

## PREPARATION OF LAYERED DOUBLE HYDROXIDES (LDHs) FOR ARSENATE AND CHROMATE REMOVAL

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### Abstract

Layer double hydroxides (LDHs) including MgFe-Cl (2:1), MgAl-Cl (2:1), ZnFe-Cl (2:1) and ZnAl-Cl (2:1) were synthesized by co-precipitation followed by calcination in air at 400 °C. The as-synthesized LDHs were characterized by powder X-Ray Diffraction, Scanning Electron Microscopy, Fourier Transform Infrared spectroscopy and Brunauer Emmett Teller nitrogen adsorption method and tested for adsorption of arsenate ( $\text{AsO}_4^{3-}$ ) and chromate ( $\text{CrO}_4^{2-}$ ). The powder X-Ray Diffraction and Scanning Electron Microscopy revealed that the synthesized LDHs possess high crystallinity and hierarchical structure. At initial concentration ( $[\text{AsO}_4^{3-}]$  or  $[\text{CrO}_4^{2-}] = 100 \text{ mg/L}$ ), more than 99 % of  $\text{AsO}_4^{3-}$  and  $\text{CrO}_4^{2-}$  were removed by MgFe-Cl and MgAl-Cl. Approximately 71.62 % of  $\text{AsO}_4^{3-}$  and 86.54 % of  $\text{CrO}_4^{2-}$  were removed by ZnAl-Cl. While the removal of  $\text{AsO}_4^{3-}$  and  $\text{CrO}_4^{2-}$  by ZnFe-Cl were 78.33 % and 90.7 %, respectively. Thus, present work has demonstrated that MgFe-Cl and MgAl-Cl is an interesting potential adsorbent application for  $\text{AsO}_4^{3-}$  and  $\text{CrO}_4^{2-}$  decontamination technology.

**Keywords.** Layered double hydroxides, arsenate, chromate, removal.

### 1. INTRODUCTION

Layered double hydroxides (LDHs) or hydrotalcite-like compounds are a class of nanostructured anionic clays. The general formula of LDHs is  $[\text{M}_{1-x}\text{M}_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  is the divalent cation,  $\text{M}^{3+}$  is the trivalent cation,  $x$  is the molar ratio of  $\text{M}^{3+}/(\text{M}^{2+}+\text{M}^{3+})$ , and  $\text{A}$  is the interlayer anion of valence  $n$ . LDHs consist of positively charged brucite-like sheets which are balanced by the intercalation of anions in the hydrated interlayer regions [1, 2]. LDHs have many applications in a variety of areas such as adsorbent, drug delivery, controlled release of herbicide, etc. LDHs have been used as such or (mainly) after calcination, the most interesting properties after calcination are large surface area, good anion exchange capacities and regeneration ability [1, 3, 4]. Due to these properties it's ensured that this

adsorbent can be excellently utilized in wastewater purification [5].

LDHs have number of advantages over other materials for environment remediation applications, as they are nontoxic, cheap and easily to prepare. Recently, LDHs have been successfully used as adsorbents for removal a variety pollutants, such as phosphate [6-10], nitrate [11-15], chromate [16-19], selenate and arsenate [20-24]. These studies have shown that feasibility of using LDHs for scavenging oxyanion in drinking water and industrial wastewater.

In this work, by taking advantage of the characteristic "reconstruction effect" of LDHs material, LDHs were synthesized by co-precipitation followed by calcination in air at 400 °C. Then, these synthesized materials were characterized by using various method including SEM, XRD, IR, BET. Furthermore, arsenate and chromate removals by

these materials were evaluated.

## 2. EXPERIMENTAL

### 2.1. Chemical

All chemicals were of analytical grade. The iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), Aluminum chloride hexahydrate ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ), Magnesium chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), Zinc chloride ( $\text{ZnCl}_2$ ), Sodium hydroxide ( $\text{NaOH}$ ), Sodium arsenate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ) and Potassium chromate ( $\text{K}_2\text{CrO}_4$ ) were purchased from Xilong Chemical Factory, Guang Dong and Shanghai Chemical Company.

### 2.2. Preparation of LDHs powder

LDHs containing MgFe-Cl, MgAl-Cl, ZnFe-Cl and ZnAl-Cl with Mg/Fe, Mg/Al, Zn/Fe, Zn/Al molar ratio of 2 were prepared by co-precipitation method using aqueous solution of  $\text{MgCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{AlCl}_3$  and  $\text{FeCl}_3$ . The solutions containing precursor compounds (Mg/Fe, Mg/Al, Zn/Fe, Zn/Al) were added dropwise at 2ml/min into alkali solution of 1M NaOH ( $\text{pH} = 11 \pm 0.2$ ) at  $65 \pm 5$  °C under vigorous stirring at 400 rpm. The pH of the solution was maintained at 11 by addition 2M NaOH. The mixture was then aged at 65 °C for 24 hours in mother liquor. The obtained materials were centrifuged, washed and dried at 65 °C for 24 h and then calcined at 400 °C for 4 h in an electric muffle furnace (Vulcan 3-103).

