

REMOVAL OF Cd(II) FROM AQUEOUS SOLUTION BY Ca-Al-HPO₄ LAYERED DOUBLE HYDROXIDE

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Abstract: Removal of aqueous cadmium ion by Ca-Al-HPO₄ layered double hydroxide (LDH) was investigated. Preparation of Ca-Al-HPO₄ LDH was performed using CaCl₂, AlCl₃ and Na₂HPO₄ by co-precipitation method at pH 4.6 and followed by hydrothermal treatment in polypropylene bottle at 90°C for 18 hours. The solid product was examined by X-ray diffraction, Fourier Transform Infrared Spectroscopy (FTIR), and elemental analysis using atomic absorption spectrometry (AAS) and UV-Vis spectrometry. Morphology of the LDH was determined using SEM. Adsorption of Cd²⁺ by the LDH was carried out using batch experiment by mixing the Cd²⁺ solution and LDH solid. After equilibrium was reached, the pH of the mixture was measured to be 7. The remaining Cd²⁺ in the solution was analyzed using AAS after being separated using a centrifuge. The amount of Cd²⁺ adsorbed by Ca-Al-HPO₄ LDH was approximately 600 mg g⁻¹, leading to the high formation of insoluble cadmium phosphate in the interlayer space of the LDH.

Keywords: Adsorption, Ca-Al-HPO₄ LDH, Cd²⁺ removal

INTRODUCTION

Heavy metals produced and released during domestic, agricultural and industrial activities may pose a serious threat to the environment. The presence of heavy metals in waste waters constitutes one of the most challenging problems in environmental today primarily because of their high toxicity and cumulative effects [1]. Recently, water pollution caused by cadmium (Cd) has attracted considerable attention. Since Cd is a very toxic element, its presence in the environment should become a serious attention. Therefore, techniques have to be developed to remove Cd in the body of water and in waste water. Most studies on heavy metal adsorption and related mechanism have been focused on synthetic mineral adsorbents such as hydroxyapatite

and other naturally occurred materials. Hydroxyapatite has been investigated as a potential adsorbent to treat heavy metal contaminated water mainly by Pb, Cd, Zn, and U [2-5]. Some researchers have reported on Cd removal with various adsorbents including peat soil, humic compounds, calcite, and hydroxyapatite. Effectiveness of other phosphatic minerals for absorption of heavy metals (Pb²⁺, Cd²⁺, and Zn²⁺) in aqueous solution has also been reported. Hydrotalcite is an anionic clay that is found naturally as hydroxycarbonate of magnesium and aluminum with the formula [Mg₆Al₂(OH)₁₆]²⁺·[CO₃²⁻·4H₂O] and brucite structure. The common formula of hydrotalcite is [M^{II}_{1-x}M^{III}_x(OH)₂]^{x-}·[Aⁿ⁻]_{x/n}·mH₂O, in which M^{II} is divalent metal such as Mg²⁺, Ca²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and M^{III} is a trivalent metal such as Al³⁺, Ga³⁺, Cr³⁺, Fe³⁺. Aⁿ⁻ is anion for example CO₃²⁻, OH⁻, Cl⁻, NO₃⁻, SO₄²⁻, PO₄³⁻ [6]. The M^{II}/M^{III} ratio is usually in the range of 1.5 ≤ R ≤ 4 [7] and the values of x are commonly to fall in the range of 0.1 ≤ x ≤ 0.05. However, pure brucite phase can only in which 0.2 ≤ x ≤ 0.33 [8].

Interests in layered double hydroxides (LDHs) and their derivative materials arise extensively due to many possible applications one of which is as adsorbents for metal pollutants. LDHs have been studied extensively for their ion-exchange, catalytic, and electrocatalytic. Phosphate containing LDHs are of interesting layered materials since phosphate interlayer anions may forms insoluble phosphate salts with heavy metal ions that can be separated as solid material. Adsorption of aqueous Cd²⁺ by Ca-Al-PO₄ may form corresponding cadmium phosphate that is formed in the interlayer gallery. This mechanism is expected to give an efficient lead removal by hydrotalcite-like compound. The current research focused on the removal of aqueous cadmium ion by Ca-Al-HPO₄ LDH. Kinetic and mechanism of the adsorption will also be discussed in this paper.

