

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

Edris Jamshidi¹, Faranak Manteghi^{1,*}

¹Department of Chemistry, Iran University of Science and Technology, Tehran, Iran

*f_manteghi@iust.ac.ir

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 LDH by sodium acetate. Layered double hydroxides are generally described as $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A_{n-x/n} \cdot mH_2O]$, 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 in all over the world. Industrial wastewaters containing artificial dyes and heavy metals are potential dangers for environment [1]. Industrial sewerage is one of the environmental pollution reasons, specially the dyes which vacated from various industrial processes like 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 dyes and heavy metals elimination in wastewater.

Considering low cost, simple design, easy working and not being sensible to toxic materials, the adsorption is using as one of the most effective methods for water purification. Usually active carbon, zeolites and mineral nanoparticles are using for dye elimination from wastewater. So it is necessary to use materials with high absorbance capacity and wide domain for contaminants in aqueous solutions.

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

By adding magnetic property to Co-Al LDHs, 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 so rare in nature. [3]

Most of the LDHs have structure formula of $[M(II)_{1-x}M(III)_x(OH)_2](A^{n-})_{x/n} \cdot H_2O$, which is similar to hydrotalcites formula, $[Mg_6Al_2(OH)_2]CO_3 \cdot 4H_2O$. 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 ethylene glycol at 313 K to form a clear brown solution under vigorously 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 Fe₃O₄.

Magnetic core-shell Fe₃O₄@CoAl LDH nanohybrid (abbreviated as Fe₃O₄@LDH) was synthesized by a coprecipitation method. Typically, the appropriate amounts of Co(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O (with the molar ratio, Co²⁺/Al³⁺=3) were dissolved in deionized water to obtain a solution with a total metal ion concentration of 0.5 mol·L⁻¹. Then, a moderate amount of Fe₃O₄ powder (3 g·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 Fe₃O₄@LDH sol was obtained. Finally, the sol was dried at 353 K to yield a product of Fe₃O₄@LDH powder.

2-2. Methyl orange adsorption

In this case, the effect of different parameters such as methyl orange first concentration, absorbance mass and contact time were studied. For isotherm adsorption survey, all the experiments have done in room temperature and in 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 mg·L⁻¹. Afterwards, the solution was shaken for 120 min in 300 rpm.

Methyl orange concentration were measured before and after adsorption by UV-vis spectroscopy in 464 nm.

Adsorption capacity is an important factor which appoints the adsorption capacity for eliminating specific amount 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 (mg.L^{-1}) and C_e (mg. 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

Fe@Co-Al LDH characterization

Figure 1 shows 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.

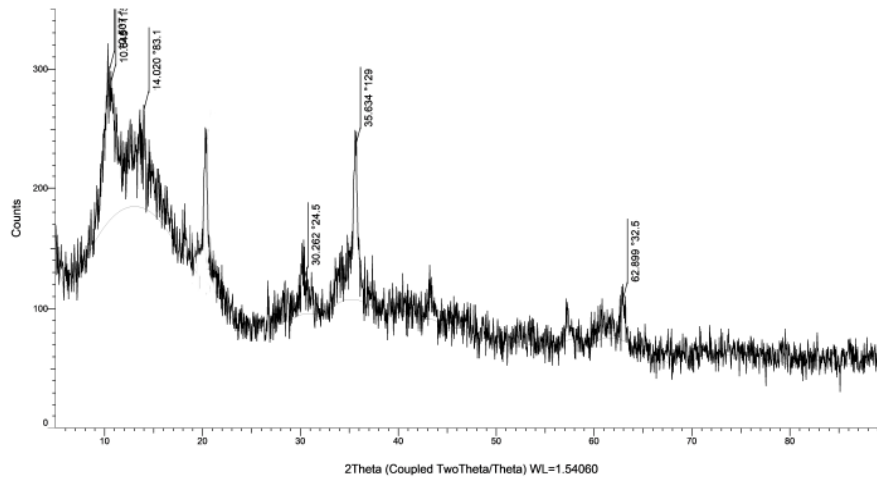


Figure 1. The XRD pattern of Fe@Co-Al LDH

The FTIR spectrum of Fe@Co-Al LDH was 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 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]

