Preparation of NiFe-LDHs Adsorbent and Its Adsorption to Methyl Orange

Xiang Zhang, Chenyong Jiang, Ruoxuan Wang, Shuyun Qian, Ye Tang, Wenchang Zhuang and Yan Xu *
School of Chemistry and Chemical Engineering, Xuzhou University of Technology, Xuzhou, China

*Corresponding author e-mail: xuyuan@xzit.edu.cn

Abstract. The Ni-Fe-LDHs adsorbent with different molar ratio of Ni/Fe was synthesized with Ni(NO₃)₂ and Fe(NO₃)₃ serving as the resource of metal ions and the ammonia water serving as the precipitant. The methyl orange (MO) was chosen to simulate the dye wastewater to study the adsorption ability of different adsorbent to MO. And XRD, FT-IR and BET were employed to characterize the prepared adsorbents. The experimental results show that LDHs with well crystalline structure can be obtained when the mole ratio of Ni/Fe of 2.3~4. The Ni₄Fe adsorbent with the Ni/Fe molar ratio of 4 shows the largest adsorbing capacity of 168.4 mg/g to MO. The XRD results of the spent adsorbent show that the LDHs structure was not destroyed. And the BET result of the fresh Ni₄Fe adsorbent proves that it is possessed with microstructure with the surface area of 125.325 m²/g.

1. Introduction

With the rapid development of chemical industry, the problem of water pollution is becoming more serious. The pollutants in water including toxic organic matter, heavy metals, ammonia nitrogen, and so on, can harm the organisms in the water, accumulate in the organisms, transmit through the food chain, and endanger human health [1]. Dye wastewater with large amount has high content of organic pollutants, which is one of the most difficult industrial waste to be treated. The common methods used to treat the dye sewage include chemical oxidation method, photocatalytic method, membrane separation, biodegradation process, and so on [2, 3]. However, these methods usually require a complex reaction system with high cost. Adsorption is an effective technology because of its low cost and insensitivity to toxic substances [4].

Hydrotalcite compounds (LDHs) are bimetallic hydroxides with layered structure, which have been widely studied in catalysis, adsorption, electrochemistry and other fields [5, 6]. LDHs are usually composed of two different valence cations (divalent and trivalent) and interlayer anions. The general formula of LDHs is $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}(\text{A}^n)^{-n/2}\cdot m\text{H}_2\text{O}$. It is reported that under alkaline conditions, LDHs compounds can be formed when the solution contains divalent metal ions and trivalent metal ions with similar radius [7]. Due to the adjustability of the divalent and trivalent metal cations, as well as the intercalation anions, LDHs can realize a variety of molecular assembly, applying to different fields. Wang et al. prepared the Fe₃O₄/Ni-Fe-LDHs by in-situ growth method, and it showed good adsorption
performance to organic dyes [8]. In this paper, NiFe-LDHs was prepared by coprecipitation method, and the effect of Ni/Fe molar ratio on its structure and adsorption performance was investigated.

2. Experimental

2.1. Reagents and instruments
Ni(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O and methyl orange (MO) used in this experiment are analytically pure, and the deionized water is self-made in the laboratory. X-ray powder diffractometer (XRD, ultima IV, Japan Science Company), infrared spectrometer (FT-IR, ALHPA, Germany Brooke company), physical adsorption instrument (BET, Autosorb iQ, USA conta instrument company), ultraviolet visible spectrophotometer (UV-5800P, Shanghai Yuanxi Instrument Co., Ltd) are employed to character the properties and adsorption ability of the sample.

2.2. Preparation of adsorbent
The preparation of NiFe-LDHs adsorbent is as follows: firstly, a certain amount of Ni(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O is dissolved in 20 mL deionized water (the total concentration of metal cations in the solution is 1 mol/L, and the molar ratio of Ni and Fe is 1:1, 2.3:1, 3:1, 4:1, respectively). Then, 100 mL, 0.5 mol/L ammonia solution is quickly added, followed by aging at 65 ℃ for 20 h under stirring condition. After that, the precipitates were centrifuged, and washed several times to neutral with deionized water and anhydrous ethanol. The obtained sample was dried at 80 ℃ for 24 h to prepare NiFe-LDHs adsorbents. According to the different molar ratio of Ni and Fe, the prepared adsorbents were labeled as Ni₁Fe, Ni₂.₃Fe, Ni₃Fe and Ni₄Fe, respectively.

