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Research paper

Removal of malachite green and crystal violet cationic dyes from aqueous solution using activated sintering process red mud

Luyi Zhang, Huayong Zhang *, Wei Guo, Yonglan Tian

Research Center for Ecological Engineering and Nonlinear Science, North China Electric Power University, Beijing 102206, China

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ABSTRACT

Acid-activated sintering process red mud (ASRM) was investigated as an adsorbent for removal of two cationic dyes, malachite green (MG) and crystal violet (CV), from aqueous solution. The adsorption behaviors of dyes were studied in batch experiments as a function of contact time, pH value, initial dye concentration and temperature. The solution with pH higher than 3.2 was favorable for the adsorption of MG and CV on the ASRM. Adsorption data fitted better using the Langmuir isotherm, and the calculated maximum adsorption capacities were 336.4 mg/g and 60.5 mg/g for MG and CV at 25 °C, respectively. The analysis of the thermodynamic parameter, ΔH, indicated that the adsorption process of MG was endothermic, whereas that of CV was exothermic. The kinetic data were better described by pseudo-second order kinetic model. These results indicated that ASRM exhibited good adsorption ability and can be used as an attractive adsorbent for the removal of cationic dyes, especially MG.

1. Introduction

Various types of synthetic dyestuffs appear in the effluents of industries, such as textiles, printing, plastics, leather and food. The removal of synthetic dyes is of great concern because most of them and their degradation products cause serious environmental problems due to their high stability and complex aromatic structures (Bulut et al., 2008; Lee et al., 2011). Their presence in water could directly affect the photosynthesis phenomenon of aquatic life due to their color, and disturb the aquatic ecosystem and food chain because of their toxicity and carcinogenicity (El-Sayed, 2011; Eren and Afsin, 2007). Therefore, the colored effluents have to be properly treated before they are discharged into the water bodies.

Adsorption has been recognized as an attractive separation technique for the removal of dyes from wastewater because of its low cost, simple design and high efficiency (Alkan et al., 2008; Kan et al., 2011). One of the most widely used adsorbents is activated carbon because of its large surface area and high adsorption capacity (Ahmad and Alrozi, 2011). However, the relatively high cost and difficult regeneration of activated carbon restrict its use in industrial wastewater treatment. This limitation has encouraged the search for inexpensive and readily available adsorbents for the removal of dyes, such as natural materials, biosorbents, and waste materials from industrial and agricultural process (Alkan et al., 2008; Bingol et al., 2010; Chakraborty et al., 2011; Kan et al., 2011; Mittal et al., 2010).

Red mud (RM) is a waste formed after the caustic digestion of bauxite ores during the production of alumina. Due to the alkaline nature (pH of 10.0 to 12.5) and the large amount, this type of solid waste presents a significant impact on the environment (Wang et al., 2005). In the past years, several studies have focused on the use of red mud as an adsorbent for the removal of dyes from wastewater because of the nature of its composition and structure, which consists of a fine-grained mixture of oxides with a relatively high specific surface area (Namasivayam et al., 2002; Pradhan et al., 1998; Zhang et al., 2012a). Namasivayam et al. (2002) reported a high efficiency for the removal of color from wastewater using red mud. Wang et al. (2005) observed that red mud had a good adsorption capacity for methylene blue. However, these studies primarily have focused on the use of Bayer process red mud. There are few studies concerning the sintering process red mud (SRM), which is another type of red mud. SRM should be given more attention because it comprises a certain percentage in the total amount of red mud, especially in developing countries (Zhang et al., 2012a).

Acid treatments have been used to neutralize the alkalinity of red mud, which could also be recognized as a method for activating the material. Pradhan et al. (1998) reported that the removal efficiency for phosphate could reach 80%–90% by RM activated by HCl from aqueous solution. Altundoğan et al. (2002) investigated the effect of acidification of RM on the adsorption of arsenic and observed that the use of 1.0 M HCl increased the adsorption efficiency. Tor and Cengeloglu (2006)

* Corresponding author. Tel./fax: +86 10 80799258.
E-mail address: stecology@gmail.com (H. Zhang).

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reported that treating red mud with 20 wt.% HCl for 20 min enhanced its BET surface area and increased the removal of Congo red. However, the effect of acid-treatment sintering process red mud (ASRM) on dye adsorption has not yet been reported.

Depending on the ionic charge of the molecules, dyes can be classified as anionic, cationic and non-ionic, and the cationic dyes are more toxic than anionic dyes (El-Sayed, 2011). Therefore in this study, two cationic dyes, malachite green (MG) and crystal violet (CV), were selected. Both of these dyes have been shown to have harmful effects on living organisms during short periods of exposure. The aim of this study was to evaluate the removal efficiencies of MG and CV from aqueous solution using ASRM. The adsorption process was investigated as the function of solution pH value, contact time, initial dye concentration and temperature. The characteristics of the adsorption isotherm, thermodynamics and kinetics were also studied through the adsorption experiments, and then the possible adsorption mechanisms were proposed.

