FTIR).

The Specific Superficial Area was determined by the BET isotherm, obtained from nitrogen adsorption experiments. For these measurements, a Quantachrome NOVA 1200 was used. The samples were previously dried under vacuum in the presence of activated silica gel. Gas was eliminated from the sample at 340 K, and the experiments were conducted from the nitrogen adsorption in its boiling point (77.35 K in liquid nitrogen bath) using about 100 mg of the sample. The measurements were carried by addition of known volumes of gaseous nitrogen into the sample support, recording its pressure after the equilibrium was reached in each case followed by.

The adsorbate Sodium Cholate was acquired from Merck (99% assay) and used without further purification. All solutions employed in the experiments were prepared with deionized water (MilliQ®), and the initial pH was adjusted by the addition of NaOH when necessary.

The adsorption experiments consisted of the addition of 400 cm^3 of Sodium Cholate solution ($C_0 = 5 \times 10^{-3}$ mol L^{-1}) to a constant mass of solid (800 mg of the prepared LDH) previously dried under vacuum. The addition was carried out under vigorous stirring, in a closed cell, in order to prevent water evaporation and contact with atmospheric CO_2. The cell was kept at a constant temperature through water circulation from a thermostatic bath. Aliquots of 25 cm^3 were collected at pre-established times, and the system was always at a constant temperature. The withdrawn aliquots were centrifuged, in order to separate the solid material. The material was separated from the supernatant solution and dried. The final solutions were then analyzed for quantification of the Cholate anions.

Quantification of Cholate anions in the solutions before and after the adsorption was performed by high performance liquid chromatography (HPLC), by adapting a method from the literature [16]. The chromatographic column was C18 RP-ODS (250 × 4.6 × 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}.

To evaluate the capacity of anion removal by sorption (simultaneous adsorption and intercalation by regeneration) the LDH was thermically treated (calcined), to remove the initially intercalated CO_3^{2-} anions. This resulted in a mixed Mg and Al oxide–hydroxide, which was employed as sorbent. Calcination of the material was carried out in a ceramic oven “EDGCON-5P” under oxygen atmosphere at 773 K for 6 h. The calcined material was then cooled to room temperature under vacuum, in the presence of activated silica gel. The resulting calcined material was subjected to those techniques used for the characterization of solids.

The same experimental procedure mentioned above was adopted for the adsorption isotherms, using the calcined LDH.

The experiments were performed by varying parameters such as temperature (298 and 323 K), initial pH of the Cholate anion solution (7.0 and 10.0), and the ionic strength with and without the addition of 0.1 mol dm^{-3} of NaCl to the initial solutions.

Results and discussion

The LDH was prepared in a Mg/Al molar ratio of 2:1. This ratio is directly related to the LDH charge density, a very important factor for the adsorption process. The specific superficial area (S_{BET}) was 41.53 m^2 g^{-1} for the prepared LDH and 200.41 m^2 g^{-1} for the calcined LDH obtained after the thermal treatment.

From the adsorption kinetics of the original LDH and the sorption kinetics study of the calcined LDH, it was possible to determine the time necessary to reach the equilibrium in each case.

Figure 1 shows that the concentrations of the solutions are practically constant after contact of the solid materials with the Cholate anion solution for 72 h. In some cases, the equilibrium was not totally reached within this period, but for comparison purposes, we can consider that 72 h was enough for the equilibrium values of the adsorption and sorption processes to be reached in each experiment.

