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Research paper

Adsorption properties and mechanisms of palygorskite for removal of various ionic dyes from water

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ABSTRACT

In this study, an acid-treated palygorskite (PAL-O) with negatively charged layers has been used as an adsorbent for the removal of various types of ionic dyes including cationic [crystal violet (CV), cationic light yellow (7GL), and methylene blue (MB)] and anionic [methyl orange (MO) and acid green 25 (AG25)] ones from water. PAL-O showed efficient performance in the adsorption of all three cationic dyes because of electrostatic interactions. As regards the two anionic dyes, PAL-O also exhibited good adsorption efficiency for MO but had almost no effect on AG25. For detailed investigation of the adsorption mechanisms, PAL-O has been further treated by soxhlet extraction, using distilled water as solvent, to remove water-soluble matter such as metal ions. The efficiencies of the purified palygorskite (PAL-P) for adsorption of cationic dyes were slightly increased, but that of MO adsorption decreased evidently. This result indicated that the metal ions on the palygorskite played an important bridging effect for adsorption of anionic dyes. However, minimal AG25 uptake may occur because this bridging effect was too weak to be bonded for much stronger electrostatic repulsions between AG25 and palygorskite. In general, the charge properties and molecular structures of dyes play important roles in their adsorption behaviors.

1. Introduction

Dye is regarded as a widely used material in a number of industries such as printing and textile, paper, leather, and plastic manufacturing. Dye effluents may present an ecotoxic risk and have potential dangers of bioaccumulation for humans and other living organisms (Ayad and El-Nasr, 2010; Lin et al., 2010). In addition, dye wastewaters are usually characterized by low biodegradability and high-salt content, thereby resulting in increasing difficulty in treatment (Alinsafi et al., 2005). Therefore, removal of this type of organic pollutants becomes a significant challenge in wastewater treatment. A number of treatment technologies have been used for dye removal over the years, such as biological treatment (Sarioglu et al., 2007; Santos and Boaventura, 2015), membrane separation (Lau and Ismail, 2009), oxidation processes (Bouafia-Chergui et al., 2010; Asghar et al., 2015), conventional coagulation/flocculation and adsorption (Santos and Boaventura, 2009; Verma et al., 2012). Among these aforementioned techniques, adsorption has a special role in practical applications because of their simplicity and cost effectiveness. Absorbent occupies a decisive function in the adsorption method; thus, many types of adsorbents have been reported and used in wastewater treatment (Yagub et al., 2014). Natural absorbents such as waste biopolymers (Cheung et al., 2009; Salleh et al., 2011), granular activated carbon (Belaid et al., 2013), and clay minerals (Errais et al., 2012; Noroozi and Sorial, 2013; Abidi et al., 2015) are economically advantageous to the water treatment as well as locally available.

Among these absorbents, natural clays have an innate characteristic of non-toxicity and high potential of ion exchange for charged pollutants because of their properties of swelling, cation exchange, and large surface capacity (Lagaly, 2006). Many researchers have studied the adsorption behaviors of high-grade clay minerals, for example, montmorillonite, sepiolite, and kaolin toward dye removal in aqueous phases (Zheng et al., 2007; Gunay et al., 2013; Santos et al., 2016; Zhu et al., 2016), which has obtained good results. However, in natural conditions, natural clays usually have a large capacity for cation exchange because of their negative charged layers, but have limitations in anion adsorption. Anion uptakes can be enhanced using modified methods such as heating, acid, and surfactant treatments (Duc et al., 2006; Chen et al., 2012; Middea et al., 2017; Moreira et al., 2017).

Palygorskite is a type of natural nanoscale rod-like hydrated magnesium aluminum silicate mineral that exhibits particular crystal microstructure of 1–5 μm and large specific surface area providing abundant active adsorption sites (Murray, 2000). In comparison with other clay minerals, its excellent salt resistance and rapid hydration rate

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have elicited considerable attention, in which case palygorskite was applied as an adsorbent to remove various contaminants, especially for metal, algae, and ionic dyes (Zheng et al., 2007; Fan et al., 2009; Liu et al., 2014; Han et al., 2015; Uddin, 2017). Various chemically or physically modified palygorskites have been adopted to disperse crystal bundles as well as import functional groups for further improvement of its adsorption performance (Liu, 2007; Zheng et al., 2007; Tang et al., 2011; Xue et al., 2011; Liu et al., 2012; Zhou et al., 2015; Zhang et al., 2016b). Its negatively charged surface brings itself cationic affinity, which broadened its applied fields (Zhang et al., 2015b, 2016a). Nevertheless, studies on the adsorption mechanisms, especially for adsorption of anionic matter, remain inadequate and need to be further investigated.

In the present study, five different types of ionic dyes were chosen as target contaminants, including three cationic [crystal violet (CV), cationic light yellow (7GL), and methylene blue (MB)] and two anionic [methyl orange (MO) and acid green 25 (AG25)] ones. The adsorption performances of an acid-treated palygorskite (PAL-O) to remove the aforementioned five dyes have been investigated in detail at various pH levels and different initial dye concentrations. To explore the adsorption mechanisms of this natural clay, PAL-O has been further treated through soxhlet extraction before adsorption, by using distilled water as the solvent, to remove water-soluble matter, such as metal ions. Further investigations related to the effects of these dissolved cationic ions on the dye uptakes were conducted. Detailed characterizations of PAL-O and further purified one (PAL-P) before and after adsorption of dyes were conducted using zeta potential (ZP), Fourier transform infrared spectroscopy (FTIR), and x-ray diffraction (XRD) to study the intrinsic rules during the adsorption processes on the basis of their distinct features of charge properties and molecular structures.

