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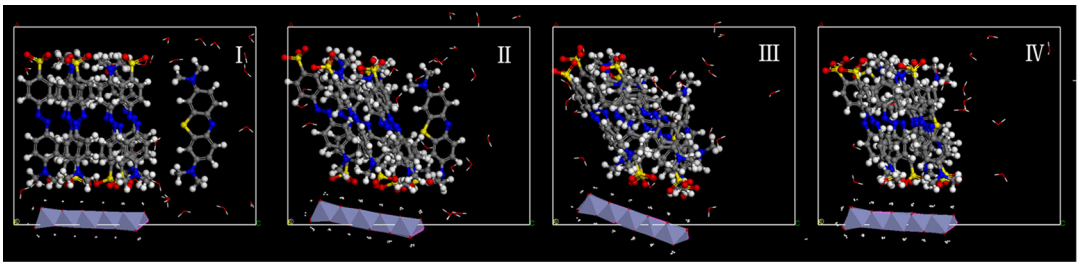
Anomalous but massive removal of two organic dye pollutants simultaneously

Zilin Meng[a,b], Yihe Zhang[a,*], Zhilei Zhang[d], Qian Zhang[a], Paul K. Chu[c], Sridhar Komarneni[b,*], Fengzhu Lv[a,*]

[a] Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China
[b] Department of Ecosystem Science and Management, Materials Research Institute, Materials Research Laboratory, the Pennsylvania State University, University Park, PA 16802, United States
[c] Department of Physics & Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China
[d] Drilling Research Institute, CNPC, Beijing, China

GRAPHICAL ABSTRACT



HIGHLIGHTS

- Removal of alkali and anionic organics simultaneously by one-pot method.
- Achieve the maximum use of charges in LDH for removal of anionic organic dye.
- Removal of two oppositely charged organic dyes simultaneously.
- Discuss the process and mechanism of removal of oppositely charged organic dyes.
- Molecular dynamic simulation was used to clearly show removal process of two dyes.

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ABSTRACT

A one-pot method to remove two organic dye contaminants and alkali simultaneously from alkaline wastewater was developed by forming Zn-Al layered double hydroxide (ZnAl-LDH). Using this process, not only alkali but also methyl orange (MO), an anionic contaminant was totally removed from wastewater. In addition, cationic contaminant, methylene blue (MB) was also removed effectively while maintaining the high removal efficiency of MO. The removal efficiency of MO was almost 100% and the pH of the treated wastewater decreased from 12 to 7.38. The charge-limited removal process, molecular arrangement of the contaminants in LDHs, and the anomalous removal mechanism were analyzed

* Corresponding authors.
E-mail addresses: zyh@cugb.edu.cn (Y. Zhang), Komarneni@psu.edu, sxk7@psu.edu (S. Komarneni), lfz619@cugb.edu.cn (F. Lv).

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experimentally and through simulation. After MO accumulated in the interlayers of LDH by electrostatic interaction, MB entered and trapped by hydrophobic interaction.

1. Introduction

Layered double hydroxides (LDHs) or anionic clays are naturally occurring inorganic lamellar compounds but they can also be synthesized easily and they have been studied extensively in recent years due to their potential applications [1]. The general formula of these compounds is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{m-})_{x/m}\cdot nH_2O$, where M^{2+} and M^{3+} are divalent and trivalent cations and A^{m-} is a charge balancing interlayer anion [2]. LDHs exhibit several properties such as ion-exchange ability [3], large specific surface area [4], and good environmental compatibility [5]. Therefore, they are often employed to remove contaminants from wastewater particularly anionic contaminants [6,7] because LDH layers are positively charged and hence can exchange with anionic contaminants. However, the removal efficiency of anionic contaminants depends on many factors such as size and charge of anions, competing anions and charge density on the layers.

Common wastewater treatment techniques with LDHs include ion exchange [8,9], exfoliation reassembly [10,11], and reconstruction [12,13], but most of these methods have drawbacks. The ion exchange process with LDHs is a slow process through the interlayers and hence the reaction time for exchange is too long. With regard to exfoliation reassembly of LDHs, long and complex steps are involved. In the case of reconstruction technique of LDHs, much energy is needed and the structure of calcined LDHs is vulnerable to CO_2 adsorption forming carbonate leading to inefficient removal of hazardous anions. Hence, it is very difficult to utilize all the positive charges on the layers of LDHs to reach the theoretical removal capacity by existing methods. Besides, anionic organic contaminants usually coexist with alkali [14,15] in alkaline wastewater, and hence the removal efficiency of anionic organic contaminants by LDH is extremely poor due to the surface potential [6].