The curve profiles were similar in all the conditions, as seen from the graphs. In all curves, there is a disturbance

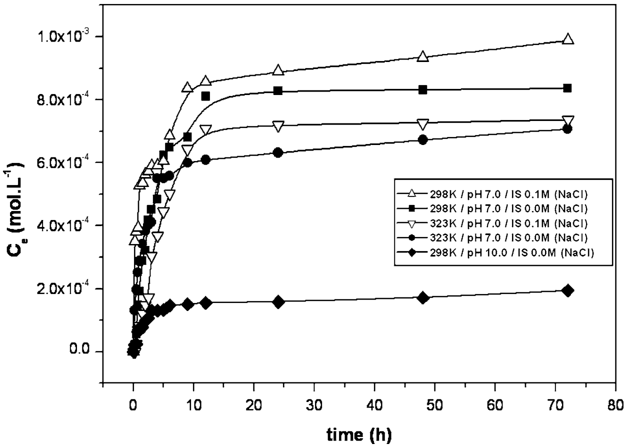

Fig. 1 Curves of cholate anion adsorption in MgAl–CO_3–LDH as a function of time at two different temperatures (298 and 323 K); two different ionic strength conditions (with and without the addition of NaCl to the solution), and at different initial pH values for the cholate anion solution (7.0 and 10.0)

when the adsorption curves reach about 90% of their adsorption capacity. This phenomenon can be explained if we split the adsorption process into two distinct stages, ruled by the second law of thermodynamics. In adsorption processes that occur by electrostatic interactions, as proposed, the predominant factor in the process is the enthalpic factor. So, it is considered that the first part of the curve (until approximately 10 h) is due to the energy of this factor. In this first part, adsorption occurs quickly and at high rates. After this stage, there is a change in the slope of the curve and the process starts to occur more slowly and at lower rates. This process is related with the entropic factor of the system, of lesser energy, but it also contributes to the adsorption process.

For the original LDH, the experimental condition that resulted in the best adsorption efficiency was the one where the adsorption temperature is 298 K, the pH value of the Cholate anion solution was adjusted to 7.0, and there is an addition of 0.1 mol dm^{-3} NaCl. Moreover, all the curves indicated a trend toward adsorbent site saturation in the last points.

A comparison of the curves reveals that an increase in temperature from 298 to 323 K caused a decrease in the amount of adsorbed Cholate anions. This effect can be seen clearly in Fig. 1. A higher temperature causes a reduction in adsorption 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 adsorption of Cholic acid anions on the surface of the LDH results in higher system organization, or a reduction in the entropy ($\Delta S < 0$), this causes a reduction in the negative value of the free energy, ruled by the negative enthalpic factor (ΔH) [17].

Figure 1 shows that an increase in the ionic strength of the system by the addition of NaCl results in a considerable increase in the amount of adsorbed cholate anions in the evaluated concentration range. The addition of NaCl, with consequent increase in the ionic strength of the medium, helps to diminish the repulsive forces between the polar groups in the Cholate molecules, thus allowing the formation of a more compact adsorbed aggregate and increasing its adsorption.

In a more alkaline pH condition ($pH = 10.0$), the amount of adsorbed Cholate anions decreases compared with the adsorption at $pH = 7.00$. This is due to the reduction in the charge of the LDH surface because of the interaction with hydroxyl anions (OH^-) from the solution.

In the experiments where the initial pH value was 7.0, there was a small dissolution of the LDH, raising the pH of the solution. However, the amount of OH^- released by the dissolution of LDH is small and does not interfere significantly in the adsorption process. After the adsorption, the pH value was approximately 7.6. On the other hand, when the initial pH value was equal to 10.0, LDH dissolution was practically null.

The adsorption efficiencies were calculated by measuring the difference between the initial concentration of the Cholate anion solution ($C_0 = 5 \times 10^{-3}$ mol L^{-1}) and the concentration of the solution after 72 h (equilibrium concentration). Table 1 shows the extraction rate values for the adsorption of the Cholate anions in MgAl–CO_3–LDH, in different conditions.

The same procedure was adopted in the case of the sorption in the calcined LDH. The only difference lay in the adsorbent, which was the original LDH previously calcined at 773 K for 6 h, in oxygen atmosphere. The other experimental conditions for the adsorption experiments were similar to those used for the original LDH but, in the case of the sorption in the calcined material, the only variable studied was the temperature, since the ionic strength and pH value could not be controlled during the regeneration process of the calcined material.

