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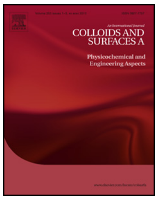


Preparation of Fe(II)–Al layered double hydroxides: Application to the adsorption/reduction of chromium

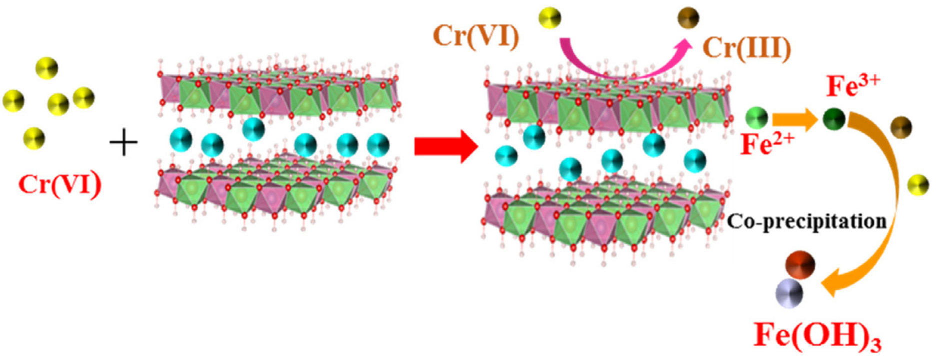
Xin He, Xinhong Qiu*, Jinyi Chen*

School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Hubei 430073, China

HIGHLIGHTS

- Fe–Al LDH showed good performances in the adsorption and reduction of Cr(VI).
- The sorption mechanism of by Fe–Al LDH was explored and proposed.
- A competitive adsorption between Cr(VI) and humic acid was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

Chromium is highly toxic and readily soluble in water. Herein, Fe(II)–Al layered double hydroxides (LDH) with Fe:Al ratios of 2:1 (LDH-2) and 3:1 (LDH-3) were synthesized by a hydrothermal synthesis method. The resulted products were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Brunauer–Emmett–Teller (BET) measurements, scanning electron microscopy (SEM), thermogravimetric analysis coupled with differential scanning calorimetry (TG/DSC), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). Highly crystalline forms with sheet structure were revealed by XRD and TEM results, while the BET surface area of the LDH-2 and LDH-3 materials were 46.85 and 53.22 m^2/g, respectively. In addition, both products showed good performances in the removal of Cr(VI), although the removal efficiency of LDH-2 was higher than that of LDH-3. Based on the characterization results, two different removal mechanism involving both adsorption and reduction processes were proposed. The Fe^{2+} ions in LDH were involved in reducing Cr(VI) to Cr(III) while simultaneously being oxidized to Fe^{3+}. pH was found to influence the adsorption of Cr(VI), with higher pH values being beneficial to the removal process. Common anions present in the environment such as SO_4^{2-}, NO^{3-}, and CO_3^{2-} showed minor influence in the adsorption performance of the LDH materials. A competitive adsorption between Cr(VI) and humic acid (HA) was observed. The crystalline structure of LDH-2 collapsed after adsorption of very high concentrations of Cr(VI), thereby demonstrating once again that Fe involved in the lamination of LDH-2 was dissolved out to a large extent promoting the Cr(VI) to Cr(III) process.

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* Corresponding authors.
E-mail addresses: qxinhong@gmail.com (X. Qiu), jychwit@163.com (J. Chen).

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1. Introduction

Chromium is highly toxic and the US Environmental Protection Agency (EPA) has issued a maximum limit of $0.1\,mg\,L^{-1}$ for total chromium in drinking water [1]. Cr(VI) is harmful to human body as it causes skin erosion, respiratory infections, and even cancer via contact with air, water, and food. Once inside the human body, Cr(VI) is transformed into Cr(III) inside the red blood cell, thereby restraining the activity of the glutathione reductase, converting hemoglobin into methemoglobin, and altering the oxidation–reduction and hydrolytic processes [2–5].

Many treatment technologies for chemical industry wastewaters containing Cr(VI) have been developed including adsorption, biological, and membrane filtration methods. Owing to the higher demand of biological methods to the external environment and the complexity of microbial proliferation, the biological methods are not widely applied in the treatment of industrial wastewaters containing Cr(VI) [6]. Membrane filtration methods seriously suffer from lack of resistance of the membranes to the harsh conditions typically found in industry wastewaters (e.g., acid, alkali, and oil). On the other hand, the adsorption method is widely applied worldwide owing to its low cost and better removal efficiency for Cr(VI) [7]. Commonly used absorbents include activated carbons [8], chitosan [9], chelate resins [10], oxide or hydroxide compound material [11,12] and clay minerals, among others. Also, those adsorbents cannot only use for the heavy metal pollution, but also can be used for organic contaminates. For example, Fei et al. [13] used the porous iron hydroxide and oxide hierarchical nanostructures for removing dyes from wastewater and Xuan et al. reported a self-propelled janus silica micromotor can separate different charged organics [14]. But for the Cr(VI), Among the different adsorbents, clay minerals are interesting materials owing to their abundance, environment protection, and reusability characteristics [15–17].

As a kind of anionic clays, layered double hydroxides (LDH) have superior removal efficiency for anionic pollutants. Their general formula is $[M^{2+}{}_{1\text{-}x}M^{3+}{}_{x}(OH)_2]^{X+}(A^{n-})_{x/n}{\bullet}mH_2O$, with M^{2+} and M^{3+} being metal cations such as Mg^{2+} and Al^{3+} [18]. A fraction of the M^{2+} ions are octahedrally restructured, with hydroxyl ions being replaced with M^{3+} and resulting in positively charged sheets. The anions in the interlayer compensate for the net positive charge. A wide variety of M^{2+}, M^{3+}, X, and A^{n-} species has generated a large number of iso-structural materials with varying physical and chemical properties. Therefore, LDH have been widely applied as adsorbents [22,23], catalysts [24,25], and polymer stabilizers [26].