2.3. Adsorption capacity test
In order to eliminate the interference of temperature and light conditions on the adsorption properties of the samples, the adsorption experiments were carried out under the conditions of avoiding light and 30 ℃ water bath. 50 mL of MO solution (100 mg/L) was used to simulate the waste, and 100 mg of adsorbent is used. After stirring the above suspension at 200 r/min of stirring speed for a period of time, 5 mL of sample was taken and measured by UV-Vis spectrophotometer to obtain its concentration. The adsorption rate (removal rate) of MO on the adsorbent was calculated by the following formula:

\[ R\% = \frac{(C_0 - C_t)}{C_0} \times 100\% \]  

Where, R% is the removal rate; C₀ is the initial MO concentration, mg/L; Cₜ is the concentration of MO at different time, mg/L.

3. Results and discussion

The MO removal rate of different adsorbents is shown in Figure 1. It can be seen that it increases with the extension of time. In the first 30 min, the MO removal rate increases rapidly, and then slows down. After 180 min, it approaches the adsorption equilibrium. At this time, the MO removal rates of Ni₁Fe, Ni₂.₃Fe, Ni₃Fe and Ni₄Fe adsorbents are 80.3%, 71.6%, 76.9% and 84.2% respectively, corresponding to the adsorption capacity to MO are 160.6 mg/g, 143.2 mg/g, 153.8 mg/g and 168.4 mg/g respectively.

The XRD spectra of the fresh adsorbent are shown in Figure 2a. It can be seen that the characteristic peaks of the hydrotalcite structure (JCPDS No. 40-0215) at 2θ = 11.5°(003), 22.9°(006), 34.8° (012) and 60.7° (110) [9] are obtained on Ni₂.₃Fe, Ni₃Fe and Ni₄Fe samples, indicating that hydrotalcite structure can be formed when the molar ratio of Ni/Fe is 2.3 ~ 4. And the low peak intensity of Ni₁Fe compound indicates the low crystallinity. In addition, the peak intensity increases with the increase of Ni/Fe molar ratio, suggesting that hydrotalcite compounds with higher crystallinity, better regularity and symmetry can be formed when Ni/Fe molar ratio is higher. It is pointed out that hydrotalcite materials have good adsorption capacity to the hydrolytic electronegative pollutants, and its adsorption capacity is related to the charge density and van der waals force of the laminate. Increasing the charge density on the laminate, the distance between adsorbed MO molecules decreases and the density increases, leading to the increasing van der Waals force. Hence, it is difficult for MO molecules to further adsorb on the
laminate of hydrotalcite materials. Therefore, in this work, although the charge density of Ni$_4$Fe adsorbent is small and the adsorption active sites are fewer, fewer Mo molecules are adsorbed. As a result, the van der Waals force between the molecules is smaller, which is conducive to the further adsorption of Mo molecules on the hydrotalcite laminate. For Ni$_1$Fe sample, its adsorption capacity is higher than that of Ni$_{2.3}$Fe and Ni$_3$Fe, which should be due to the larger charge density and more active sites. The FT-IR results of fresh adsorbent are shown in Figure 2b. It can be seen that the FT-IR spectra of all adsorbents are similar. The absorption peak at 3447 cm$^{-1}$ is the expansion vibration peak of O-H on the laminate, and the absorption peak at 1640 cm$^{-1}$ is the bending vibration peak of O-H on the laminate. The absorption peak at 1384 cm$^{-1}$ is the asymmetric expansion vibration peak of NO$_3^-$. In addition, the absorption peak below 800 cm$^{-1}$ is mainly caused by Ni-O, Ni-O-Ni, Fe-O, Fe-O-Fe and Ni-O-Fe on the laminated plates [10]. It can be inferred that NO$_3^-$ deriving from metal nitrate is the interlayer anion of the prepared adsorbent. Ammonia provides the alkaline environment and interlayer OH$^-$ ion. The molecular formula of the prepared sample in this work is [Ni$_{1-x}$Fe$_x$(OH)$_2$]$^x$$(\text{NO}_3)_x$, where X is 0.5, 0.3, 0.25 and 0.2, respectively, corresponding to the Ni/Fe molar ratio of 1/1, 2.3/1, 3/1 and 4/1.

The N$_2$ isothermal adsorption-desorption curve of the fresh Ni$_4$Fe adsorbent is shown in Figure 3. It is the type IV isotherm in IUPAC classification, which is the mesoporous structure with a hysteresis loop caused by capillary condensation in the region of low relative pressure. The porous structure may be formed by the accumulation of lamellar structure of Ni$_4$Fe hydrotalcite. And the specific surface area, average pore size and pore volume of the prepared Ni$_4$Fe adsorbent are 125.325 m$^2$/g, 3.4 nm and 0.029 cc/g, respectively. So it has better adsorption performance.
Figure 3. The N\textsubscript{2} adsorption - desorption of Ni\textsubscript{4}Fe

The XRD spectra of the spent adsorbent are shown in Figure 4. It can be seen that, consistent with the fresh adsorbent, Ni\textsubscript{2.3}Fe, Ni\textsubscript{3}Fe and Ni\textsubscript{4}Fe adsorbents have obvious hydrotalcite structural with characteristic peaks at 2\(\theta\) = 11.5°(003), 22.9°(006), 34.8°(012) and 60.7°(110). It is worth noting that the diffraction peak intensity of fresh Ni\textsubscript{4}Fe adsorbent is significantly higher than that of Ni\textsubscript{3}Fe, and they are almost the same after MO adsorption, which may be due to MO replacing part of the interlayer anions, affecting the regularity and symmetry of its structure.