### 2.3. Characterization of LDHs powder

X-ray diffraction (XRD) patterns of materials were recorded on a Bruker D8 Advance diffractometer. The patterns with the  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54051$  Å) at 40 kV and 40 mA were recorded in the region of  $2\theta$  from 5° to 70°. Specific surface area (BET surface area) of materials was measured with Quantachrome Autosorb 1 apparatus. Scanning Electron Microscopy (SEM) images were obtained using JEOL microscope with an accelerating voltage of 20 kV. Fourier Transform Infrared (FT-IR) spectra were recorded using KBr pallet technique in the region  $4000\text{-}400$   $\text{cm}^{-1}$  on a Bruker Vector 22 spectrometer.

### 2.4. Arsenate and chromate adsorption

The arsenate ( $\text{AsO}_4^{3-}$ ) and chromate ( $\text{CrO}_4^{2-}$ ) sorption experiments were conducted with 0.5 g of LDHs powder in 100 mL solution at concentration of

$\text{AsO}_4^{3-}$  or  $\text{CrO}_4^{2-}$  100 mg/L. The studies were carried out at ambient temperature ( $28 \pm 2$  °C). All experiments were performed in triplicate. Contact time was set at 8 h; the samples were taken and filtered through a 0.45  $\mu\text{m}$  membrane filter. The concentration of  $\text{AsO}_4^{3-}$  and  $\text{CrO}_4^{2-}$  were analyzed by atomic absorption spectrometry (AAS, Shimadzu 6800, Japan). The sorption capacity ( $q$ ,  $\text{mg} \cdot \text{g}^{-1}$ ) was calculated using the following equation:

$$q = \frac{C_i - C_f}{m} \times V \quad (1)$$

where  $C_i$  ( $\text{mg L}^{-1}$ ) is the initial concentration of the arsenate or chromate in solution;  $C_f$  ( $\text{mg L}^{-1}$ ) is the final arsenate or chromate concentration in aqueous phase,  $V$  (L) is the volume and  $m$  (g) is the mass of the adsorbent.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of materials

XRD patterns of as-synthesized and calcined LDHs materials are shown in Figs. 1 and 2, respectively. It is obviously seen that almost all diffraction peaks were sharp and symmetrical, indicating a good crystallinity. Several characteristic peaks were located at  $11.20^\circ$  (003),  $22.50^\circ$  (006),  $35^\circ$  (009) and  $60^\circ$  (110) (Fig.1), which can be indexed to typical brucite-like LDH materials [25]. These peaks are consistent with the report data [26]. The basal spacing and BET surface areas of materials are presented in table 1.

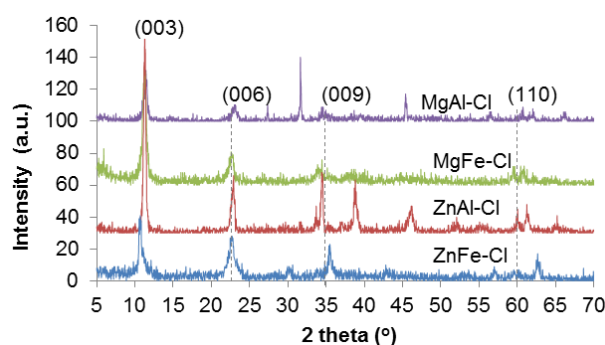


Figure 1: XRD patterns of as-synthesized LDHs

The morphology of materials is shown in Fig. 3. SEM images proved that MgFe-Cl and MgAl-Cl had a polygon structure which has similar shape with ZnAl LDH [26], while ZnFe-Cl and ZnAl-Cl materials had a rod structure.

FT-IR spectra of MgFe-Cl, MgAl-Cl, ZnFe-Cl and ZnAl-Cl are displayed in Figure 4. The board