MATERIALS AND METHODS

Ca-Al-HPO₄ LDHs were synthesized by co-precipitation method. A 250 mL aqueous solution with Ca²⁺ to Al³⁺ molar ratio of 3 was prepared by mixing 0.01 M AlCl₃ and 0.03 M CaCl₂ in the three-necked flask equipped with magnetic stirrer. A portion of 100 mL solution of 0.25 M Na₂HPO₄ was added and vigorously stirred for 1 hour under nitrogen gas atmosphere. The mixed suspension was treated hydrothermally at 90 °C for 18 hours in poly propylene bottle with self-produced pressure. The solid product was separated by centrifuge at spinning rate of 2500 rpm for 10 minutes. The product was washed 3 times using doubly distilled water before being dried at 70 °C in air oven for 72 hours.

The layered structure of the material were confirmed by XRD (using CuKα 1.54060 Å, 45 kV, 30 mA) on Shimadzu 6000 X-Ray Diffractometer. The IR spectra were recorded with KBr pellet on Shimadzu FTIR-8201 PC. Electron microscopy was performed for grounded samples on a JEOL-JSM 6300 electron microscope equipped with EDAX. The elemental analysis was done using Perkin Elmer atomic absorption spectrometer (AAS) and UV-Vis spectrometer. Gravimetric method was applied to analyze water content in the LDH.

The isotherm adsorption of aqueous lead ion was done in centrifuge tube. The solution of Cd ion with certain concentration measuring 25 mL was adjusted to pH 4.0. A 0.05 g of LDH powder was added to the tube and was agitated using a mechanical shaker for 24 hours at room temperature. The solid was separated by centrifuge at spinning rate of 2500 rpm for 10 minutes. The left over lead ion in the supernatant was analyzed by AAS.

RESULTS AND DISCUSSION

The pH of the solution was monitored during the reaction process. The material basal spacing (d_{003}) of 7.47 Å was attributed to the basal spacing of phosphate LDH (Fig. 1). It was reported that LDHs with simple anions can have basal spacing in the range 7.4-8.2 Å and depend on the kind of anions [8].