2. Materials and methods

2.1. Adsorbent

The sintering process red mud was obtained from Shandong Aluminum Corporation. The preliminary experiment revealed that 0.5 mol/L HCl was optimal for red mud to improve its adsorption capacity. Therefore, ASRM was obtained using the following procedures. The SRM was blended with 0.5 mol/L HCl at a solid-to-liquid ratio of 1/20 in a jacketed glass reactor, and stirred under atmospheric pressure using a digitally controlled stirrer for 0.5 h at 25 °C in a constant temperature water bath. After stirring, the acid dispersion was centrifuged for 10 min at 10,000 rpm, and the residue was rinsed three times with distilled water to remove the residual acid on the surface of the sample. Finally, the residue was dried overnight at 100 °C to reach constant weight and sieved through 100 mesh. After these treatments, the powder was directly used in the following experiments without further treatment.

The compositions of the samples were determined using a Philips PW2404 X-ray fluorescence spectrometer (XRF). N_2 adsorption/desorption isotherms were measured to determine the porous properties and the surface areas of the samples (Quadrasorb SI, Quantachrome). X-ray diffraction patterns (XRD) were measured using a Rigaku miniflex diffractometer with Co Kα radiation. The surface morphology and microstructure were observed by scanning electron microscopy (SEM) using a Hitachi S-3000 N field emission scanning electron microscope. The zeta potential was determined using a Zetasizer 2000 instrument (Malvern) in the pH range of 2.0 to 10.0. FTIR spectra were recorded using the KBr pressed disk technique on a NICOLET 750 FTIR spectrophotometer in the range of 4000 cm^{-1} to 400 cm^{-1}.

2.2. Adsorbate

Two cationic dyes, malachite green (C.I.: 42,000, FW: 365.00, λ_{max}: 618 nm) and crystal violet (C.I.: 42,555, FW: 407.99, λ_{max}: 584 nm), were used. The dyes were purchased from Tianjin Reagent Corporation and used without prepurification. The chemical structures of MG and CV were shown in Scheme 1. The concentrations of the dye solutions ranged from 10 mg/L to 500 mg/L, and the solutions were prepared by dissolving accurately weighted amounts in distilled water.

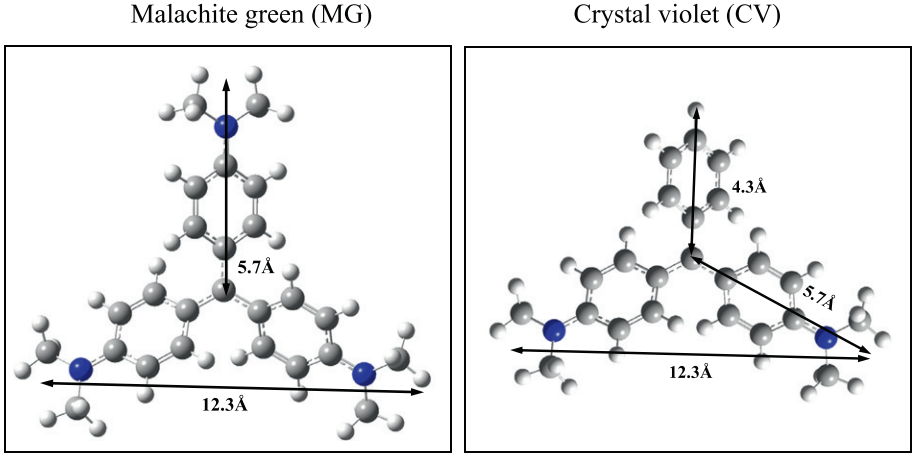
2.3. Batch adsorption studies

Batch experiments were conducted to evaluate the adsorption behaviors of MG and CV using the ASRM from aqueous solution. In all experiments, except for the initial concentration impact experiment, 0.25 g of adsorbent was added into a 250-mL stoppered conical flask containing 50 mL of 100 mg/L dye solution. These flasks were shaken in a shaker at 180 rpm. The contact time was selected as 180 min according to the preliminary experiment for all of the equilibrium tests. After being shaken, the dispersions were centrifuged for 5 min at 10,000 rpm. The residual concentrations of dyes in the supernatants were analyzed by measuring the OD at λ_{max} using a UV–vis spectrophotometer. The amount of adsorbed dye, q_e (mg/g), was calculated using Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of the dye (mg/L) respectively, V is the volume of the solution (L), and m is the mass of the adsorbent (g).

The effect of the contact time was investigated by varying the contact time from 0 to 360 min at 25 °C. The effect of the initial pH of the dye solution was studied over a range of 2.0 to 10.0. The pH values of the solutions were adjusted using HCl (1 mol/L) and NaOH solutions (1 mol/L) and monitored with a pH meter (DDS-11A, LIDA, China). To study the effect of the initial dye concentration, the experiments were performed at various dye concentrations ranging from 10 to 500 mg/L (10, 20, 40, 60, 100, 150, 200, 300, 500 mg/L). The adsorption studies were also conducted at different temperatures (15, 25, 35 and 45 °C) to examine the effect of temperature.



Scheme 1. The chemical structure of dyes.