Journal of Hazardous Materials 243 (2012) 152–160

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Efficient removal of dyes by a novel magnetic Fe_3O_4/ZnCr-layered double hydroxide adsorbent from heavy metal wastewater

Dan Chen[a], Yang Li[a], Jia Zhang[a], Wenhui Li[b], Jizhi Zhou[a], Li Shao[a], Guangren Qian[a,*]

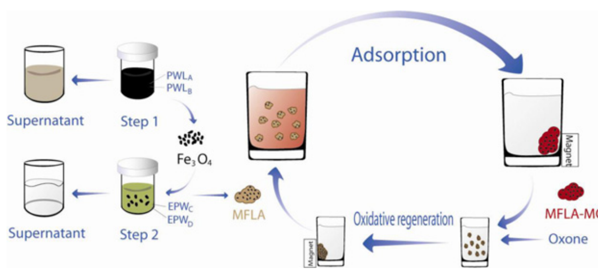
[a] School of Environmental and Chemical Engineering, Shanghai University, No. 99 Shangda Road, Shanghai 200444, PR China
[b] Department of Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China

HIGHLIGHTS

- Fe_3O_4/ZnCr-layered double hydroxide adsorbent was produced from wastewater.
- RSM was successfully applied to the optimization of the preparation conditions.
- The maximum adsorption capacity of MO was found to be 240.16 mg/g.
- The MO adsorption mechanism on MFLA was certified.
- MFLA could be recycled after catalytic regeneration by the oxidation technology.

GRAPHICAL ABSTRACT

To purify heavy metal wastewater (pickling waste liquor (PWL_A and PWL_B) and electroplating wastewater (EPW_C and EPW_D)), a novel magnetic Fe_3O_4/ZnCr–LDH material was formed via two-step microwave hydrothermal method (Step 1 and Step 2) and applicable for organic dyes wastewater treatment.



ARTICLE INFO

Article history:
Received 12 June 2012
Received in revised form
20 September 2012
Accepted 6 October 2012
Available online 13 October 2012

Keywords:
Heavy metal wastewater
Fe_3O_4/heavy metal-layered double hydroxide
Adsorption
Dye
Response surface methodology

ABSTRACT

A novel magnetic Fe_3O_4/ZnCr-layered double hydroxide adsorbent was produced from electroplating wastewater and pickling waste liquor via a two-step microwave hydrothermal method. Adsorption of methyl orange (MO) from water was studied using this material. The effects of three variables have been investigated by a single-factor method. The response surface methodology (RSM) based on Box–Behnken design was successfully applied to the optimization of the preparation conditions. The maximum adsorption capacity of MO was found to be 240.16 mg/g, indicating that this material may be an effective adsorbent. It was shown that 99% of heavy metal ions (Fe^{2+}, Fe^{3+}, Cr^{3+}, and Zn^{2+}) can be effectively removed into precipitates and released far less in the adsorption process. In addition, this material with adsorbed dye can be easily separated by a magnetic field and recycled after catalytic regeneration with advanced oxidation technology. Meanwhile, kinetic models, FTIR spectra and X-ray diffraction pattern were applied to the experimental data to examine uptake mechanism. The boundary layer and intra-particle diffusion played important roles in the adsorption mechanisms.

1. Introduction

Nowadays, heavy metal contaminations in freshwater systems have become a global environmental issue because of its influence on public health. Among all water contaminants, heavy metal ions, such as Cr^{3+}, Cr^{6+}, Cu^{2+}, Fe^{3+}, Fe^{2+}, and Zn^{2+}, have become one of the major concerns because they are toxic to animals and human beings, and are the main cause for freshwater systems degradation. Therefore, the removal of heavy metal ions from wastewater has become a crucial issue. Various traditional technologies, such as chemical precipitation [1], physisorption [2], electrochemistry [3], nano-membrane technology [4], and biosorption [5,6], have been developed to remove the heavy metal ions from wastewater. However, during the removal process, the potential application value

* Corresponding author. Tel.: +86 21 66137758; fax: +86 21 66137758.
E-mail addresses: grqian@shu.edu.cn, grqian@staff.shu.edu.cn (G. Qian).

0304-3894/$ – see front matter © 2012 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.jhazmat.2012.10.014

of the heavy metal of wastewater is ignored. Recently, to utilize those heavy metal ions, we investigated that heavy metal ions can form two kinds of materials, ferrite and heavy metal-layered double hydroxide (heavy metal–LDH) [7–10].

Heavy metal–LDH is obtained from the heavy metal solidification/stabilization and generally expressed as $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$ where M^{2+} represents divalent metal cation (Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, etc.), M^{3+} trivalent metal cation (Fe^{3+}, Cr^{3+}, etc.) and A^{n-} an anion ($CO_3{}^{2-}$, $SO_4{}^{2-}$, $NO_3{}^{-}$, Cl^-, OH^-, etc.), and x is the molar ratio of trivalent metal ion to total metal ion, i.e. $M^{3+}/(M^{2+}+M^{3+})$ [11]. This charge excess is produced by isomorphic substitution of divalent by trivalent cations and compensated by the introduction of anions (together with water) in the interlayer space. This particular structure characteristic allows heavy metal–LDH to have a powerful ability to capture organic or inorganic anions in aqueous solutions [12–14].

Ferrite general formula can be expressed as XY_2O_4, where X is a divalent ion (Fe^{2+}, Ni^{2+}, Co^{2+}, or Zn^{2+}) or their combination, Y mainly stands for Fe^{3+} but can be substituted by any of trivalent ions (Co^{3+}, Cr^{3+}) [15]. One important characteristic of ferrites is high values of magnetism, which makes them ideal for high frequency applications, such as electronic components, electrode and drug-loading materials [16].

