Methyl Orange Adsorption by Fe₂O₃@Co-Al-Layered Double Hydroxide [†]

Edris Jamshidi and Faranak Manteghi *

Department of Chemistry, Iran University of Science and Technology, Tehran 1684613114, Iran; edj439@gmail.com

* Correspondence: f_manteghi@iust.ac.ir

[†] Presented at the 23rd International Electronic Conference on Synthetic Organic Chemistry, 15 November 2019–15 December 2019; Available online: <https://ecsoc-23.sciforum.net/>.

Published: 26 January 2020

Abstract: A magnetic composite consisting of iron oxide and a cobalt–aluminum-layered double hydroxide, Fe₂O₃@Co-Al-layered double hydroxide was prepared through linking of Fe₂O₃ to Co-Al layered double hydroxide (LDH) by sodium acetate. Layered double hydroxides are generally described as [M²⁺_{1-x}M³⁺_x(OH)₂] [Aⁿ⁻_{x/n}·mH₂O], where M²⁺ and M³⁺ are divalent and trivalent metal cations, respectively, and A is an n-valent interlayer guest anion. The composite was characterized by XRD, FTIR and UV-Vis. spectroscopy methods. Afterwards, the composite was used for methyl-orange adsorption in aqueous solution. The UV-Vis spectrum indicates that the adsorption process was satisfying. In effect, after several washings of the composite, no decrease of the adsorption capacity was observed.

Keywords: composite; Fe₂O₃@Co-Al LDH; methyl orange; adsorption

1. Introduction

Environmental pollution is one of the three biggest social problems all over the world. Industrial wastewaters containing artificial dyes and heavy metals are potential dangers for the environment [1]. Industrial sewerage is one of the environmental pollution reasons, specially the dyes, which are vacated from various industrial processes such as paper, plastic, textile and food industries. Among the dyes in wastewater, methyl orange is a very harmful contaminant for human and aquatic animals. [2] Therefore, different methods such as physical adsorption, chemical decomposition, and microbiological decomposition are developed for the elimination of dyes and heavy metals in wastewater.

Considering low costs, with a simple design, easy handling and no sensitivity to toxic materials, the adsorption is one of the most effective methods for water purification. Usually active carbon, zeolites, and mineral nanoparticles are used for dye elimination from wastewater. Thus, it is necessary to use materials with high absorbance capacity and a wide domain for contaminants in aqueous solutions.

Layered double hydroxides (LDHs) have a favorable adsorption capacity of dye molecules and can compete well with other adsorbants. LDHs have shown a high capability for dye elimination by adsorption [3].

By adding magnetic property to Co-Al LDHs, the collecting of the particles becomes much easier. LDHs are named as hydrotalcite-like materials (because of the structure similarity) or named anion clays and lamellar host–guest materials which are very rare in nature [3]

Most of the LDHs have a structure formula of [M(II)_{1-x}M(III)_x(OH)₂] (Aⁿ⁻)_{x/n}·H₂O, which is similar to the hydrotalcites formula, [Mg₃Al₂(OH)₂] CO₃·4H₂O. In the LDH formula, M(II) and M(III) are di-

and trivalent metals, respectively, $0.2 < x < 0.33$ and A^{n-} is the anion which is transferable between layers.

2. Experimental Method

2.1. Synthesis of $Fe_3O_4@CoAl$ LDH

Magnetic Fe_3O_4 microspheres were prepared by a modified solvothermal route [4]. Initially, 3.24 g of $FeCl_3 \cdot 6H_2O$ and 8.64 g of $CH_3COONa \cdot 3H_2O$ were dissolved in 80 mL of ethylene glycol at 313 K to form a clear brown solution under vigorous stirring [5]. The solution was sealed in a stainless steel reactor with polytetrafluoroethylene liner. The reactor was then heated for 8 h at 473 K. After cooling down, the resultant suspension was attracted by a magnet and then washed three times at intervals with deionized water and ethanol solution. The precipitate was dried at 333 K overnight to yield a black powder of Fe_3O_4 .

The magnetic core-shell $Fe_3O_4@CoAl$ LDH nanohybrid (abbreviated as $Fe_3O_4@LDH$) was synthesized by a coprecipitation method. Typically, appropriate amounts of $Co(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (with the molar ratio, $Co^{2+}/Al^{3+} = 3$) were dissolved in deionized water to obtain a solution with a total metal ion concentration of $0.5 \text{ mol} \cdot L^{-1}$. Then, a moderate amount of Fe_3O_4 powder ($3 \text{ g} \cdot L^{-1}$) was ultrasonically dispersed into the mixed salt solution for 5 min. An ammonia–water solution (volume ratio of 1:4) was slowly poured into the suspension under stirring until precipitation at pH 9–10, and then a precipitate was produced. After standing at room temperature for 1 h, the suspension was filtered and then washed four times with deionized water. The filter cake was sealed at 353 K in an oven for about 24 h, and $Fe_3O_4@LDH$ sol was obtained. Finally, the sol was dried at 353 K to yield a product of $Fe_3O_4@LDH$ powder.

2.2. Methyl Orange Adsorption

In this case, the effect of different parameters such as methyl orange first concentration, on the absorbance mass and contact time were studied. For the isotherm adsorption survey, all the experiments were completed at room temperature and in a dark environment by adding 10 mg of $Fe@Co-Al$ LDH to 30 mL of methyl orange solution with first concentration of 100, 250, 500, and 750, $1000 \text{ mg} \cdot L^{-1}$. Afterwards, the solution was shaken for 120 min in 300 rpm.

