Journal of Industrial and Engineering Chemistry 21 (2015) 561–568

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Highly efficient removal of three red dyes by adsorption onto Mg–Al-layered double hydroxide

Ran-ran Shan [a], Liang-guo Yan [a,*], Yan-ming Yang [b], Kun Yang [a], Shu-jun Yu [a], Hai-qin Yu [a], Bao-cun Zhu [a], Bin Du [a]

[a] School of Resources and Environment, University of Jinan, Jinan 250022, PR China
[b] Shandong Cadre Institute of Science & Technology, Jinan 250014, PR China

ARTICLE INFO

Article history:
Received 30 October 2013
Accepted 9 March 2014
Available online 18 March 2014

Keywords:
Adsorption kinetics
Adsorption isotherm
Reactive red
Congo red
Acid red 1

ABSTRACT

The Mg–Al-CO_3-LDH with Mg^{2+}/Al^{3+} molar ratio of 2 was prepared via coprecipitation method at constant pH of 9–10 and used to remove three red dyes by batch adsorption method. The results showed the Mg–Al-LDH were well crystallized and can adsorb the red dyes effectively. The optimal adsorbent dosage and contact time were 1.0 g and 60 min, respectively. Adsorbed amount hardly changed when pH < 10. The adsorption kinetics fit the pseudo-second order kinetic models well and isotherms correspond to Langmuir model strictly. All the relevant mechanisms were studied and manifested as anion exchange and also electrostatic attraction for CR.

1. Introduction

Industrial effluents are one of the major causes of environmental pollution, especially effluents discharged from various dyestuff manufactures, plastic, and paper making industries. These effluents can give rise to certain hazards and environmental problems for their highly colored suspended organic solid. Dye effluents are not only aesthetic pollutants, but coloration of water by the dyes may affect photochemical activities in aquatic systems by reducing light penetration [1–3]. It has been also reported that several commonly used dyes are carcinogenic and mutagenic for aquatic organisms [4]. Therefore, removing dyes from effluents is of significant importance.

The conventional wastewater treatment methods for removing dyes include coagulation and flocculation, ozonation, electrochemical techniques, filtration, membrane separation, ion-exchange, aerobic and anaerobic microbial degradation, fungal decolorization [3,5,6]. Some of these methods suffer from one or more limitations in removing the dyes from wastewater thoroughly. For example, coagulation and flocculation, ozonation, membrane separation and ion-exchange are generally not feasible on a large scale due to the consideration of expense, complexity and additional chemicals [6]. Comparing with other wastewater treatment, adsorption as purification and separation technique has been shown to be one of the effective and economic methods to eliminate dyes with magnificent advantages, such as high efficiency, simple operation, and easy recovery or reuse of adsorbent. It is a powerful physiochemical wastewater treatment process which involves passive separation of adsorbate from an aqueous phase onto a solid phase [7]. Many adsorbent materials have been prepared in the removal of dyes from wastewater, including bentonite [3,5], sagaun sawdust [8], alginate [9], surfactant-modified natural zeolite [10], tin sulfide nanoparticle loaded on activated carbon [11], Mg–Fe-based hydrotalcites [12], modified chitin [13], etc.

Layered double hydroxides (LDHs), also known as hydrotalcite like compounds or anionic clay, have attracted considerable attention in recent years due to the presence of large interlayer spaces, positively charged layers and a significant number of exchangeable anions [14]. The chemical composition of LDHs can be expressed as the general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[A_{x/n}^{n-}]^{x-}\cdot mH_2O$ [15]. The divalent cations M^{2+} (Ca^{2+}, Mg^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, etc.) are partially substituted by trivalent ones M^{3+} (Al^{3+}, Fe^{3+}, Co^{3+}, Mn^{3+}, Ni^{3+}, Cr^{3+}, etc.), leading to the generation of a

* Corresponding author. Tel.: +86 531 82767617.
E-mail addresses: yanyu-33@163.com, chm_yanlg@ujn.edu.cn (L.-g. Yan).

http://dx.doi.org/10.1016/j.jiec.2014.03.019
1226-086X/

positively charged layer [15,16]. As a consequence, anions can be intercalated into the interlayer space of the LDHs to maintain charge neutrality [15]. Nowadays, LDHs has become a research focus on removing dyes from aqueous solutions. Ahmed and Gasser [17] synthesized an Mg–Fe-LDH as the adsorbent of congo red. They found that Mg–Fe-LDH was particularly efficient for removing congo red. $NiFeCO_3$ hydrotalcites were synthesized by Saiah et al. [18]. They concluded that Ni–Fe-LDH can be used effectively for removing evans blue from aqueous solutions. Extremera et al. [19] found that calcined Mg–Al LDHs can be used effectively for the removal of acid orange (AO10) from aqueous solutions. And there are few studies on the comparison of removing different red dyes from aqueous solutions by Mg–Al-LDH. Auxilio et al. [20] synthesized Mg–Al-LDH and only used it to adsorb Acid Blue 9 efficiently.

In this study, the feasibility of using Mg–Al-LDH as adsorbent for red dyes (RR, CR and AR1) removal was examined. The physical structure and chemical properties of Mg–Al-LDH were characterized by XRD, BET, FTIR, SEM and XPS. The red dyes adsorption properties (dosage of adsorbent, effect of initial solution pH, contact time and adsorption isotherms) were evaluated by the batch experimental methods. This could provide the basis for the treatment of actual dye wastewater.