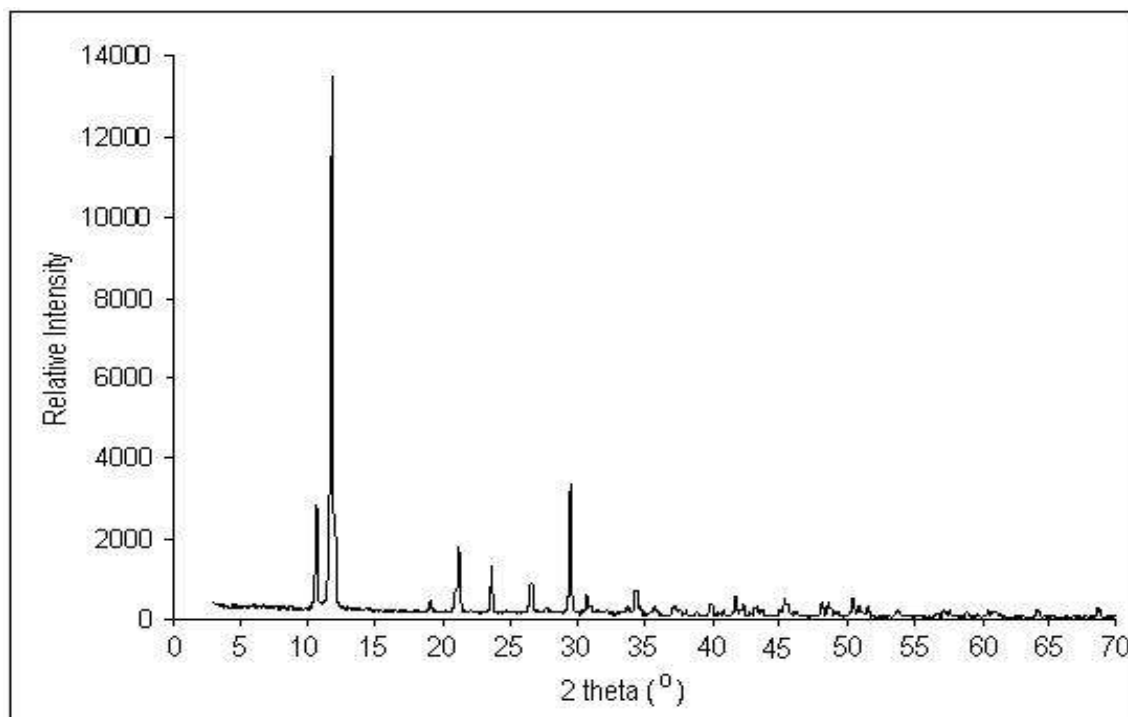


Fig. 1: XRD patterns of synthetic Ca-Al-HPO₄ LHD prepared at pH 4.6 followed by hydrothermal treatment at 90°C for 18 hours.

Synthesis of phosphate LDH was carried out with precipitation method using Na₂HPO₄ and the metal salts. The formation of phosphate LDH is pH dependent since phosphate can exist as monohydrogenphosphate, dihydrogenphosphate, and metaphosphate. At pH 4.6, it is conceivable that dihydrogenphosphate is present in the interlayer gallery. In alkaline condition, metaphosphate can easily form hydroxyapatite-like compounds. As revealed by XRD, the authors have followed the formation of phosphate LDH at various pHs and found that the best crystalline phosphate LDH was formed at pH 4.6. It was reported that LDH with a better crystalline structure can be synthesized at pH 5-6 [9-10]. The growth of LDH crystalline structure was assisted by hydrothermal treatment.

The absorption band near 3500-3600 cm⁻¹ can be assigned as stretching mode of O-H group in the LDHs and/or interlayer water (Fig.2). The small peak appeared around 3000 cm⁻¹ was due to hydrogen bonding between H₂O and the anion in the interlayer space. Absorption at 1651 cm⁻¹ can be ascribed to H₂O as well as hydroxide bending. The intensity of these last two vibration modes have been known to depend on the type of anion and the amount of water. The vibration occurred between 1000 cm⁻¹ and 1100 cm⁻¹ was caused by the presence of phosphate ion. In the 400-1000 cm⁻¹ region there is some bands related to vibrations of the anions and some related to metal-oxygen vibration.