2. Experimental

2.1. Materials and reagents

The palygorskite, treated by a dilute hydrochloric acid aqueous solution, was purchased from Nanjing Yadong Auto Mining Co. Ltd., in which SiO_2, MgO, Al_2O_3, Fe_2O_3, Na_2O, K_2O, CaO, MnO, TiO_2, and discretionary reduction rates were 55.6–60.5%, 10.7–11.35%, 9.0–10.1%, 5.7–6.7%, 0.03–0.11%, 0.96–1.30%, 0.42–1.95%, 0.61%, 0.32–0.63%, and 10.53–11.80%, respectively, provided by the manufacturer. Furthermore, CV, MB, and, MO were all obtained from Tianjin Institute of Chemical Reagents, whereas 7GL and AG25 were from Xingwu Chemical Co. Ltd. and Shanghai Jingchun Reagent Co. Ltd. (China), respectively. The structures and relative parameters of the five target dyes are shown in Table 1. Hydrochloric acid (HCl), sodium hydrate (NaOH), and other reagents used in this study were all A.R.-grade reagents obtained from Nanjing Chemical Reagent Co. Ltd. (China). Distilled water was used in all experiments.

2.2. Preparation and characterization of absorbents

PAL-O was fully dried before use. In addition, PAL-O was further purified through soxhlet extraction for 48 h, using distilled water as the solvent, to partially remove some water-soluble substances. The purified PAL-O was named PAL-P.

Zeta potentials (ZP) of PAL-O and PAL-P with concentration of 1.0 g/dm^3 at different pH levels, adjusted by dilute HCl or NaOH aqueous solutions, were measured by using a Malvern Zetasizer Nano ZS90 (United Kingdom). The extracted solvent after soxhlet extraction was detected to further analyze the extracted cationic content of PAL-O by using inductively coupled plasma mass spectrometry (ICP-MS, PE Optima 5300DV, United States). In addition, these two absorbents before and after adsorption of dyes were characterized using FTIR (Bruker Model IFS 66/S) and XRD (ARL X'TR, Switzerland). The range of scanning wavenumbers in FTIR measurement was 600–4000 cm^{-1} and the scanning range of 2θ in XRD was 3–70°.

2.3. Adsorption experiments

2.3.1. Effects of initial solution pH

The effects of initial solution pH on the adsorption of five different dyes by PAL-O were conducted at 298 K. The initial pH was adjusted by diluting HCl or NaOH aqueous solutions to 2.0–12.0 for CV, 7GL, MB, and AG25 but 5.0–12.0 for MO because MO would precipitate at strong acidic media (Li et al., 2016), thereby resulting in inaccurate experiment data. Approximately 0.03 g of dried adsorbent was dispersed in 30.0 cm^3 of dye solution at various initial pH levels under continuous stirring for 1 h and then the mixed solution was settled for 12 h to achieve the adsorption equilibrium according to the results of our preliminary experiments. The initial concentrations of CV, 7GL, MB, MO, and AG25, were 500, 500, 200, 500, and 200 mg/dm^3, respectively, given that they could reach saturated adsorption below these concentrations based on their adsorption isotherms. The final concentrations of dyes were determined by a visible spectrophotometer, and the absorbance rates of CV, 7GL, MB, MO, and AG25, were measured at the wavelengths of 581, 415, 662, 463, and 642 nm, respectively. All results were measured in triplicate, and the result was the average of the three runs, with the relative error lower than 5%.

Equilibrium adsorption capacity (q_e, mg/g) was calculated from the dye concentration change in the adsorption process. The calculation equation is represented as follows:

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

where C_0 and C_e (mg/dm^3) are the dye concentrations before adsorption and after reaching adsorption equilibrium, respectively; V (dm^3) is the volume of solution; and m (mg) is the dried weight of adsorbent.

2.3.2. Adsorption equilibrium study

Adsorption equilibrium experiments of PAL-O and PAL-P for the removal of five dyes were conducted at 298 K with different initial dye concentrations that varied from 20 to 1000 mg/dm^3. A total of 0.03 g of dried adsorbent was dispersed in 30.0 cm^3 dye solution under continuous stirring for 1 h and then the mixture was settled for 12 h to achieve the adsorption equilibrium. The dye concentrations at equilibrium were detected by using the same aforementioned methods. The dye uptakes were calculated based on Eq. (1).

3. Results and discussion

3.1. Adsorption performance of palygorskite

Palygorskite is a phyllosilicate clay mineral whose ideal formula is $Si_8(Mg,Al,Fe)_5O_{20}(OH)_2(OH_2)_4{\cdot}4H_2O$. It consists of ribbons of 2:1 (SiO_4 tetrahedron and octahedral sites principally occupied by Mg^{2+}) units, which could be replaced by Al^{3+} or Fe^{3+} cations due to isomorphic substitution. The main metal oxide contents of PAL-O are described in the Experimental section of this study. Furthermore, the rupture of *Si*-O-Si on the external surface and isomorphism endow palygorskite with permanent negative charge, thereby resulting in high affinity to positively charged pieces (Zheng et al., 2007; Zhu et al., 2016).

Then, PAL-O was used as an adsorbent for the removal of five different dyes including cationic and anionic ones. Obviously, pH is a crucial factor that affects adsorption effectiveness of the ionic adsorbents by changing the surface charges and ionization degrees of the adsorbents. The pH dependence of PAL-O for the adsorption of various dyes has been measured and shown in Fig. 1.

As shown in Fig. 1, PAL-O had a decent adsorption capacity towards