Recently, the combination of ferrite and LDH, a magnetic composite, has been developed to apply in photo-catalysis, adsorption and drug delivery. For example, it has been reported that a Fe_3O_4/MgAl–LDH core/shell nanocomposite was applied in photodegradation of HCH [17]. It has been developed recyclable Fe_3O_4/hydroxyapatite (HAP) composite as a novel photocatalyst support [18]. It has been synthesized a core–shell structural Fe_3O_4@DFUR–LDH particle for magnetically controlled drug delivery and release [19]. Although great success has been achieved in the magnetic composite, the application in purification of heavy metal wastewater through formation of this composite is still difficult due to Al^{3+} in the structure of LDH. We have lately reported the synthesis of magnetic Fe_3O_4/ZnCr-layered double hydroxide composite with enhanced adsorption and photocatalytic activity [20]. Thus, we discovered that this novel material combines the best of both worlds: (A) heavy metal ions could be tightly bound in the crystal lattice of ferrite and LDH, and (B) Fe_3O_4/ZnCr-layered double hydroxide composite have the potential for the further environmental application.

The organic contamination is another concern. In particular, organic dye pollutants by cosmetics and textile industries have gained so much attention due to high toxicity and perturbation in aquatic life [21]. Low-cost adsorbents with high adsorption capacities for removal of dye will be in high demand. So it has become a trend that wastes instead of the chemicals synthesize foundational material. Therefore, our idea is to transfer heavy metals to useful low-cost adsorbents, ferrite/layered double hydroxide, and discuss the removal activity and mechanism of dye. And none of the reports involved the low-cost adsorbent which obtained from the heavy metal stabilization of wastewater.

Herein our study (i) fabricates this novel magnetic Fe_3O_4/ZnCr–LDH adsorbent (MFLA) using two kinds of wastewater laden with various heavy metals ions, pickling waste liquor (PWL) and electroplating wastewater (EPW), via two-step microwave hydrothermal method; (ii) investigates the optimization of the preparation conditions by using response surface methodology (RSM) and assess the effects of synthetic parameters (pH, contact time, and temperature), for the adsorption capacity of methyl orange (MO) onto MFLA; (iii) shows that MFLA can be separated from the MO solution by the magnetic field and enable its recycling by combining with the sulfate radical oxidation for decomposition of the dyes; and (iv) demonstrates the removal mechanism of MO on MFLA.

2. Materials and methods

2.1. Materials

Two typical pickling waste liquors (PWL_A and PWL_B) and two typical electroplating wastewaters (EPW_C and EPW_D) were obtained from Shanghai Second Steel Co., Ltd. and Shanghai Hazardous Waste Management Centre (Shanghai, China), respectively. The main components of four wastewaters were shown in Table 1. Methyl orange (MO) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification.

2.2. RSM experimental design

Response surface methodology (RSM) was applied to optimize the adsorption process and investigated the related effects of pH of the mixture solution (X_1), the microwave hydrothermal contact time (X_2) and temperature (X_3) because they were considered as significant factors on the second step microwave hydrothermal preparation process (formation of MFLA). In this research, the experimental design involved three parameters (X_1, X_2, and X_3), at three levels separately. Coded −1, 0, and +1 stands for low, middle and high concentrations respectively (Table 2).

In the study, the statistical software of Design-Expert (version 7.1.6, STAT-EASE Inc., Minneapolis, MN, USA) was used for designing and analyzing the experimental data. For statistical calculations, the transformation of independent variables (X_i) into coded corresponding variables (x_i) was calculated by Eq. (1).

$$x_i = \frac{(X_i - X_0)}{\Delta X} \tag{1}$$

where X_0 is the value of X_i at the center point and ΔX represents the step change.

The response variable (adsorption efficiency) was fitted by a second-order polynomial equation according to Eq. (2).

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i=1}^{k-1}\sum_{j=i+1}^{k} b_{ij} x_i x_j \tag{2}$$

where Y is the response variable, i and j are the index number for pattern, b_0 is the constant coefficient, b_i, b_{ij} and b_{ii} are the linear, interaction and quadratic coefficients, x_i and x_j are the coded levels of process factors studied.

2.3. Preparation of the adsorbents via a two-step microwave hydrothermal method

Synthesis of Fe_3O_4: the experimental procedure for the synthesis of Fe_3O_4 was similar to that description in the literature [22]. Typically, 1 mL of PWL_A and 3 mL of PWL_B were mixed together. The pH values were adjust with $NH_3{\cdot}H_2O$ (20%, v/v) to 9 controlled by pH meter (Shanghai Leici Instrument, China). The mixed solution obtained was carried out in the sealed reactor with teflon liner, transferred to the microwave digestion system (WX-4000, Shanghai Yi-Yao Instruments, China). The microwave hydrothermal treatment was performed at 150 °C, pressure of 30 psi for 30 min. After cooling down, precipitates were washed repeatedly by distilled water and dried in the oven at 80 °C overnight.

Formation of MFLA: typically, 10 mL of EPW_C and 100 mL of EPW_D was mixed and Fe_3O_4 nanoparticles of 10 mg were dispersed to 25 mL of the mixture wastewater. Meanwhile, $NH_3{\cdot}H_2O$ (20%, v/v) was used to adjust the pH values under ultrasonication to obtain precursors. The obtained precursors were put into teflon liner reactors, moved to the microwave digestion system