

Removal of Cadmium from Polluted Water Using Layered Double Hydroxides as Effective Adsorbents

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Abstract—Layered double hydroxides (LDHs) are layered materials containing a positively charged layer and exchangeable anions in the interlayer. In this study, LDHs intercalated with chelating agents were synthesized by anion exchange reaction. The materials synthesized in this work were characterized by chemical analysis, Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and powder X-ray diffraction (XRD). Adsorption experiments from aqueous solutions containing known amounts of some heavy metallic ions onto the adsorbent were explored in a batch system. The amount of metallic ions adsorbed by LDHs intercalated with EDTA and LDHs without EDTA were determined by atomic absorption spectrometry (AAS). In order to examine the adsorption capacity of LDHs intercalated with chelating agents, the adsorption experiment was investigated under the optimum condition.

Keywords— Layered double hydroxides, Ion exchange, Chelating agents, Sorbents, Cadmium contamination.

I. INTRODUCTION

Layered double hydroxides (LDHs), also known as hydrotalcite (HT)-like materials, are a class of synthetic two-dimensional nanostructured anionic clays whose structure can be described as containing brucite-like layers, where a fraction of the divalent cations coordinated octahedrally by hydroxyl groups have been replaced isomorphously by trivalent cations, giving positively charged layers with charge-balancing anions between them; some hydrogen bonded water molecules may occupy any remaining free space in the interlayer region [1,2]. LDHs may be represented by the general formula $[M^{2+}_x M^{3+}_y(OH)_z]^{x+y} (A^{n-})_{x/n} \cdot nH_2O$, where M^{2+} (M = e.g. Mg, Fe, Co, Cu, Ni, or Zn) and M^{3+} (M = e.g. Al, Cr, Ga, Mn or Fe) are di- and trivalent cations respectively; the value of x is equal to the molar ratio of $M^{2+}/(M^{2+} + M^{3+})$ and is generally in the range 0.2–0.33; A^{n-} is an anion. As a result, a large class of isostructural materials, which can be considered complementary to alumina silicate clays, with widely varied physicochemical properties can be obtained by changing the nature of the metal cations, the molar ratios of M^{2+}/M^{3+} as well as the type of interlayer anions. Layered double hydroxides exhibit anion-exchange properties, i.e., anions in the interlayers may be exchanged for the other ones. At temperatures of approximately 300 – 500 °C, layered double hydroxides are decomposed to form mixed oxides of MII and MIII metals. In Rehydration of these mixed oxides takes place in an aqueous solution containing the anion to be intercalated, resulting in the reconstruction of the layered LDH structure along with the intercalation of anions from the solution into interlayers [3,4]. This unique property of layered double hydroxides can be employed for preparation of compounds

intercalated with various anions or in removal of anions from solutions. The often used group name “hydrotalcite-like compounds” is related to the mineral hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$). There are some other natural minerals and a great number of synthetic compounds with an analogous layered crystal structure combining various MII and MIII metal cations in hydroxide layers and various anions intercalated in the interlayers.

II. RELATED WORK

Cadmium is a soft white solid metal with an oxidation state of +2. It is chemically similar to zinc and occurs naturally with zinc and lead in sulfide ores. Cadmium metal is used mainly as an anticorrosive, electroplated onto steel. Cadmium sulfide and selenide are commonly used as pigments in plastics [5-7]. Cadmium compounds are used in electric batteries, electronic components and nuclear reactors. Cd can enter into the wastewater from industrial processes such as electroplating, Cd-Ni batteries, fertilizers, pesticides, ore mining, plastics, pigments, dyes, etc. Consumption of Cd containing food leads to its accumulation in living tissues causing various diseases and disorders [8-10].

One of the cases of environmental pollution is due to heavy metal contaminants such as copper, lead, cadmium, chromium, arsenic, zinc, etc. Heavy metals are of major concerns because of their strong toxicity even at low concentrations. Surface water pollution and groundwater contamination are some of the environmental problems today. Heavy metal ions have high toxicity and poor biodegradability for plants and animals at higher concentrations [11,12]. There is no evidence indicating its

essentiality to humans. Cd is toxic, even in extremely low levels, it accumulates especially in the kidney and is a potent cause of cancer and cardiovascular diseases. Cd can cause cough, headaches, and nausea followed by vomiting in low dose intakes, while in large doses, accumulation in the liver and kidneys take place; while its replacement of calcium in bones, culminates in painful bone disorders, renal failure, and implications in human hypertension. Chronic anemia can be caused by prolonged exposure to drinking water contaminated with Cd. The binding of protein, metallothionein, into excess essential metals renders their non-availability to human blood supply. However, it gets bound to copper and zinc when it is induced to activity by Cd (Environmental Protection Agency [EPA], 1999). In their study on Egypt, Salem, Ewieda, and Farag (2000) revealed that drinking of water contaminated with lead and Cd strongly correlated with patients suffering from renal failure. A variety of cost effective adsorbents have been extensively employed for the successful removal of Cd from effluents.