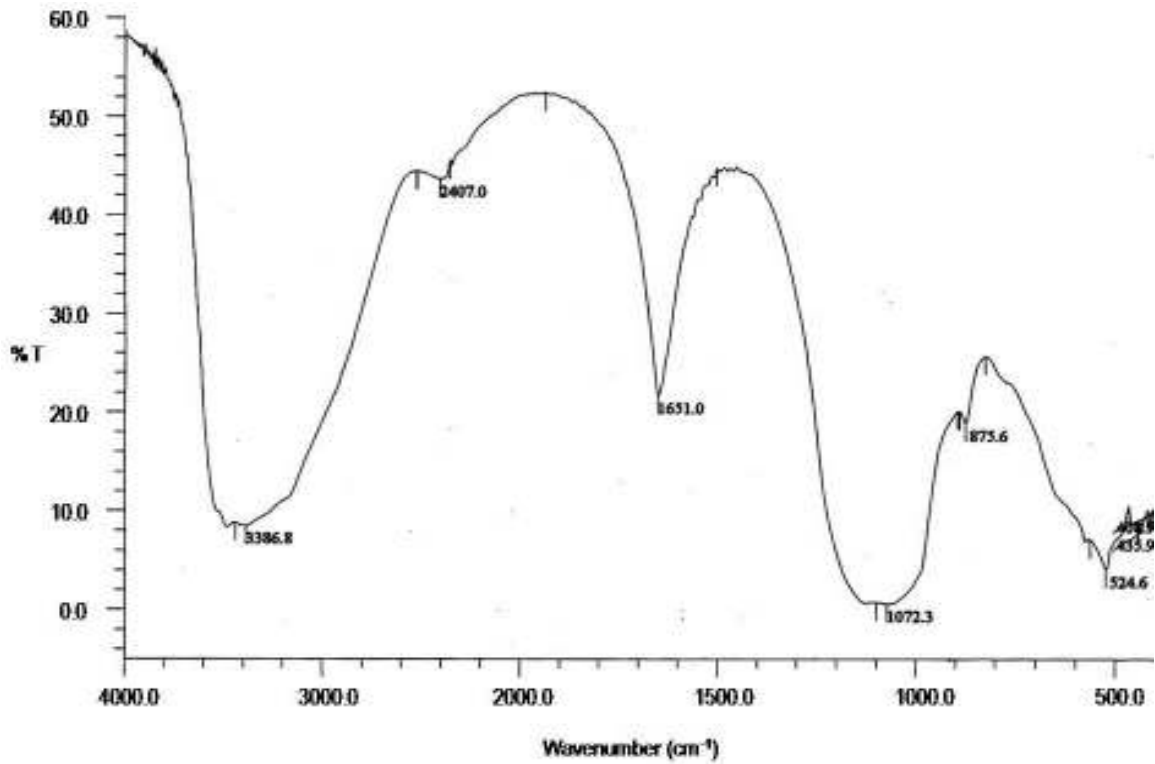


Fig. 2: FTIR spectra of synthetic Ca-Al-HPO₄ LDHs.

