Microporous and Mesoporous Materials 234 (2016) 230–238

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

# A novel CoFe layered double hydroxides adsorbent: High adsorption amount for methyl orange dye and fast removal of Cr(VI)

Faling Ling [a, b], Liang Fang [a, c, *], Yi Lu [a, d], Jiemei Gao [a], Fang Wu [a, **], Miao Zhou [b], Baoshan Hu [e]

[a] *State Key Laboratory of Mechanical Transmission, College of Physics, Chongqing University, Chongqing, 400044, PR China*
[b] *College of Optoelectronic Engineering, Chongqing University, Chongqing, 400044, PR China*
[c] *Institute of Materials Science and Engineering, Sichuan University of Science and Engineering, Zigong, Sichuan Province, 643000, PR China*
[d] *National Engineering Research Center for Magnesium Alloys, College of Materials Science and Engineering, Chongqing University, Chongqing 400044, PR China*
[e] *College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 401331, PR China*

## ARTICLE INFO

*Article history:*
Received 4 April 2016
Received in revised form
17 June 2016
Accepted 10 July 2016
Available online 12 July 2016

*Keywords:*
CoFe-Layered double hydroxides
Adsorption
Methyl orange
Cr(VI)

## ABSTRACT

CoFe-nitrate-layered double hydroxides (LDHs) with $Co^{2+}/Fe^{3+}$ molar ratios of 2, 3 and 4 were synthesized by a simple co-precipitation method. The as-prepared CoFe-LDHs exhibited a high adsorption activity to the methyl orange (MO) dye and Cr(VI). The adsorption characteristics including adsorption kinetics and isothermals were investigated. Structure analysis of the as-synthesized LDHs before and after adsorption revealed that adsorption proceeds in two processes: external surface adsorption and interlayer anion exchange. The results of MO adsorption experiments showed that LDHs with $Co^{2+}/Fe^{3+}$ molar ratios of 4 worked best with the largest MO adsorption amount up to 1290 mg/g at an initial concentration of 300 mg/L due to the porous structures. We have also noted that Cr(VI) in a range of 2–25 mg/L can be quickly removed with the maximum adsorption capacity of 27.62 mg/g in the initial 5 min, much faster than other LDH materials. Therefore, CoFe-LDHs are potential cost-effective adsorbents for both MO dye and Cr(VI).

## 1. Introduction

Industrial effluents are one of the major causes of environmental pollution, especially dyes discharged from various industrial processes, such as food, paper, carpet rubber, plastics, cosmetics, and textile [1–3], and heavy metal derived from metal finishing and leather tanning activities [4]. Among these effluents, MO dye and Cr(VI) are commonly identified hazardous contaminant because of their hazards to the aquatic ecosystem and human beings [5–7]. Moreover, the nondegradable nature and stability toward light and/or oxidizing agents of dyes and the mobility of Cr(VI) complicate the selection of a suitable method for removal [8,9]. For these reasons, economic and effective techniques to remove MO and Cr(VI) from wastewaters have been sought urgently in recent years.

Several techniques have been employed to remove dyes and Cr(VI) from wastewater systems. In terms of dyes removal, the most widely used methods include biological treatment, coagulation, chemical oxidation, ozonation, membrane filtration, ion exchange methods, photo-catalysis, and adsorption [10]. For Cr(VI) removal, the most commonly applied treatment techniques are adsorption over activated carbons, clay materials and modified ones, oxide/hydroxide nanomaterial, precipitation with soluble chemicals, and bioprocesses [11]. Among all these techniques, the adsorption process is the preferred method, while other methods suffer from drawbacks like high capital and operational cost and problems in disposal of the residual metal-containing sludge [12]. LDHs, known as anion exchange clay materials, can be considered as potential cost-effective adsorbents for removal of hazardous anions in drinking water and industrial wastewater. LDHs can be nominally expressed as the chemical formula: $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot H_2O$, where $M^{2+}$ ($Ca^{2+}$, $Mg^{2+}$, $Zn^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, etc.) represents any divalent metal

---

* Corresponding author. Chongqing University, College of Physics, Chongqing 400044, PR China.
** Corresponding author.
*E-mail addresses:* lfang@cqu.edu.cn (L. Fang), fang01234@163.com (F. Wu).

http://dx.doi.org/10.1016/j.micromeso.2016.07.015

cations, $M^{3+}$ ($Al^{3+}$, $Fe^{3+}$, $Ga^{3+}$, $Cr^{3+}$, etc.) any trivalent metal cations and $A^{n-}$ any anions (inorganic or organic) [10], and *x* is the molar ratios between divalent and trivalent cations $M^{3+}/(M^{2+}+M^{3+})$ in the range 0.2–0.33. LDHs consist of cationic brucite-like layers and exchangeable interlayer anions, where a portion of the divalent cations is replaced by trivalent cations. The positive charges, as a result of isomorphous substitution of trivalent cations for divalent cations, are balanced by interlayer anions that can be exchanged for other anions [13–15]. Since the relatively large specific surface areas (30–150 $m^2/g$), high charge density (25–50 $Å^2$ per charge) and exchangeable interlayer anions [16], LDHs are considered as good anion exchangers to adsorb anionic organic and inorganic pollutants from water.