The sorption efficiency was higher in the calcined LDH compared with the original LDH. This efficiency was higher at 298 K. In other words, increasing the temperature

Table 1 Cholate anion extraction efficiency by the original LDH, in different conditions

Temperature (K)	0.1 M (NaCl)	pH	Extraction efficiency (%)
298	Yes	7.0	19.8
298	No	7.0	16.8
323	Yes	7.0	14.7
323	No	7.0	14.1
298	No	10.0	3.9

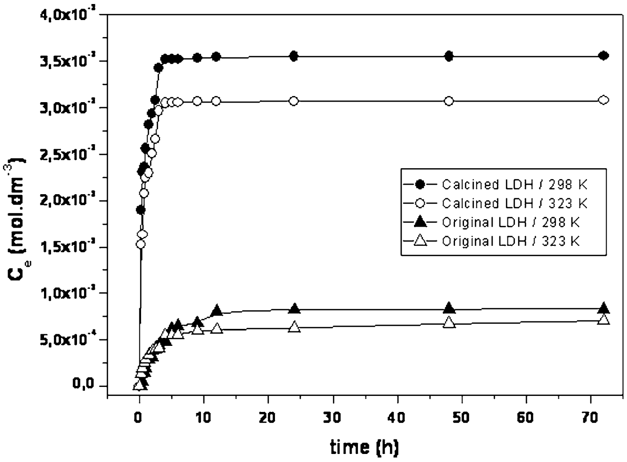

Fig. 2 Comparison between the rate of cholate anion removal by the original and calcined LDH, at two different temperatures

Table 2 Cholate anion extraction efficiency by the calcined LDH, at different temperatures

Temperature (K)	Extraction efficiency (%)
298	71.1
323	61.4

causes a decrease in the adsorption of Cholate anions, as already explained. The saturation region is reached more quickly (in approximately 4 h) in the case of the calcined material. Figure 2 shows a comparison between the Cholate anion adsorption curves for the original LDH and the Cholate anion sorption curves for the calcined LDH, at two different temperatures.

Table 2 shows the rate of Cholate anion extraction by the calcined LDH at different temperatures. The sorption efficiencies are higher than the adsorption ones. This can be explained by two facts: (i) During the sorption process both adsorption and intercalation occur due to the regeneration of the calcined precursor (also called "memory effect") [14] and (ii) the specific surface area of the calcined LDH is almost five times larger than that of the uncalcined one, resulting in higher extraction rates.

The solids obtained before and after adsorption were characterized by powder X-ray diffraction (PXRD). The PXRD patterns are depicted in Fig. 3. The prepared LDH has a basal spacing of 7.56 Å, characteristic of this kind of material [14]. The PXRD patterns of the LDH obtained after the adsorption are not significantly different from those of the pure MgAl–CO_3–LDH. In all the analyzed conditions, the calculated basal spacing was 7.56 Å, so substitution of the interlayer anion (CO_3^{2-}) did not occur. Adsorption of Cholate anions may happen only due to electrostatic interactions.

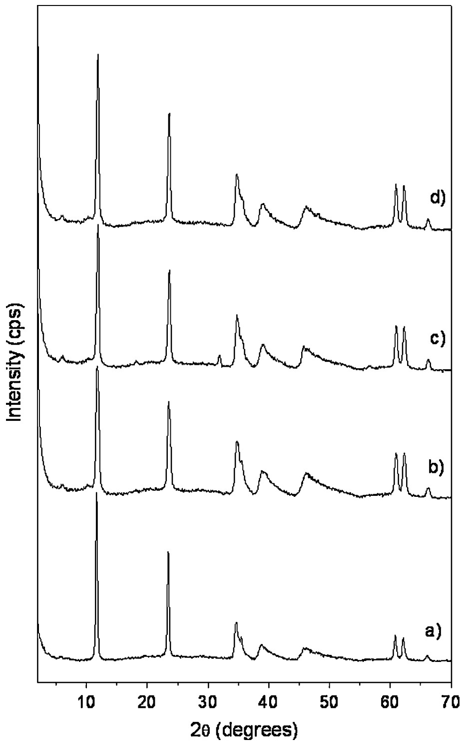

Fig. 3 PXRD for the original LDH in different conditions. (a) pure; (b) adsorbed with cholate at 298 K in pH 10; (c) adsorbed with cholate at 323 K in pH 7; (d) adsorbed with cholate at 298 K in pH 7 with the addition of NaCl