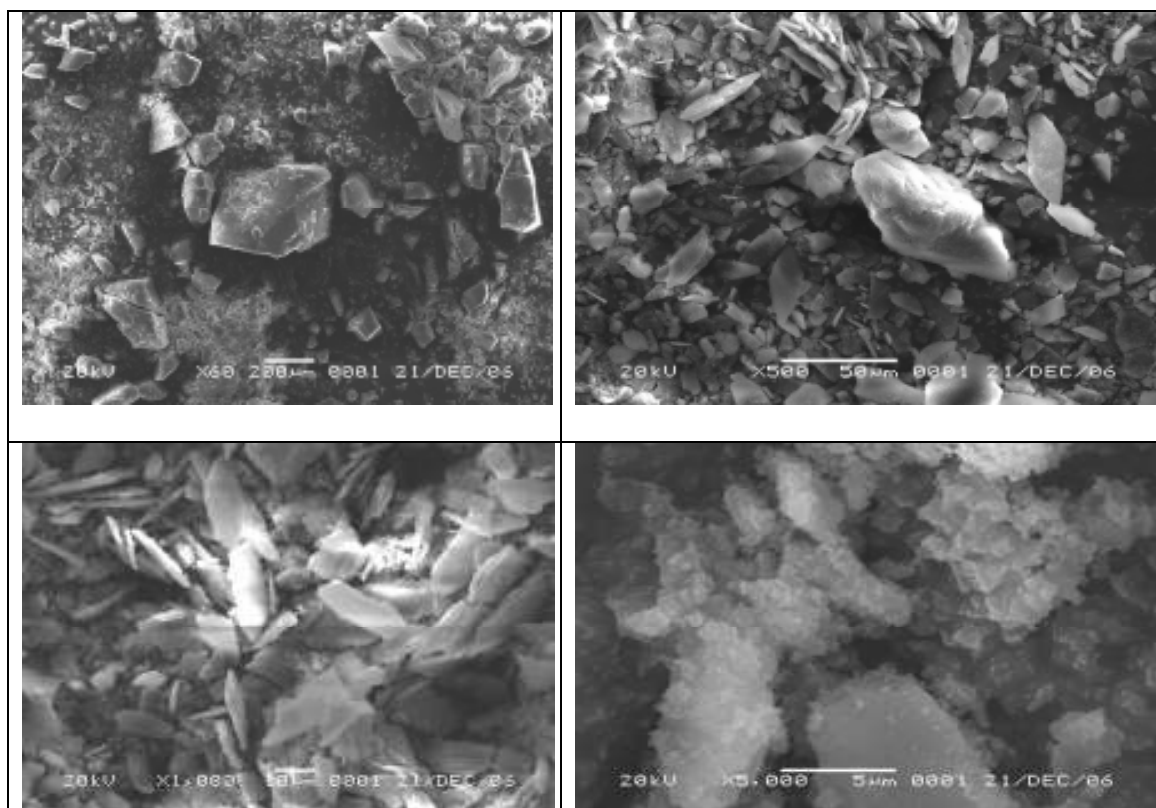


Fig. 3: SEM images of Ca-Al-HPO₄ LDH powder.

The slab of the LDH is estimated to have particle size about 5 μm (Fig. 3). This indicates that the nucleation process takes place very rapidly leading to large aggregation of LDH particle. The plot of concentration of Cd²⁺ in the adsorbent at various initial concentrations of Cd²⁺ versus the remaining Cd²⁺ in the solution will give the maximum adsorption capacity for each gram LDH, using 0.05 g of LDH and final volume of the mixture 25 mL (Fig. 4). From the plot, it shows that the amount of Cd²⁺ adsorbed was 600 mg g⁻¹, which is considerably very high.

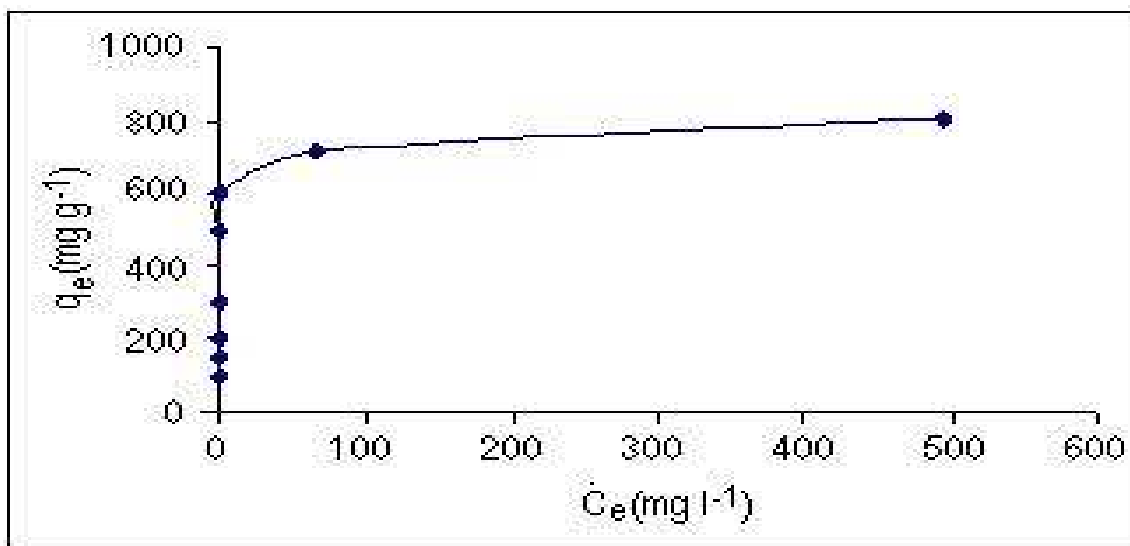


Fig. 4: The adsorption maxima of Cd²⁺ by Ca-Al-HPO₄ LDH at different initial concentrations.