Compared to Cr(III), Cr(VI) is more virulent and pernicious [19]. Common LDH like Mg–Al/LDH and Ca–Al/LDH adsorb Cr(VI) while being inactive for the transformation of Cr(VI) into less toxic Cr(III). LDH materials able to simultaneously perform adsorption/reduction of Cr(VI) require M^{2+} species having reducibility characteristics. Since both M^{2+} and M^{3+} can be replaced by different metal ions, LDH with different capacity can be prepared by replacing M^{2+} and M^{3+} species [20,21]. As previously described, Fe^{2+} can be transformed into Fe^{3+} via loss of an electron which is used for the Cr(VI) to Cr(III) process [27–29].

In this study, Fe(II)–Al-LDH (Fe:Al = 2:1, LDH-2) and Fe(II)–Al-LDH (Fe:Al = 3:1, LDH-2) were synthesized by a hydrothermal synthesis method [30]. The resulted products were characterized by several techniques and subsequently applied to the removal of Cr(VI). The removal mechanism of Cr(VI) was carefully discussed based on the X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron microscopy (XPS), and Fourier transform infrared spectroscopy (FTIR) results of solid residues. In addition, several factors with influence such as the pH and the co-existence of anions and humic acid (HA) during the removal process were also studied.

2. Materials and methods

2.1. Chemicals

Ferrous chloride ($FeCl_2{\cdot}4H_2O$), aluminum chloride ($AlCl_3{\cdot}6H_2O$), potassium dichromate ($K_2Cr_2O_7$), diphenylcarbazide ($C_{13}H_{14}N_4O$), acetone (C_3H_6O), sodium carbonate (Na_2CO_3), sodium nitrate ($NaNO_3$), sodium sulfate (Na_2SO_4), and sodium hydroxide (NaOH) were of analytical reagent grade and used as received (Sinopharm Chemical Reagent Co., Ltd., China).

2.2. Methods

2.2.1. Synthesis of Fe(II)–Al-LDH

Fe^{2+}-Al-LDH were synthesized by a hydrothermal synthesis method. The LDH sample with a Fe:Al molar ratio of 2:1 was synthesized with 8.0 g (0.040 mol) of $FeCl_2{\cdot}4H_2O$ and 4.8 g (0.020 mol) of $AlCl_3{\cdot}6H_2O$. 4.8 g of $AlCl_3{\cdot}6H_2O$ and 8.0 g of $FeCl_2{\cdot}4H_2O$ were successively dissolved in 150 mL of deionized water (900 rpm, 25 °C) while adding 4 mol/L of a NaOH solution to create an alkaline reaction environment. The as-generated turbid solution was transferred into 100 mL Teflon tubes and brought to a draught drying cabinet at 120 °C for 24 h as soon as the pH was 7. In order to get the solid product, the generated precipitated was centrifuged, washed for 3 times, and subsequently dried at 40 °C for 12 h. For the synthesis LDH samples with a Fe:Al molar ratio of 3:1, 9.0 g of $FeCl_2{\cdot}4H_2O$ and 3.6 g of $AlCl_3{\cdot}6H_2O$ were used. The LDH samples were denoted as LDH-m, with m representing the Fe/Al molar ratio (m = 2 and 3). The samples were conserved under anaerobic environment.

2.2.2. Extraction and characterization of HA

HA was extracted from a black soil previously grinded at a screen mesh of 60 after and dried at low temperature. A certain amount of black soil was put into a beaker and a 0.5 mol/L HCl solution was added into the soil at a solid to liquor mass–volume ratio of 10. The mixture was stirred at room temperature for 5 h. The supernatant was subsequently removed after standing the mixture for 5 h. The remaining residue was centrifuged at 10,000 rpm for 5 min. The soil was isolated after washing 3 times with deionized water. A 0.4 mol/L NaOH solution was subsequently added into the above soil at a solid to liquor mass–volume ratio of 10. After 5 h of stirring and 5 h of standing, the mixture was filtered to get the roux solution containing HA. A 6 mol/L HCl solution was added to the roux solution to fix the pH at 2 resulting in the precipitation of HA, which was collected for using in this experiment.

The FTIR spectrum of HA is shown in Fig. 1. The two small peaks observed at around 1400 and $1200\,cm^{-1}$ were likely ascribed to the C—O stretching vibration of hydroxyl and carboxyl groups. In addition, the band at around $1600\,cm^{-1}$ was assigned to the C=C stretching vibration of an aromatic ring skeleton. The broad band at around $3300\,cm^{-1}$ was attributed to the O—H stretching vibration of carboxylic and alcoholic groups. Thus, these results indicated that HA contained hydroxyl, alkyl, carbonyl, and methoxy functional groups that determine the complexation ability of HA with Cr or Fe ions [31].

2.2.3. Adsorption experiments

Adsorption experiments were carried out with LDH-2 and LDH-3 in a 1 mmol/L $K_2Cr_2O_7$ solution. The pH of the $K_2Cr_2O_7$ solution was adjusted to 7.00 using 1 mol/L NaOH before adding the LDH samples. Subsequently, 0.05 g of LDH was added to 15 mL of the $K_2Cr_2O_7$ solution followed by shaking at 150 rpm and 25 °C in a shaking incubator. Sampling was carried out at 15, 30, 60, and 90 min. The supernatants were filtered with a sand core filter unite (0.45 μm). The concentrations of Cr(VI) and Cr(III) were measured by an ultraviolet-visible (UV–vis) spectrophotometer