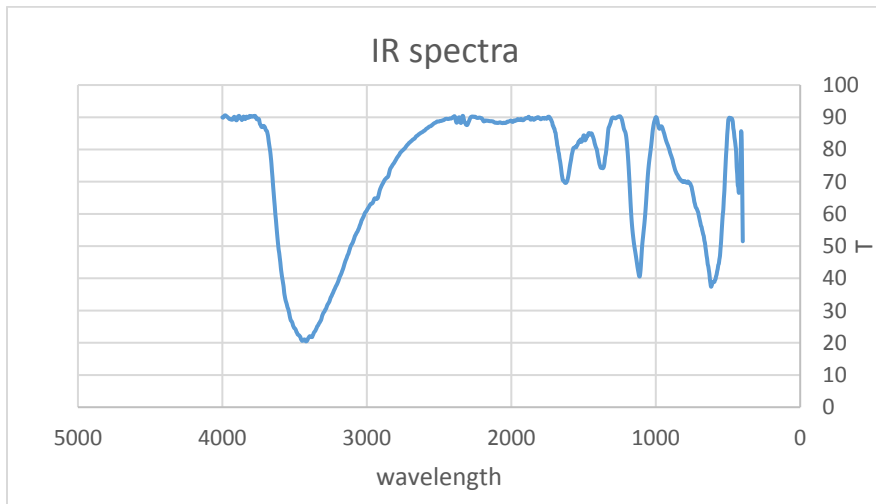


Figure 2. FTIR spectrum of Fe@Co-Al LDH.

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]

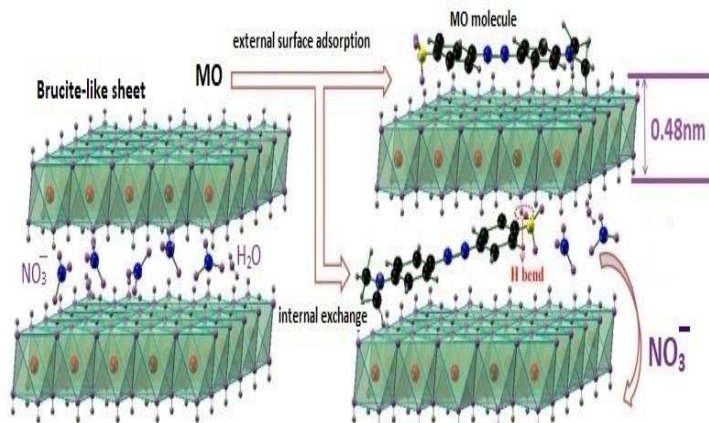


Figure 3. The LDH structure and methyl orange adsorbed between the layers

UV-vis Adsorption diagram

UV-visible diagram based on changes of dye concentration according to adsorption is shown in figure 4. 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.