The maximum capacity of Cd²⁺ adsorption by Ca-Al-HPO₄ LDH can also be inferred from Table 1. The total volume of the mixture and the weight of the LDH were kept constant at 25 mL and 0.05 g, respectively. It was believed that the formation of insoluble cadmium phosphate in the interlayer space of the LDH was responsible for this high adsorption capacity.

Table 1: Adsorption of Cd²⁺ by phosphate LDH using various initial concentration.

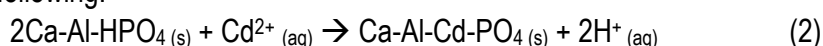
Initial Cd ²⁺ in solution (mg)	Mass of LDH (g)	Volume of the mixture (mL)	Cd ²⁺ remaining in solution (mg)	Cd ²⁺ adsorbed/gram adsorbent (mg g ⁻¹)	Cd ²⁺ adsorbed/initial (%)
5.0	0.05	25	0.002	99.96	99.96
7.5	0.05	25	0.010	149.81	99.87
10.0	0.05	25	0.002	199.96	99.98
15.0	0.05	25	0.002	299.96	99.99
25.0	0.05	25	0.004	499.92	99.98
30.0	0.05	25	0.004	599.92	99.99
37.5	0.05	25	1.660	716.75	95.57
52.5	0.05	25	12.358	802.83	76.46

Mechanism reaction of Cd adsorption by Ca-Al-HPO₄ has yet not been understood. The authors believe that the formation of cadmium phosphate in the interlayer space is the main reason. From FTIR spectra it is proven that the interlayer space of LDH is filled with hydrogen phosphate anion to balance the charge of the LDH sheets. Formation of cadmium phosphate may be supported by some other work where the pH of the solution lower after cadmium ion was adsorbed as presented in Table 2. In general, addition of Cd²⁺ to the suspension of LDH leads to lowering the pH of the solution. It was reported that adsorption of metal ion by iron oxyhydroxide is written as follows.



This reaction will produce hydrogen ion that eventually will reduce the pH of the suspension.

Reaction between phosphate LDH (in the interlayer as HPO₄²⁻ anion) and Cd²⁺ can be proposed as the following.



Taking into account this reaction, the pH of the system will also be affected by the hydrogen ion released during the reaction. The authors found that if the initial pH was 10 after addition of Cd²⁺ it would drop to just over 7. Similarly, when the initial pH was 8, the final pH of the mixture was about 7. However, this did not work well for the acidic solution. In more acidic condition, the species of phosphate was probably dihydrogen phosphate. Since phosphate can have the buffering effect, the mixture of dihydrogen phosphate, monohydrogen phosphate, and metaphosphate ions will give pH around 7.

Table 2: Influence addition absorbent towards pH aqueous solution Cd.

<i>Cd²⁺ concentration (mg l⁻¹)</i>	<i>pH initial</i>	<i>Mass of LDH added (g)</i>	<i>Total Volume (mL)</i>	<i>pH final</i>
100	2.0	0.05	0.025	5.4
100	4.0	0.05	0.025	6.8
100	5.2	0.05	0.025	6.8
100	6.0	0.05	0.025	6.9
100	8.0	0.05	0.025	7.2
100	10.0	0.05	0.025	7.3

More proofs can be seen from the XRD pattern of the adsorbent after reaction. Compared to that before the reaction we observed that the main product of the reaction was hydroxyapatite-like material. This suggested that cadmium ion reacted with the interlayer phosphate anion to form cadmium phosphate having hydroxyapatite-like structure. Fig. 5 also revealed that there was major change in the structure of LDH after adsorption of Cd²⁺. The OH stretching narrowed after the adsorption. As well, vibration spectra of phosphate near 1000-1100 cm⁻¹ sharpened and narrowed.