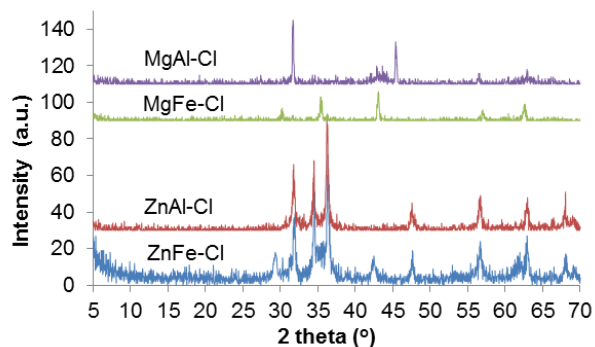


Figure 2: XRD patterns of LDHs calcined at 400 °C

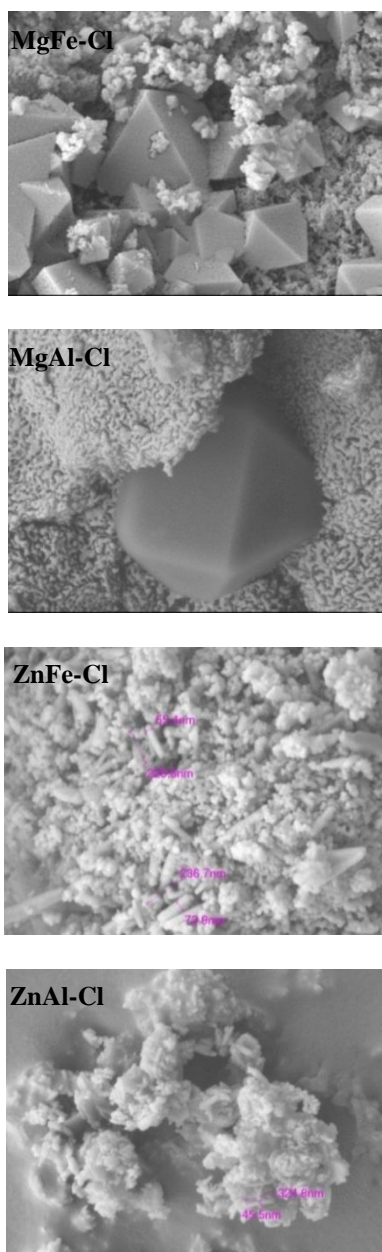


Figure 3: SEM images of as-synthesized LDHs (magnification, X 30 000; bar, 100 nm)

absorption bands in these compounds appeared in the ranges of 3417-3451  $\text{cm}^{-1}$  and 1627-1635  $\text{cm}^{-1}$

which belongs to the stretching vibration of structure -OH groups and bending vibration of H-O-H, respectively [26].

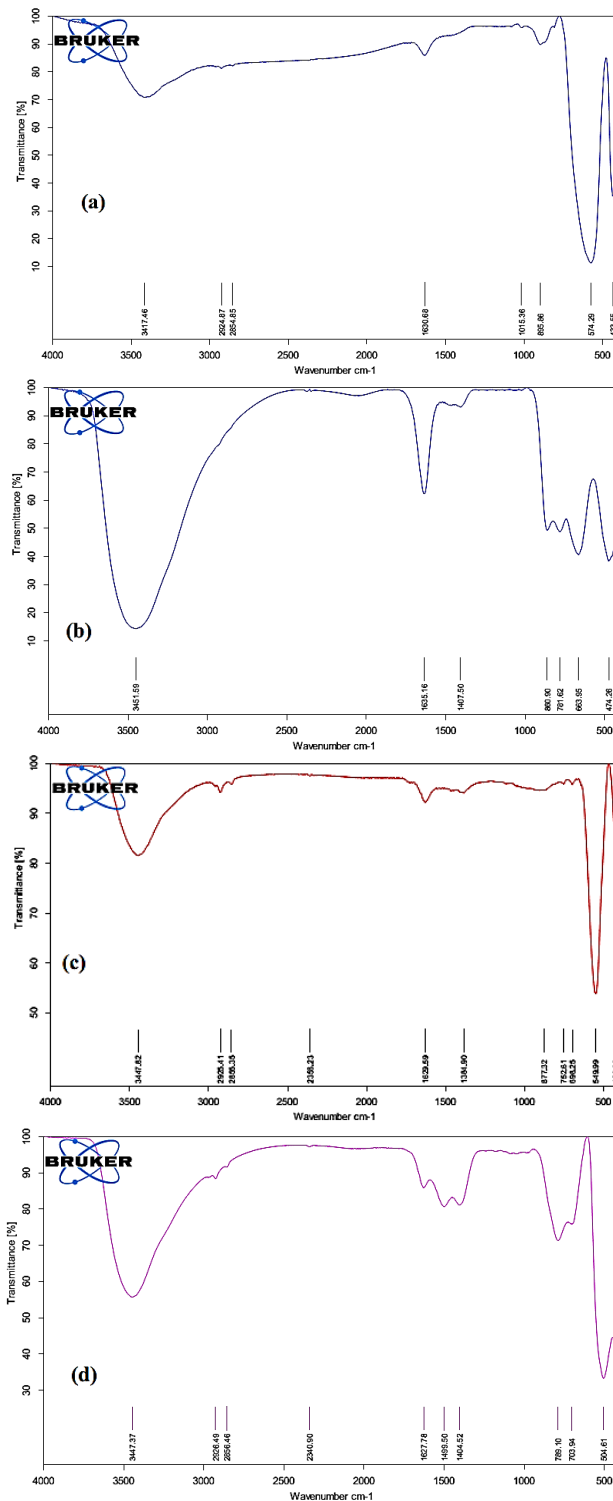


Figure 4: FT-IR spectra of as-synthesized LDHs (a) MgFe-Cl, (b) MgAl-Cl, (c) ZnFe-Cl, (d) ZnAl-Cl

