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High performance NiFe layered double hydroxide for methyl orange dye and Cr(VI) adsorption

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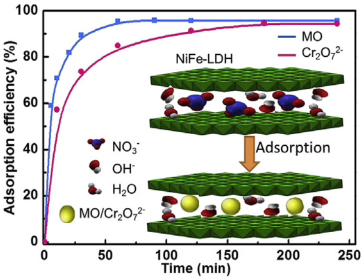
HIGHLIGHTS

- NiFe-LDHs were synthesized from non-noble salt solutions by coprecipitation method.
- NiFe-LDH is an effective adsorbent for the removal of MO and $Cr_2O_7^{2-}$ in aqueous solutions.
- The adsorption mechanisms of MO and Cr(VI) were proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

The NiFe layered double hydroxides (LDHs) with different mole ratio of Ni/Fe (4:1, 3:1, 7:3 and 1:1) were prepared by a simple coprecipitation method. The adsorption performance were evaluated by the removal of methyl orange (MO) dye and hexavalent chromium(VI) heavy metal ion. It is found that Ni_4Fe_1-LDH can remove more than 92% of MO in 10 min at the 10 mg/L MO initial concentration, and 97% of Cr(VI) in 1 h at 4 mg/L $Cr_2O_7^{2-}$ initial concentration. The saturated adsorption capacity of Ni_4Fe_1-LDH is found to be as large as 205.76 mg/g for MO and 26.78 mg/g for Cr(VI). The adsorption behavior of this new adsorbent is fitted well with Langmuir isotherm and the pseudo-second-order kinetic model, indicative of a monolayer and chemical adsorption that synergistically originates from exchangeable anions mechanism and layer charge density. Due to the excellent removal capacity of MO and Cr(VI), the NiFe-LDHs could be a promising adsorbent for wastewater treatment.

1. Introduction

Environment pollution is one of the three biggest social problems around the world. Wastewater effluents from industries containing synthetic dyes and heavy metals cause a potential hazard to the environment. Therefore, a variety of techniques such

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as adsorption, chemical decomposition, microbiological decoloration, have been developed to remove dyes and heavy metals in wastewater (Rafatullah et al., 2010; Swaminathan et al., 2013; Kornaros and Lyberatos, 2006). Due to the low initial cost, simple design, ease of operation and insensitive to toxic substances, adsorption is considered to be a very effective and superior separation technique for water treatment. Conventionally, bentonite (Lian et al., 2009), activated carbon (Ghaedi et al., 2013), zeolites (Faki et al., 2008) and inorganic nanoparticles (Wang et al., 2012; Bai et al., 2012) have been used to remove dyes from wastewater, but their uptake capacity are low and they usually adsorpt only a few special species of contaminants. Thus, it is still indispensable to exploit some novel adsorbent materials with higher adsorption and capacity to capture a range of pollutants adsorbates in aqueous solutions.

As a specific layered 2D structure material, layered double hydroxides (LDHs) have been received considerable attention for their potential application in the fields of catalysts, drug delivery materials, adsorption and flame retardants (Sherman, 2015). LDH materials can be represented by the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent metal cations (Mg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, etc.) and trivalent metal cations (Al^{3+}, Fe^{3+}, Ga^{3+}, Cr^{3+}, etc.), respectively. The cations occupy the octahedral sites within the hydroxide layers. x is the molar ratio of trivalent cations, $M^{3+}/(M^{2+}+M^{3+})$, with various values between 0.2 and 0.33, while A^{n-}(Cl^-, OH^-, NO_3^-, SO_4^{2-}, etc.) is the interlayer anion with charge (Ma et al., 2012a; Ai et al., 2011). As adsorbents, due to high surface area, facile manipulation of adsorption sites (electronic density, alkaline intensity) and morphology/pore structure, LDHs provide the possibility of a high adsorption capacity. MO and $Cr_2O_7^{2-}$, which are anionic dye and anionic metal contaminants in aqueous solutions, were often used to study the adsorption performance of LDHs. For example, Ni et al. (2007) prepared ZnAl-layer double oxides (LDO) with a capacity of 181.9 mg/g for the adsorption of MO. An Au/ZnAl-LDO nanocomposite was reported to increase the MO adsorption capacity to 627.51 mg/g (Zhang et al., 2013). And the calcined graphene/MgAl-LDH was found to remove Cr(VI) with capacity of 172.55 mg/g (Yuan et al., 2013). Although the Au/ZnAl-LDH system and graphene/MgAl-LDH have significantly improved their adsorption performance, they are so expensive and difficult to prepare, disadvantageous to the broad application. NiFe-LDH is a classical material in electrocatalysis (Tang et al., 2014) and can be synthesized by different growth methods, such as hydrothermal synthesis (Saiah et al., 2009) and solvothermal method (Sherman, 2015). To the best of our knowledge, the removal of MO and $Cr_2O_7^{2-}$ by NiFe-LDH has not been reported in other papers.