This paper takes a look at the direct application of the LDH produced by coprecipitation method for the adsorption of Cadmium ions.

III. METHODOLOGY

Synthesis of LDH

Carbonate form of Mg-Al LDH was synthesized by coprecipitation method. A 50 ml aqueous solution containing 0.3 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.1 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with Mg/Al ratios 4:1, was added drop wise into a 50 ml mixed solution of NaOH (2M) + Na_2CO_3 (1M) with vigorous stirring and maintaining a pH of greater than 10 at room temperature. After complete addition which last between 2 hours 30 minutes to 3 hours, the slurry formed was aged at 60°C for 18 hours. The product was centrifuged at 5000 rpm for 5 minutes with distilled water (3-4 times) and dried by freeze drying.

Characterization of layered double hydroxide

The morphology and microstructure of the sample were characterized by a Scanning Electron Microscopy (SEM) (Jeol JSM 840A scanning electron microscopy), X-ray diffraction (XRD, Jeol JDX8P powder diffractometer and Fourier transformation infrared spectra (Nicolet model Impact 400D FTIR spectrometer, KBR pellets resolution 4 cm^{-1}).

Preparation of aqueous solution of heavy metal

All reagents used for this study were analytical reagent grade, 1000 mg/l aqueous solutions of the metals ion was prepared as stock from their salts (CdSO_4). From the stock, working solutions of 0.08g/L Cd, 0.12g/L Cd and 0.16g/L Cd were prepared from appropriate aliquots diluted to the appropriate concentration. The total concentration of each metal ion in the aqueous solution was confirmed by analysis using Atomic Absorption Spectrometer (AAS).

IV. RESULTS AND DISCUSSION

The PXRD pattern shows the following broad reflections for planes (003), (006) and (110). The corresponding interlayer spacings "d" are calculated and listed in the table. The PXRD pattern of Mg-Al- NO_3 and Mg-Al-EDTA is represented in a table 1. The prepared intercalated compound in (b) is different from that of the precursor sample with nitrate anion in the interlayer (a), but both are characteristic of a layered phase with the basal diffractions mainly due to planes of (003) and (006). These patterns also indicate that the intercalation of EDTA in Mg-Al- NO_3 gives rise to an increase in basal spacing from $d=7.77 \text{ \AA}$ to $d=14.98 \text{ \AA}$. The subtraction of 4.8 \AA as the hydrotalcite-layer thickness, from the $d=14.4 \text{ \AA}$ gives 10.18 \AA as interlayer space occupied by EDTA. On the other hand, the values for Mg-Al- NO_3 decrease slightly from Mg-Al-EDTA which agrees with the reported classical values for Mg-Al-EDTA [13]. This suggests that the ligand is probably accommodated in the interlayer space of the LDHs. To confirm the chelation of metal cations in the interlayer, the PXRD patterns of the products Mg-Al-EDTA-M were obtained, but no significant change in the basal spacing of the adsorbent material was observed (PXRD not shown). In addition, the basal spacing is very similar to that found in previous reports [14]. The results suggest that the M-EDTA complexes are formed and accommodated into the interlayer without apparent deformations. The sorption experiments of Cd^{2+} on Mg-Al-EDTA were carried out suspending duplicate samples of 0.1 g of Mg-Al-EDTA in 50 ml of aqueous solution of chromium chloride salt at various concentrations of 0.1-20 mg shaken in a thermostatic water bath at 20, 30, 40, and 50°C for 5, 10, 15, 20, 25 and 30 min. The pH was varied in the range of 3-8. It was determined for the optimum initial pH, contact time and concentration of metal salts. The supernatants were separated to determine the amount of metal Cd^{2+} adsorbed by colorimetric method using s-diphenyl carbazide. This amount was determined from the difference between initial and final concentration of the metal ion in the supernatant solutions. Metal solutions without adsorbent (blank samples) were also shaken under the same experimental conditions.

The Percent uptake (%) = $\frac{\text{conc. of Cd in the solid phase}}{\text{conc. of Cd in aqueous phase}} \times 100$. Effect of initial metal concentration was investigated using initial Cd concentration varied from 0.1 to 20 mg/100 ml. In experiments concerning the effect of adsorbent dose, a range of solid material samples (0.5, 1, 2, and 5 g) were used. For contact time experiments, the same procedure above was followed, with the difference that the phases were separated after a determined period of contact time. The temperature was optimized at 35°C for all adsorption experiments. The Cd ion uptake was affected by pH of the solution as the pH increases the uptake increases reaching a maximum of 82% and 80%, respectively at pH 8.0 and pH 7. The sorption capacities of metal ions at the optimal temperature of 35°C are, 50%, 65%, 67%, 78%, 80% and 82% at pH 2, 3, 4, 5, 6, 7 and 8 respectively. The capacity

is relatively constant for pH 6-7. Thus, the optimum pH was chosen to be 7 to avoid any false uptake at pH 8 or above due to the formation of metal hydroxides. This order of uptake clearly shows the pH dependence and the sorption increases with increasing pH value of solution as expected trend for heavy metal ions. The effect of contact time between adsorbent and a Cd solution with an initial concentration of 100 mg/L, 1g of solid material and pH 6.5 at 30°C is presented in Figure 3.