The infrared spectrum obtained for the MgAl–CO_3–LDH after 72 h in contact with the solutions is shown in Fig. 4 in different conditions. This spectrum displays a wide band in the 3,400 cm^{-1} region, attributed to the water and hydroxyl groups present in the layers of the LDH and in the Cholate anions. The bands located between 2,750 and 3,000 cm^{-1} can be associated with the hydrogen bonds taking place between the cholate anion dimers present in the structure.

The bands located in the 1,500 cm^{-1} region indicate the presence of carboxylate in the material. Compounds with intermolecular hydrogen bonding between carboxylic acids have a band due to C=O in the 1,700 cm^{-1} region. Bands in the 1,250 cm^{-1}region, related to C–O stretching, are also observed, as well as wide bands between 1,400 and 920 cm^{-1} due to deformation of the O–H bond [18].

The average particle size of the last points in each curve is shown in Table 3. The Scherrer method was employed to this end [19]. The average particle size is always larger for the solids obtained after adsorption compared with pure LDH.

The X-Ray patterns obtained for the calcined material adsorbed with Cholate anions after 72 h are depicted in Fig. 5, at different temperatures. The patterns show the

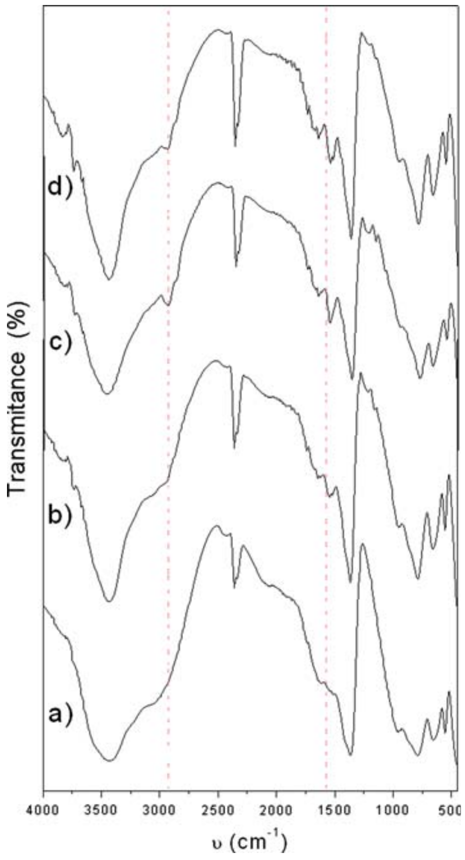

Fig. 4 FT-IR for the original LDH in different conditions. (a) pure; (b) adsorbed with cholate at 298 K in pH 10; (c) adsorbed with cholate at 323 K in pH 7; (d) adsorbed with cholate at 298 K in pH 7 with the addition of NaCl

Table 3 Average particle size for the original LDH adsorbed in different conditions

Sample	Average particle size (Å)
Pure LDH	433.5
298 K; pH 10; IS 0.0	454.6
323 K; pH 7; IS 0.0	481.9
323 K; pH 7; IS 0.1	482.6
298 K; pH 7; IS 0.0	495.6
298 K; pH 7; IS 0.1	496.2

reconstruction of the calcined LDH structure when it is placed in contact with the Cholate anion solutions. The appearance of two discrete peaks is noticed at $2\theta = 7.5$ and 16.3°. Compared with the X-Ray pattern obtained for the pure sodium Cholate (shown in Fig. 6), there are two peaks at the same 2θ values. Therefore, because a large amount of Cholic acid anions were sorbed by the calcined LDH, crystals may have been formed together with the LDH structure.