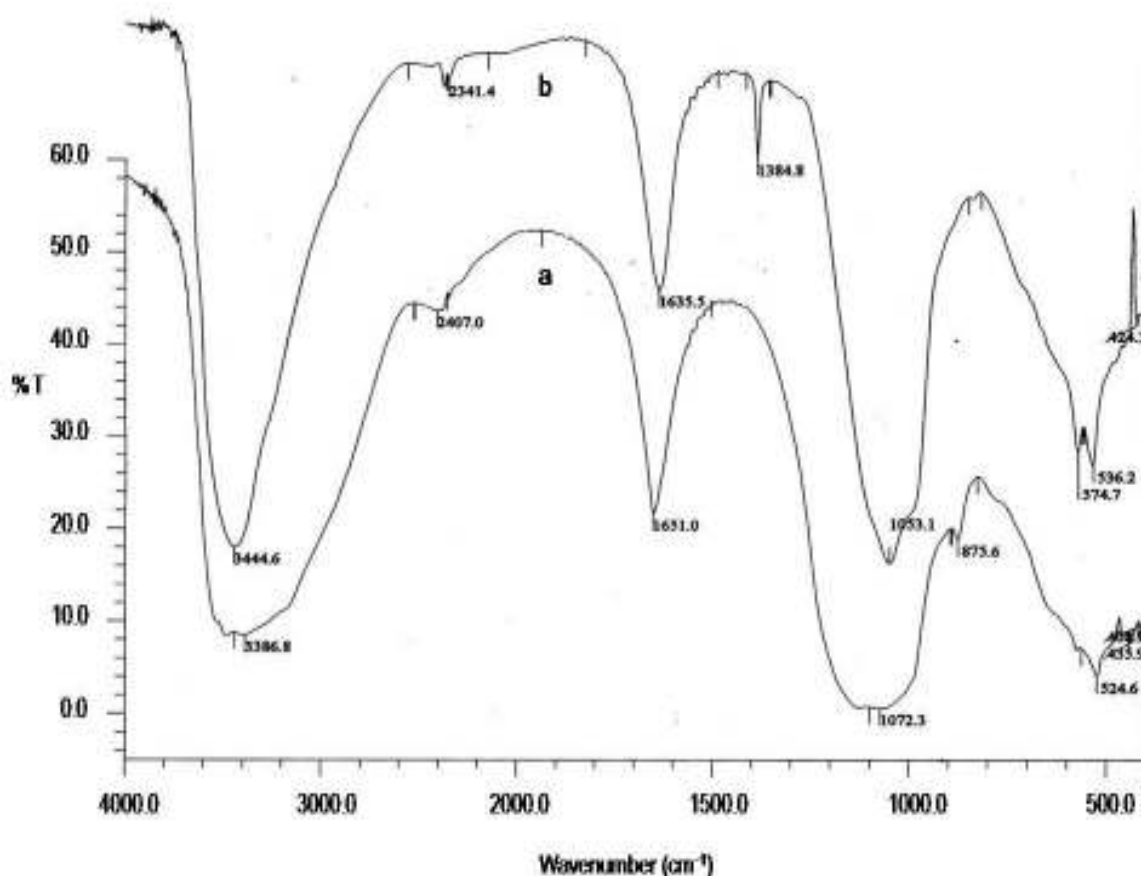


Fig. 5: FTIR spectra of Ca-Al-HPO₄ LDH before (a) and after (b) adsorption of Cd²⁺.

CONCLUSIONS

Synthesis of Ca-Al-HPO₄ LDHs can be performed by the direct co-precipitation method using salts of calcium and aluminum chloride and sodium hydrogen phosphate with suitable molar ratio. Ca-Al-HPO₄ layered double hydroxide is an efficient adsorbent for the adsorption of aqueous Cd²⁺. The estimated adsorption capacity is 600 mg g⁻¹ more than half of the weight of adsorbent itself. Adsorption of Cd²⁺ by Ca-Al-HPO₄ LDH is believed to happen due to formation of insoluble cadmium phosphate that has similar structure to hydroxyapatite as proven by XRD pattern and FTIR spectra.

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