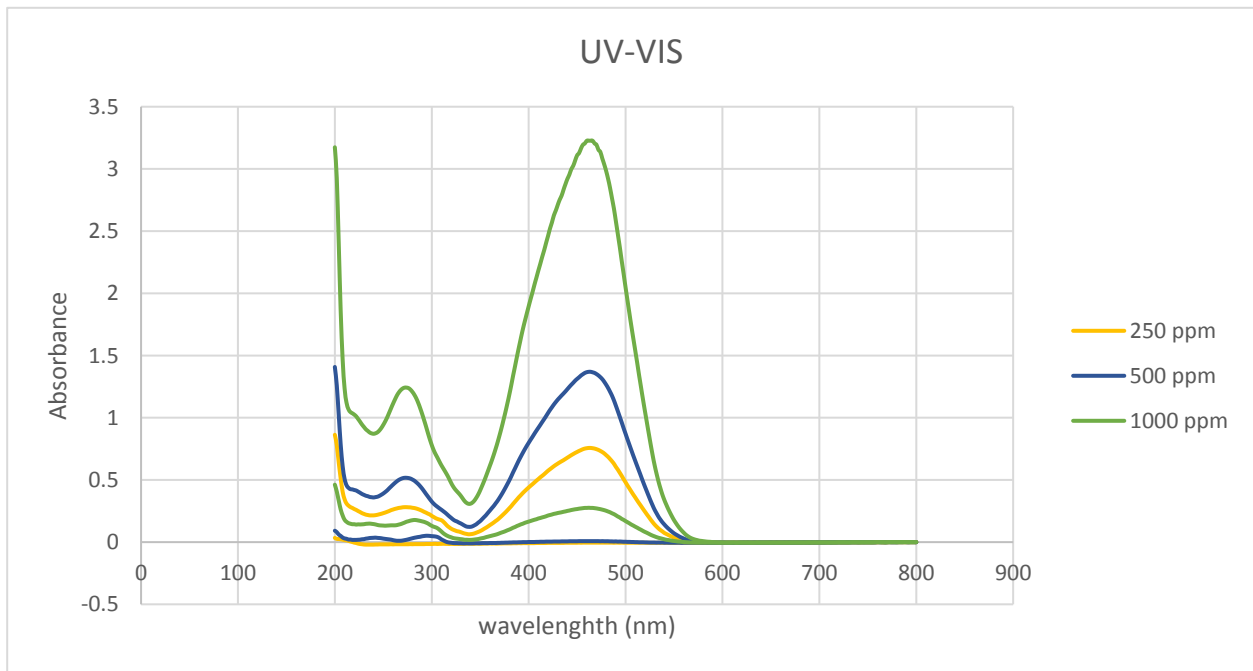
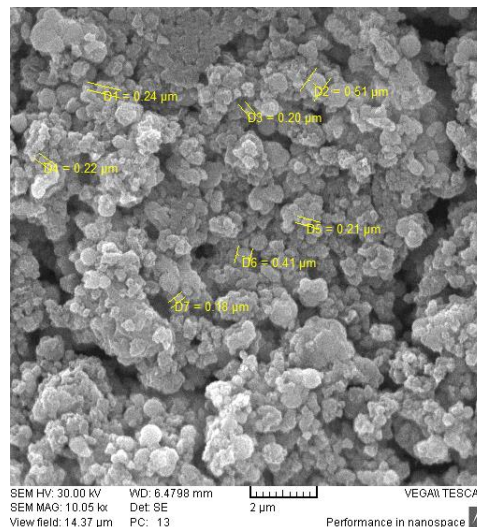


Figure 4. UV-vis spectrum of Fe@Co-Al LDH.

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 5, 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 .



Conclusion

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] Y. Lu, B. Jiang, L. Fang, F. Ling, J. Gao, F. Wu and X. Zhang, *Chemosphere*, **152** (2016)415-422.
- [2] F. Ling, L. Fang, Y. Lu, J. Gao, F. Wu, M. Zhou and B. Hu, *Microporous and Mesoporous Materials*, **234** (2016)230-238.
- [3] A. Jaiswal, R.K. Gautam and M.C. Chattopadhyaya, *Advanced Materials for Agriculture, Food and Environmental Safety*, (2014)1-26.

- [4] Y-H. Deng, C-C. Wang, J-H. Hu, W-L. Yang, S-K. Fu, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **262** (2005) 87-93.
- [5] S.J. Palmer, R.L. Frost and T. Nguyen, *Coordination Chemistry Reviews*, **253** (2009)250-267.
- [6] Y. Li, H. Bi, X. Mao, Y. Liang, H. Li, *Applied clay sciences*, **162** (2018)230-238.