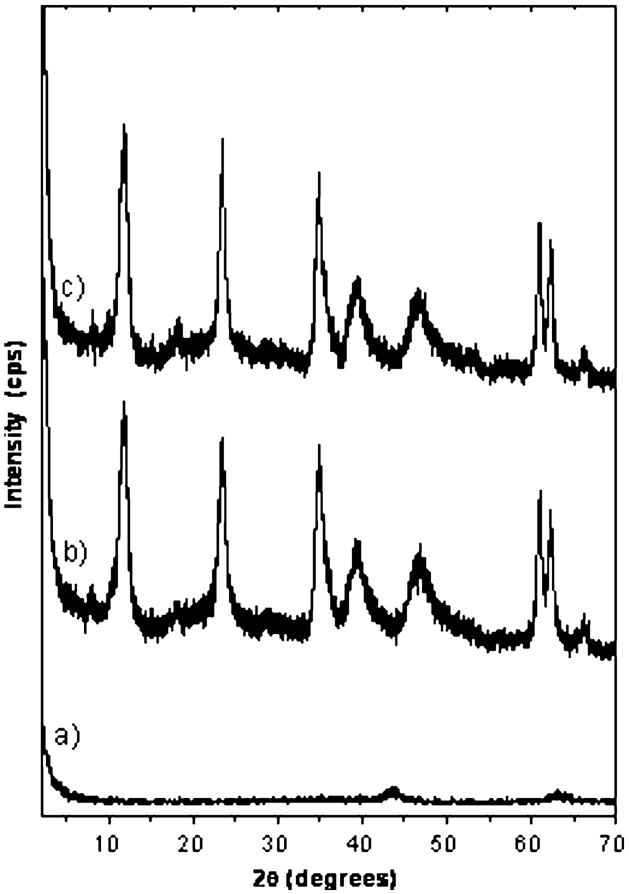

Fig. 5 PXRD for the calcined LDH in different conditions. (a) pure; (b) adsorbed at 323 K; (c) adsorbed at 298 K

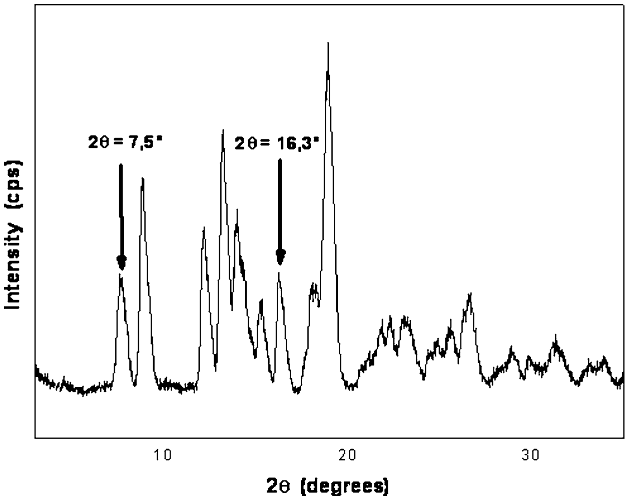

Fig. 6 PXRD for the pure sodium cholate salt

Conclusions

The results show that the sorption of Cholate anions in calcined LDH can remove a considerable amount of these anions. The adsorption of this cholesterol derivative in uncalcined LDH also occurs, but at lower amounts. The adsorption/sorption kinetic study shows that Cholate anion removal efficiency is significantly dependent on the studied variables. In the conditions investigated here, adsorption diminishes when the temperature is increased. Addition of NaCl, with a consequent increase in ionic strength, increases the rate of Cholate anion removal. The initial pH value of the Cholate anion solutions also exerts influence on the adsorption. Higher pH values significantly decrease Cholate anion removal.

In conclusion, LDHs have potential applications in the pharmaceutical field, such as their use as adsorbent of Cholate anions produced in excess by the human organism.

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