Herein, a simple and fast one-pot method, which fully utilizes almost all the positive charges was designed and developed. In this method, anionic organic contaminants were used to balance the charge on the layers during the synthesis of LDHs by co-precipitation utilizing the alkali available in the wastewater. The removal amount of methyl orange (MO) by this one-pot method is much larger than the amounts reported previously by other techniques (see Table 1) [16–31]. The precipitates synthesized in MO solution were analyzed by XRD, SEM and Molecular Simulation. To elucidate the extraction mechanism, wastewater containing MO (anionic organic contaminant) and methylene blue (MB, cationic organic contaminant) was also studied and several isotherm models were used to fit the data. The obtained precipitates were also analyzed by XRD and SEM. Molecular dynamics simulation of MB molecules entering the ZnAl-LDH interlayers was presented by a video.

2. Experimental section

2.1. Materials

Organic dyes of MO and MB were purchased from Jingwen Chemical Corporation while $Zn(NO_3)_2\cdot 6H_2O$, $Al(NO_3)_3\cdot 9H_2O$, NaOH, and other reagents were obtained from Beijing Chemical Reagent Factory, China. They were all of analytical grade and used without further purification. Synthetic wastewater was prepared and its pH for all wastewater was adjusted to a pH of 12 by NaOH.

Table 1
Archival data for MO removal by LDHs.

Name	Modified	Removal Amount (mg/g)	Refs.
$Co_{5.84}Fe_{2.16}$-LDH		76.0	[16]
Mg_2Al-LDH		1187.0	[12]
Mg_2Al-LDH		1144.5	[17]
Mg_2Al-LDH	Calcined	726.7	[12]
Mg_3Al-LDH	Calcined, 200 °C, 4 h	490.0	[18]
Mg_2Al-LDH	dodecanoic acid	10.2	[19]
Mg_2Al-LDH	hydrothermal synthesized	148.3	[20]
MgNiAl-LDH		118.5	[21]
MgNiAl-LDH	Calcined, 500 °C, 4 h	375.4	[21]
Ni_2Al-LDH		903.4	[22]
Ni_2Al-LDH	Calcined, 500 °C, 5 h	186.6	[22]
Ni_2Al-LDH	graphene oxide	210.8	[23]
Zn_3Al-LDH		949.2	[24]
Zn_4Al-LDH		752.8	[24]
$Zn_{0.67}Al_{0.33}$-LDH		817.5	[25]
Zn_3Al-LDH	Calcined, 500 °C, 6 h	181.9	[26]
Zn_2Al-LDH	Au	627.5	[27]
Zn_2Al-LDH	MnOx	617.3	[28]
ZnMgAl-LDH		883.2	[29]
Zn_2Cr-LDH	Fe_3O_4	528.0	[30]
Zn_2Cr-LDH	Microwave	240.1	[31]

2.2. MO and alkali removal

Twenty five mL each of $Zn(NO_3)_2\cdot 6H_2O$ (0.2 mmol, 0.0595 g) and $Al(NO_3)_3\cdot 9H_2O$ (0.1 mmol, 0.0375 g) were added dropwise to 100 mL of MO solutions with different concentrations from 0.1 mmol/L to 8 mmol/L under vigorous stirring and the precipitate was collected immediately without aging. The precipitates were separated by centrifugation, washed with deionized water, dried at 80 °C for 24 h, and denoted as ZnAl-(MO)LDH-x where x indicates the concentration of MO. To determine the effects of time of LDHs on MO removal, 2 mL of the suspensions were withdrawn immediately after the addition and at 30 min intervals and centrifuged to separate the solid (4000 rpm for 2 min). The MO concentration in the supernatant was determined by UV–vis spectroscopic measurement at the wavelength of 465 nm. A control sample of ZnAl-LDH with NO_3^- in the interlayer was used to test for adsorption of MO.

2.3. MO, MB and alkali removal

Different amounts of MB were dissolved in 100 mL of MO solution to make different synthetic wastewater samples. In these wastewater samples, MO concentration was 1 mmol/L which is equal to the total anion exchange capacity of the forming LDHs during reaction and MB concentration was in the range of 0.01–0.5 mmol. A 25 mL each of $Zn(NO_3)_2\cdot 6H_2O$ (0.2 mmol) and $Al(NO_3)_3\cdot 9H_2O$ (0.1 mmol) were dropped into the wastewater under vigorous stirring. A precipitate was formed quickly, which was collected immediately, rinsed with deionized water, and dried at 80 °C for 24 h. The product was denoted as ZnAl-(Mixed)LDH-x where x indicates the concentration of MB. For example, ZnAl-(Mixed)LDH-0.1 means that the LDH was formed in the wastewater with 1 mmol/L MO and 0.1 mmol/L MB. To determine the effects of aging on MO and MB removal, 2 mL of the suspensions were with-