Nowadays, LDHs have become a research focus to remove various pollutants in water. Ai et al. [17] synthesized a MgAl-LDH with an MO adsorbent capacity of 148 mg/g, and the MgNiAl-LDH prepared by Hassina et al. [18] showed an increased MO adsorption amount to 375 mg/g. Moreover, LDO (layered double oxide, derived from calcination of LDH) and LDH-based nano-composites used as adsorbents have been reported by numerous researches. Zhang et al. [19] found that Au/ZnAl-LDO can effectively adsorb MO with a capacity of 627.51 mg/g. And the calcined graphene/MgAl-LDH nanocomposite obtained by Yuan et al. [20] can remove Cr(VI) with the capacity up to 172.55 mg/g. Although the adsorption performance of LDHs has been gained thorough calcinations or compositing with other materials, the high cost and difficulty to operate limit their practical application. Therefore, developing new binary LDHs with low cost and sample operation is quite essential. To the best of our knowledge, adsorption performance of MO dye and Cr(VI) by CoFe-LDH is still unknown. Thus, in this work, CoFe-LDHs with different $Co^{2+}/Fe^{3+}$ molar ratios were prepared by a simple co-precipitation method. The morphology and structure of the obtained LDHs were carefully investigated and the removal behaviors of MO and Cr(VI) were evaluated.

## 2. Experimental

### 2.1. Materials

All chemicals were of reagent grade. $Co(NO_3)_2 \bullet 6H_2O$, $Fe(NO_3)_3 \bullet 9H_2O$ and $K_2Cr_2O_7$, were purchased from Aladdin (Shanghai, China). Ammonia ($NH_3 \bullet H_2O$, 25–28%), and methyl orange ($C_{14}H_{14}N_3O_3SNa$, >80.0%) were purchased from Chongqing Chuandong Chemical Co Ltd, China. All the chemicals were used in our experiments without further treatment. All solutions were prepared using deionized (DI) water.

### 2.2. Preparation of samples

Our CoFe-nitrate-LDHs are designated as Co*X*Fe1-LDH, where *X* is the $Co^{2+}/Fe^{3+}$ molar ratios in the synthesis mixture. Co*X*Fe1-LDH ($X = 2$, 3 and 4) compounds with different $Co^{2+}/Fe^{3+}$ molar ratios were synthesized by the co-precipitation method. In a typical procedure, 20 mL of the solutions containing $Fe(NO_3)_3 \bullet 9H_2O$ and $Co(NO_3)_2 \bullet 6H_2O$ were prepared with the desired $Co^{2+}/Fe^{3+}$ molar ratios, reaching a total cation concentration of 1.0 M. Aqueous alkali was prepared by dissolving 0.05 mol of ammonia aqueous solution in 100 mL of deionized water. Afterwards, the mixed salt solution was added dropwise into the basic alkaline solution at a rate of 2 mL/min under constant stirring condition. The mixture was stirred for 30 min after the addition. The resulting suspensions were aged at 65 °C for 18 h, stirring constantly. Precipitates were separated by centrifugation, washed thoroughly with deionized water several times to remove the unreacted nitrates, and the wet solid was dried in an oven at 65 °C for 24 h to collect the solid Co*X*Fe1-LDH product.

### 2.3. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded using a Bruker D8 Advance diffractometer under the following conditions: 40 kV, 40 mA, Cu Ka ($\lambda = 0.154$ nm). Elemental analysis of metals in LDHs was performed using an inductively coupled plasma optical emission spectroscopy (ICP-OES; Thermo Scientific ICAP 6300 Duo) at the Analysis Centre of Chongqing University. Prior to analysis, as-synthesized samples were dried once again at 65 °C for 2 h, and solutions were prepared by dissolving the samples in nitric acid (1:1). The specific surface area and pore size distribution measurements were obtained with a Quantachrome instrument. $N_2$ gas was introduced as the adsorbate at 77.3 K. The Brunauer–Emmett–Teller (BET) method was adopted to measure the specific surface area by a multipoint method, and the Barrett–Joyner–Halenda (BJH) desorption method was employed to calculate the pore size distribution [10]. Samples were degassed at 150 °C for 23 h to remove any adsorbed species before analysis. The structure and morphology of the samples were investigated by transmission electron microscopy (TEM, ZEISS LIBRA 200). The samples were prepared by dropping LDH powder dispersed in ethanol onto commercially available TEM grids (Ted Pella, lacey carbon 300 mesh Cu grids) using micropipettes and were dried under ambient conditions. Fourier transform infrared (FT-IR) spectra (KBr pellets, 1 mg in 100 mg of KBr) were recorded in the range 4000–400 $cm^{-1}$ on a Nicolet iS50 Fourier transform spectrometer. The spectra were taken using a DTGS KBr detector with an optical resolution of 8 $cm^{-1}$ and 40 scans.

### 2.4. Adsorption experiments

Prior to adsorption, the samples were grounded for 30 min in an agate ball mill to produce fine particles which are in the size range of a few hundred nanometers. Batch adsorption experiments were carried out under constantly magnetic stirring at 250 rpm in air with bottles open under condition of continuous darkness. In order to keep a constant ambient temperature (25 ± 1 °C), the beakers were put into a container with water at constant 25 °C. For MO adsorption, solutions with different concentrations (5–300 mg/L) of MO were prepared in advance. The adsorption experiments were conducted by adding 20 mg adsorbents powder in 100 mL ready-prepared MO solution with initial indicated concentrations. After an appropriate time intervals, the suspensions were centrifuged. The dye concentrations in the supernatants were measured by UV–visible spectrophotometer (UV-3600 Shimadzu, Japan) at 464 nm. Various Cr(VI) concentration solutions were prepared by dissolving $K_2Cr_2O_7$ in distilled water. For Cr(VI) adsorption, adsorbents powder (20 mg) was used to adsorb Cr(VI) at a concentration from 2 to 25 mg/L. The subsequent procedure was similar to that for MO adsorption noted earlier. The concentrations of Cr(VI) in the supernatant were determined with ICP.

The adsorption capacity ($Q_t$) and removal percentage (*R%*) of the adsorbents were calculated according to the following equations [21].

$$Q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

$$R = 100 \times \frac{(C_0 - C_t)}{C_0} \tag{2}$$