An intense broad band at 3417-3451  $\text{cm}^{-1}$  might be due to physically adsorbed water. The spectrum of these compound showed an intense band at

around 860-895  $\text{cm}^{-1}$  associated with the chloride ion vibration [27]. A weak peak recorded at 2926 - 2924  $\text{cm}^{-1}$  has been ascribed to the OH stretching mode of inter layered water molecules [28]. The lattice stretching and bending vibrations ascribed to O-M and O-M-O bonds were also observed at absorption band below 800  $\text{cm}^{-1}$ .

Table 1: Basal spacing  $d_{003}$  and BET surface area of materials

Materials	$d_{003}$ (Å)	BET surface area ( $\text{m}^2/\text{g}$ )
MgFe-Cl	7.835	49.02
MgAl-Cl	7.711	52.80
ZnFe-Cl	7.836	49.00
ZnAl-Cl	7.580	47.30

### 3.2. Arsenate and chromate adsorption

The adsorption of  $\text{AsO}_4^{3-}$  and  $\text{CrO}_4^{2-}$  by synthesized LDHs was evaluated at constant initial concentration ( $[\text{AsO}_4^{3-}]$  or  $[\text{CrO}_4^{2-}] = 100 \text{ mg/L}$ ). The results for removing  $\text{AsO}_4^{3-}$  and  $\text{CrO}_4^{2-}$  as well as sorption capacity of synthesized LDHs are presented in table 2.

Table 2:  $\text{AsO}_4^{3-}$  and  $\text{CrO}_4^{2-}$  adsorption on LDHs (mean value,  $n = 3$ )

Materials	% removal	$q$ (mg/g)
$\text{AsO}_4^{3-}$		
MgFe-Cl	99.97	20.00
MgAl-Cl	99.91	20.00
ZnFe-Cl	78.33	15.66
ZnAl-Cl	71.62	14.33
$\text{CrO}_4^{2-}$		
MgFe-Cl	99.04	19.81
MgAl-Cl	99.40	19.90
ZnFe-Cl	90.70	18.14
ZnAl-Cl	86.54	17.31

The results of this study has shown that the removal efficiency of  $\text{AsO}_4^{3-}$  and  $\text{CrO}_4^{2-}$  by MgFe-Cl and MgAl-Cl were significantly high, more than 99 %. The sorption capacity of MgFe-Cl and MgAl-Cl were about 20 mg/g for  $\text{AsO}_4^{3-}$  and 19.8-19.9 mg/g for  $\text{CrO}_4^{2-}$ . While ZnAl-Cl removed about 71.62 % and 86.54 % for  $\text{AsO}_4^{3-}$  and  $\text{CrO}_4^{2-}$ , respectively.

Sorption capacity of ZnAl-Cl was 14.33 mg/g for  $\text{AsO}_4^{3-}$  and 17.31 mg/g for  $\text{CrO}_4^{2-}$ . In case of ZnFe-Cl,  $\text{AsO}_4^{3-}$  removal rate was about 78.33 % while it was about 90.7 % for  $\text{CrO}_4^{2-}$ . Sorption capacity of ZnFe-Cl was 15.66 mg/g for  $\text{AsO}_4^{3-}$  and 18.14 mg/g for  $\text{CrO}_4^{2-}$ . It has been observed from previous studies that the capacities of  $\text{MgAlCO}_3$  LDH for chromate adsorption of  $\sim 17 \text{ mg/g}$  [17] and arsenate adsorption range from 15.8 to 32.6 mg/g [24]. Therefore, MgFe-Cl and MgAl-Cl in this study demonstrated excellent  $\text{AsO}_4^{3-}$  and  $\text{CrO}_4^{2-}$  sorption efficiency.

### 4. CONCLUSION

Layered double hydroxides (LDHs) including MgFe-Cl, MgAl-Cl, ZnFe-Cl and ZnAl-Cl has been successfully synthesized by coprecipitation method. The XRD, SEM of these LDHs illustrated high crystallinity. The above findings indicate that both MgFe-Cl and MgAl-Cl are an interesting potential adsorbent which is suitable for further exploration in order to fully realize its application to  $\text{AsO}_4^{3-}$  and  $\text{CrO}_4^{2-}$  decontamination technology.

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