In present work, a simple method and non-noble metals (Ni, Fe) salt solution were used to synthesize high performance NiFe-LDH materials. The morphology and structure of the LDHs were investigated and the adsorption capacity of MO and $Cr_2O_7^{2-}$ were evaluated. This could provide some basic information for the treatment of actual wastewater.

2. Experimental section

2.1. Preparation of NiFe-LDHs

$Ni_{1-x}Fe_x$-NO_3-LDHs with different molar ratio ($x = 0.2, 0.25, 0.3, 0.5$) were prepared by co-precipitation method and marked as Ni_4Fe_1-LDH, Ni_3Fe_1-LDH, Ni_7Fe_3-LDH, Ni_1Fe_1-LDH, respectively. Specifically, 20.0 mL of metal salt solution containing $Ni(NO_3)_2\cdot 6H_2O$ and $Fe(NO_3)_3\cdot 9H_2O$ (99%, Aladdi, Shanghai, China) were added into a vigorously stirred ammonia (25–28%, Aladdi, Shanghai, China) solution (100.0 mL, 0.5 M) drop by drop. The total concentrations of cations in the salt solution were maintained at 1.0 M. The obtained suspension (yellow brown precipitate) was stirred mechanically for a further 18 h at 65 °C, then centrifuged and washed thoroughly with deionized water, and finally dried overnight at 60 °C under vacuum. The characterization methods are presented in the Supplementary Material.

2.2. Adsorption experiments

In order to study the adsorption kinetics, batch adsorption experiments were carried out by adding 20 mg NiFe-LDH samples into 100 mL MO solution, whose initial concentrations ranging from 10 to 180 mg/L. The mixture was stirred at room temperature and dark place during the adsorption process. The concentrations of MO in the supernatant before and after adsorption were determined using a UV–visible spectrophotometer (UV-3600 Shimadzu, Japan) at 464 nm. The equilibrium adsorption capacity (q_e) and the MO removal efficiency ($R\%$) were evaluated by using the equations (1) and (2) (Wang et al., 2012):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

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

where C_0 and C_e (mg/L) are the initial and equilibrium concentration of MO, C_t is the concentration of MO at time t, m (g) is the mass of the adsorbent, and V (L) is the volume of solution. In the adsorption of Cr(VI), the initial concentrations of $Cr_2O_7^{2-}$ were ranged from 4 to 20 mg/L and the concentrations of Cr(VI) were measured by ICP. Adsorption experiments were replicated at each tested condition and average values were reported.

3. Results and discussion

3.1. Characterization of as-synthesized NiFe-LDHs

The crystallite phases of NiFe-LDHs with different molar ratio were illustrated in Fig. 1a. The sample b, c and d (Ni/Fe = 7:3, 3:1 and 4:1, respectively) display the characteristic diffraction peaks of well crystallized hydrotalcite-like LDH materials (JCPDS no. 40-0215) (Saiah et al., 2009) with a series of (00*l*) harmonics at low angle. But the sample a (Ni/Fe = 1:1) has a tendency to form amorphous compounds, indicating that the reevesite structure LDHs were easy to be achieved with the molar ratio (x) between 0.2 and 0.33 by the coprecipitation method. The calculated lattice parameters of the as-synthesized samples assuming a 3R stacking ($c = 3d_{(003)}$ and $a = 2d_{(110)}$) (Bookin and Drits, 1993) are shown in Table S1. The cell parameter a, a function of the average radii of the metal cations value, decreases with increasing the Fe^{3+} content. This effect may be explained, beared in mind that a divalent cation Ni^{2+} (0.69 Å) in the lattice was replaced by a smaller trivalent cation Fe^{3+} (0.550 Å for low spin configuration or 0.645 Å for high spin configuration), thus leading to a decrease of unit-cell volume (Zhao et al., 2002). The lattice parameter c does not enhance with the increase of Ni/Fe molar ratio, which attributed to the size, number, strength and orientation of the bonds between the anions and the hydroxyl groups in the LDH layer (Uzunova et al., 1994). The different aspect ratios between the values of a and c in each sample with different metal contents indicate that the crystalline domains were not equivalent in all crystallographic directions. The layer charge density augments with the increase of Fe^{3+} content, so the area per unit charge decreases from 0.3937 nm^2 to 0.3047 nm^2 as the content of Fe^{3+} increases from 20 at.% (Ni:Fe = 4:1) to 30 at.%