2. Materials and methods

2.1. Materials

The reactive red and congo red used for this study were purchased from Tianjin damao reagent factory, and acid red 1 was purchased from the Aladdin industry corporation in China. The structures of the dyes were shown in Fig. 1. Na_2CO_3, NaOH, $Al(NO_3)_3$, $Mg(NO_3)_2$, HNO_3 were all of analytical grade. The desired pH was adjusted by adding 1:10 HNO_3 or 20% NaOH solution.

2.2. Preparation of Mg–Al-LDH

The Mg–Al-LDH was prepared via low saturation coprecipitation method. Solution A containing 64.01 g of $Mg(NO_3)_2{\cdot}6H_2O$ and 46.64 g of $Al(NO_3)_3{\cdot}9H_2O$ with a Mg^{2+}/Al^{3+} molar ratio of 2:1 dissolved in 150 mL distilled water. Solution B containing 10.00 g of NaOH and 26.62 g of $NaCO_3$ dissolved in 150 mL distilled water. Solution A and B were added dropwise to a vessel containing stirred distilled water (100 mL), which controlled the pH of the reaction mixture at 9–10. The resulting precipitate was aged for 18 h, washed by distilled water until the solution was neutral, then centrifuged and dried at 80 °C in the oven. All products were ground with an agate mortar and pestle and passed through 100 mesh sieve prior to be analyzed and used in dye adsorption.

2.3. Characterization methods

The Mg–Al-LDH was characterized by XRD, BET, FTIR, SEM, XPS and Zeta potentials. XRD patterns of the LDH were obtained by using a D/MAX 2200 X-ray diffractometer (Rigaku, Tokyo) with Cu$K\alpha$ radiation (40 kV, 300 mA, $\lambda = 0.154$ nm) to confirm the structure of the material. Data were collected in a scan range from 5° to 70° (2θ) with a step size of 0.03°. Surface area was measured by nitrogen physisorption using ASAP 2020 surface area and porosity analyzer (Micromeritics, United States). The samples were out-gassed overnight (12 h) under nitrogen prior to adsorption measurement. Pore distributions and pore volume were calculated using the adsorption branch of the N_2 isotherms based on the BJH model. Specific surface area was calculated by the BET equation. FTIR spectra were recorded in the spectral range of 4000–400 cm^{-1} on a Spectrum One FTIR spectrometer (Perkin-Elmer, United States). Mg–Al-LDH was coated with Au under vacuum in an argon atmosphere for SEM microscopy (Hitachi S570, Tokyo, Japan). XPS was performed on ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. Zeta potentials were measured by using a Nano ZS90 Zetasizer analyzer (Malvern, UK) with the 0.001 mol/L $NaNO_3$ electrolyte.

2.4. Adsorption experiments

All the adsorption experiments were carried out in a series of glass centrifuge tubes containing 20 mL of dye solution (RR, CR and AR1) by batch technique. The desired pH of the suspensions in each tube was adjusted by adding 1:10 HNO_3 or 20% NaOH solution. The Mg–Al-LDH was added in the test tubes to achieve the desired concentrations. For the kinetic experiments, the above suspensions were withdrawn at appropriate time intervals and the supernatant

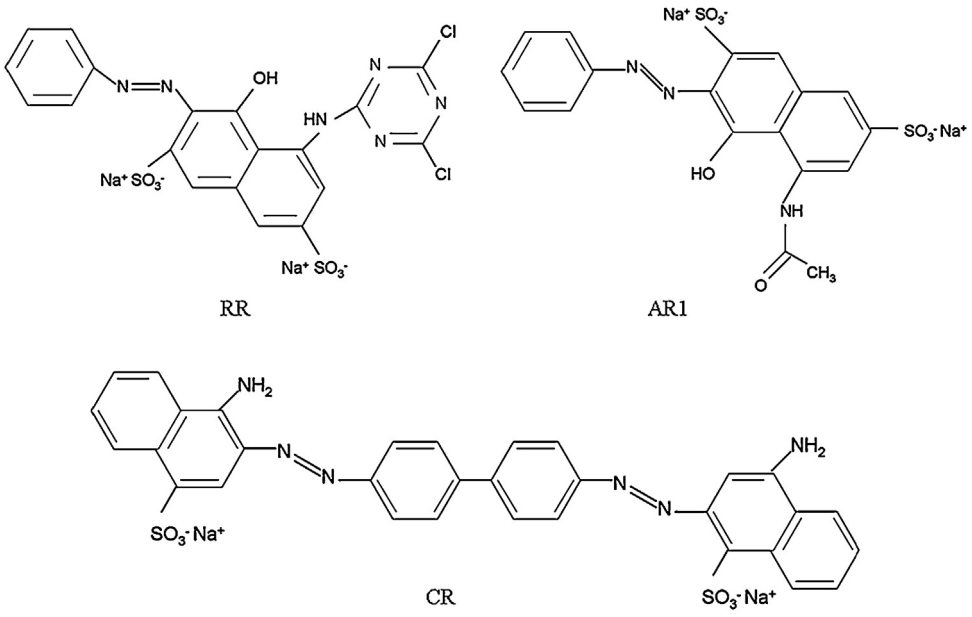

Fig. 1. The molecular structure of RR, CR and AR1.