The methyl orange concentrations were measured before and after adsorption by UV-vis spectroscopy in 464 nm.

The adsorption capacity is an important factor which appoints the adsorption capacity for eliminating specific amounts of contaminants. The following Equations (1) and (2) state the contaminant elimination percentage:

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

in which C_0 ($\text{mg} \cdot L^{-1}$) and C_e ($\text{mg} \cdot L^{-1}$) are the first concentration and equivalent concentration of contaminants, respectively. V (mL) introduces as solution volume, m (g) as adsorbant mass and q_e (mg/g) as surface equivalent adsorption capacity [6].

2.3. Results and Discussion

The characterization of $Fe@Co-Al$ LDH and adsorption of methyl orange was performed by the following methods.

2.3.1. XRD Pattern

Figure 1 shows the XRD pattern which indicates that the $Fe@Co-Al$ LDH was directly synthesized. Two sharp peaks in different 2θ 9.98 and 20.13 were referred to (003) and (006) plates,

respectively. Wide peaks at 2θ 34.47, 39.54 and 26.28 were referred to (012), (015), (018) sheets and two peaks at 2θ 60.67 and 61.13 were attributed to (110) and (113) sheets.

Figure 1. The XRD pattern of Fe@Co-Al layered double hydroxide (LDH).

2.3.2. FTIR Spectrum

The FTIR spectrum of Fe@Co-Al LDH is shown in Figure 2. The widespread and intense band in the 3446 cm^{-1} area is due to the stretch vibrations of O–H groups present in the interlayer and water molecules which are in layers. The 1625 cm^{-1} is related to water bending vibrations. The sharp bands in 1379 cm^{-1} and 827 cm^{-1} are related to stretch and bending vibration of the interlayer nitrate anion, respectively. However, the band seen in 1357 cm^{-1} is related to CO_3^{2-} which is caused by existing CO_2 in deionized water [4].

Figure 2. FTIR spectrum of Fe@Co-Al LDH.

Along the adsorption on the outer surface, the interlayer NO_3^- ions are replaced with methyl orange by interlayer anion exchanges, as shown in Figure 3 [2].

Figure 3. The LDH structure and methyl orange adsorbed between the layers.

2.3.3. Scanning Electron Microscopy

The method was selected to investigate the morphology and particle size of Fe@Co-Al LDH. The result was shown in Figure 4, in which the particles have no distinct shape, but are relatively isomorph, additionally their sizes are in the range of 0.2–0.5 μm .

Figure 4. Figure caption. The SEM image of Fe@Co-Al LDH, with the size of particles

2.3.4. UV–Vis Adsorption Spectroscopy

UV-visible diagram based on changes of dye concentration according to adsorption is shown in Figure 5. The diagram shows that methyl orange has maximum absorbance in 464 nm and its absorbance is quenched after adsorption on Fe@Co-Al LDH. Actually, the concentration of methyl orange was 250, 500, and 1000 ppm, and the three higher curves were taken before adsorption, and the other three were taken after adsorption. The best result was for blue 500 ppm and 250 ppm of methyl orange which were totally adsorbed on Fe@Co-Al LDH.

Figure 5. UV-vis spectrum of methyl orange before and after absorption on Fe@Co-Al LDH

3. Conclusions

A composite of an LDH based on cobalt and aluminum with Fe_3O_4 was prepared and applied to remove methyl orange as a toxic and dangerous dye. The results of UV-vis spectroscopy shows that the best removal is for 250 and 500 ppm methyl orange which is completely adsorbed on the composite.

References

1. Jiang, Y.L.B.; Fang, L.; Ling, F.; Gao, J.; Wu, F.; Zhang, X. High performance NiFe layered double hydroxide for methyl orange dye and Cr (VI) adsorption. *Chemosphere* **2016**, *152*, 415–422.
2. Ling, F.; Fang, L.; Lu, Y.; Gao, J.; Wu, F.; Zhou, M.; Hu, B. A novel CoFe layered double hydroxides adsorbent: High adsorption amount for methyl orange dye and fast removal of Cr (VI). *Microporous Mesoporous Mater.* **2016**, *234*, 230–238.
3. Jaiswal, A.; Gautam, R.K.; Chattopadhyaya, M.C. Layered Double Hydroxides and the Environment: An Overview. *Advanced Materials for Agriculture, Food, and Environmental Safety* **2014**, 1–26, doi:10.1002/9781118773857.ch1.
4. Deng, Y.H.; Wang, C.C.; Hu, J.H.; Yang, W.L.; Fu, S.K. Investigation of formation of silica-coated magnetite nanoparticles via sol-gel approach. *Colloids Surf. A Physicochem. Eng. Asp.* **2005**, *262*, 87–93.
5. Palmer, S.J.; Frost, R.L.; Nguyen, T. Hydrotalcites and their role in coordination of anions in Bayer liquors: Anion binding in layered double hydroxides. *Coord. Chem. Rev.* **2009**, *253*, 250–267.
6. Li, Y.; Bi, H.Y.; Mao, X.M.; Liang, Y.Q.; Li, H. Adsorption behavior and mechanism of core-shell magnetic rhamnolipid-layered double hydroxide nanohybrid for phenolic compounds from heavy metal-phenolic pollutants. *Appl. Clay Sci.* **2018**, *162*, 230–238.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).