Figure 4. The XRD patterns of the spent adsorbents

4. Conclusion
NiFe-LDHs with nitrate as interlayer anion were prepared with Ni(NO\textsubscript{3})\textsubscript{2} and Fe(NO\textsubscript{3})\textsubscript{3} as divalent and trivalent metal cation sources and ammonia as precipitant. The experimental results show that the hydrotalcite structure could be formed when the Ni/Fe ratio is 2.3 ~ 4, and the crystallinity increase with the increase of Ni/Fe ratio. When the Ni/Fe ratio was 1, the diffraction peak intensity is low and broad, which might be the amorphous structure. And there is a close relationship between the adsorption capacity to MO and the charge density, as well as the van der Waals force in the NiFe-LDHs. The charge density of Ni\textsubscript{4}Fe is smaller, and the van der Waals force between adsorbed MO molecules is also smaller, which is conducive to the further adsorption of MO on the laminate. Therefore, Ni\textsubscript{4}Fe has the highest adsorption performance for MO in this work.

Acknowledgments
This work was financially supported by the innovation and entrepreneurship training program of college student of Xuzhou University of Technology (xcx2020137), the Natural Science Foundation of Jiangsu
Province (BK20171168, BK20171169), Natural Science Foundation of Jiangsu Higher Education Institutions of China (17KJB530010, 17KJB150038 and 18KJA430015).

References
[1] Z. Tang, K. Tong, S. Xie, et al. Experimental Study on Adsorption of U(VI) by Mesoporous Molecular Sieve Fe-MCM-41 and Cu-MCM-41, Sci. Technol. Eng. 18 (2018) 193-198.
[2] L. Cheng, M. Wei, L. Huang, et al. Efficient H2O2 Oxidation of Organic Dyes Catalyzed by Simple Copper(II) Ions in Bicarbonate Aqueous Solution. Ind. Eng. Chem. Res. (53) 2014 3478-3485
[3] H. Wang, X. Yuan, Y. Wu, et al. Synthesis and applications of novel graphitic carbon nitride/metal-organic frameworks mesoporous photocatalyst for dyes removal. Appl. Catal. B: Environ. 174 (2015) 445-454.
[4] X. Tao, D. Liu, W. Cong, Controllable synthesis of starch-modified ZnMgAl-LDHs for adsorption property improvement, Appl. Surf. Sci. 457 (2018) 572-579.
[5] F. Khodam, Z. Rezvani, A.R. Amani-Ghadim, Enhanced adsorption of Acid Red 14 by co-assembled LDH/MWCNTs nanohybrid: Optimization, kinetic and isotherm. J. Ind. Eng. Chem. 21 (2015) 1286-1294.
[6] S. Gundekari, K. Srinivasan, In situ generated Ni(0)@boehmite from NiAl-LDH: An efficient catalyst for selective hydrogenation of biomass derived levulinic acid to γ-valerolactone, Catal. Commun. 102 (2017) 40-43
[7] H. Chen, Z. Zhan, Synthesis, characterization and catalysis of Co-Ni-Fe hydrotalcite like compounds, Chem. Res. Appl. 18 (2009) 1189-1192.
[8] W. Wang, H. Yu, Y. Xu, et sl. Influence of Ni:Fe ratio on the adsorption of Fe3O4/Ni-Fe-LDHs hierarchical structure[J]. New Chem. Mater. 46 (2018) 211-213.
[9] Y. Xu, Y. Chen, J. Li, et al, Improved low-temperature activity of Ni-Ce/γ-Al2O3 catalyst with layer structural precursor prepared by cold plasma for CO2 methanation, Int. J. Hydrogen Energ. 42 (2017) 13085-13091.
[10] J. Nandhini, P. Neeraja, S.R.J Rajkumar, et al, Comparative Studies of Microwave and Sol-Gel-Assisted Combustion Methods of NiFe2O4 Nanostructures: Synthesis, Structural, Morphological, Opto-magnetic, and Antimicrobial Activity[J]. J. Supercond. Nov. Magn. 30 (2016) 1-8.