V. CONCLUSION AND FUTURE SCOPE

Layered double hydroxides are good adsorbent materials for the effective removal of heavy and toxic metal ions. EDTA intercalated Mg-Al-LDH is successfully used for the removal of the Cadmium from the contaminated water. The interlayer spacings of layered double hydroxides are responsible for the intercalation and deintercalation of many heavy and toxic metal ions.

Figures and Tables

Table 1: Interlayer spacing of the samples

Sample name	d(003) Å	d(006) Å	d(110) Å
(a) Mg-Al-NO ₃ -LDH	7.77	3.86	1.55
(b) Mg-Al-EDTA-LDH	14.98	7.38	1.56

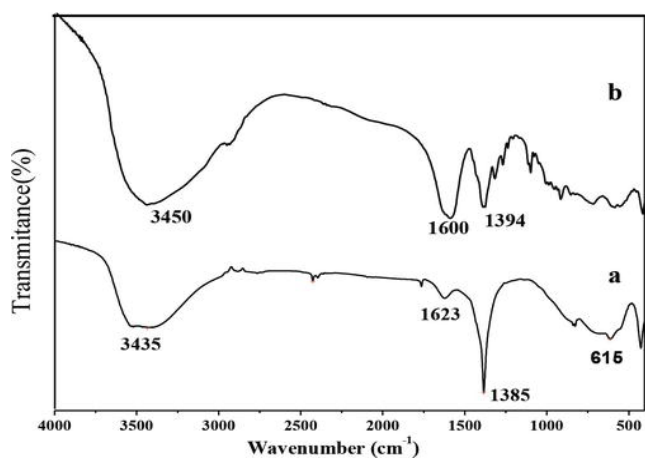


Fig: 1. FTIR Spectra of (a) Mg-Al-Ldh (b) EDTA intercalated Mg-Al-Ldh

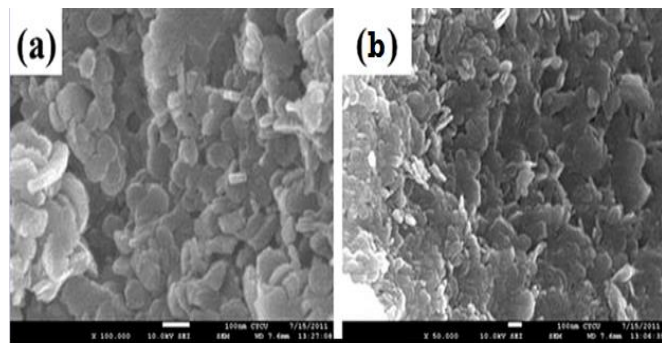


Fig: 2. Scanning Electron micrographs of (a) Mg-Al-Ldh (b) EDTA intercalated Mg-Al-Ldh

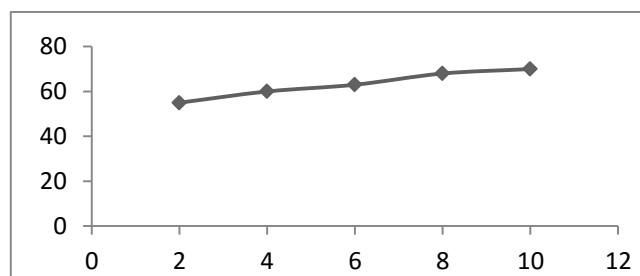


Fig:3. Percent uptake of Cd as a function of pH

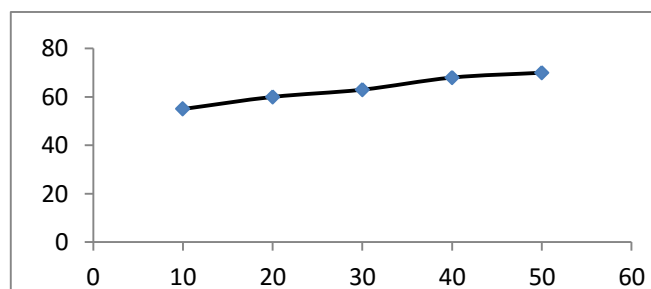


Fig:4. Percent uptake of Cd as a function of time (min)

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