



Research paper

Structures of nonionic surfactant modified montmorillonites and their enhanced adsorption capacities towards a cationic organic dye

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ABSTRACT

This work aims to prepare and characterize novel organo-montmorillonites (OMTs) using a nonionic surfactant - octylphenol polyoxyethylene ether (OP-10), and apply the materials for the removal of cationic organic dyes. The nonionic surfactant OP-10 can be successfully intercalated into the interlayer of montmorillonite and the obtained OMTs still keep cation exchange capacity. The structural configuration of surfactant molecules between clay mineral layers varies from the surfactant loadings. Moreover, OMTs with higher surfactant loadings have higher organic carbon content but lower specific surface area. The prepared OMTs showed enhanced adsorption capacities towards cationic organic dye methylene blue (MB), and the adsorption amount increases with an increase of surfactant loading. The high adsorption capacity can be attributed to the fact that the novel OMTs still keep cationic exchange capacity and OP-10 has plentiful polyoxyethylene ether chains in its molecule structure, which can capture MB molecules through hydrogen bonding. A probable mechanism for the removal of MB was proposed to be a synergistic effect of ion exchange, partition adsorption, hydrogen bonding and electrostatic interactions. Kinetic and isotherm data could be fitted with pseudo-second order model and Langmuir isotherm. The adsorption thermodynamics study has proved the spontaneous and endothermic nature of the adsorption process. The nonionic surfactant modified OMTs could be promising candidate adsorbents for the removal of cationic organic dyes.

1. Introduction

Nowadays, organic dyes and their effluents have become one of the main sources of water pollution due to the greater demand in industry such as textile, paper, and plastic (Srilakshmi and Saraf, 2016; Zhou et al., 2010). It is reported that over 100,000 kinds of commercial dyes are used with an annual production over 9 million tonnes (Liang et al., 2017). These organic dyes are composed of certain organic compounds, which are toxic to microorganism, aquatic life, and human beings (Wang and Zhu, 2007). Therefore, removal of organic dyes from wastewater is an urgent and necessary environmental issue.

Montmorillonite (Mt), a kind of natural abundant clay mineral, has been widely used in environmental remediation because of its excellent swelling capacity, large specific surface area and high cation exchange capacity (Ma et al., 2016). Natural Mts show a slight adsorption capacity towards organic dyes due to ion exchange. Organic modification is a common method to improve the adsorption capacities of natural Mt

for organic dyes. In the past two decades, cationic surfactants modified Mts have been the most widely studied organo-montmorillonites (OMTs) because the interlayer exchangeable cations can be substituted easily with cationic surfactants. It converts Mt surface from hydrophilic to hydrophobic, which is in favor of the adsorption of organic dyes (Borisover et al., 2008). However, the substitution of inorganic exchangeable cations by organic cations in the interlayer of Mts is irreversible. After modification with cationic surfactants, the interlayer cationic surfactants are not readily exchangeable (Ma et al., 2016). Compared with the natural Mts, the adsorption capacities of cationic surfactant modified OMTs for organic dyes do not increase obviously and even show a dramatic decrease for cationic organic dyes. Therefore, effective OMTs adsorbents with high adsorption capacities for organic dyes especially for cationic organic dyes are still needed to be developed.

Previous studies showed that the type of organic modifier used could remarkably influence the structure and adsorptive behavior of

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OMts (Celis et al., 2000; Xue et al., 2013). Thus, if OMts are modified with surfactants which do not carry ionic and chemisorbing functional groups, such as nonionic surfactants, the resultant OMts may have a wide range of cation exchange capacities as well as high organic carbon contents, which may increase the adsorption capacities towards cationic organic dyes through both ion exchange and partition mechanism. Octylphenol polyoxyethylene ether is a kind of nonionic surfactant, which consists of a long carbon chain and a polyoxyethylene ether chain. It has the characters of high water solubility, biodegradability and low toxicity, which is beneficial to the environment. Previous works have proven that hydrogen bond can be formed between polyoxyethylene ether chain and siloxane surfaces (Huang et al., 1996; Mathur and Moudgil, 1998; Postmus et al., 2007; Shen, 2001; Somasundaran et al., 1991), which also demonstrated that nonionic surfactant octylphenol polyoxyethylene ether can intercalate into the interlayer of Mts through hydrogen bonding instead of ion exchange. In addition, the long carbon chain can function as a partition medium for organic compounds. Thus, it might be expected that novel OMts modified with nonionic surfactants have a high adsorption capacity for cationic organic dyes. Considering that few reports were focused on the nonionic surfactants modified Mts and the adsorption mechanism, fundamental research on nonionic surfactants modified Mts and the adsorption mechanism is worth studying.

In this study, octylphenol polyoxyethylene ether with 10 CH₂CH₂O radicals (OP-10) was chosen as the nonionic surfactant to prepare the OMts. The structural information of OMts, which is very important to understand the adsorption mechanism, was obtained by XRD, TG, FT-IR and BET analysis. A typical cationic organic dye methylene blue (MB) was selected as the target pollutant to determine the adsorption properties of the OMts. The influence of initial pH, kinetic, isotherms and thermodynamics of the adsorption process was investigated. In addition, the adsorption mechanism involved in the adsorption process for MB by the OMts was also explored. The results of this work might provide novel information for developing new OMts adsorbents with high adsorption capacities towards organic dyes.

2. Materials and methods

2.1. Materials

The montmorillonite used in this study is from Liaoning province, China. The cation exchange capacity (CEC) is 64.13 meq/100 g. The nonionic surfactant selected for this study is octylphenol polyoxyethylene ether (OP-10) with a purity of 99%, which was obtained from Usolf Chem. Co., China. Methylene blue was purchased from Beijing Reagent Co. (Beijing, China). All reagents are analytical grade and used without further purification.

2.2. Preparation of the OMts

4 g of Mt was dispersed in 300 mL of deionized water. After 30 min of vigorous magnetic stirring to form a homogeneous dispersion at room temperature, a predissolved stoichiometric amount of surfactants were firstly dissolved in 100 mL of deionized water and then slowly introduced to the clay mineral dispersion. The mixtures were treated for 30 min at 60 °C on an ultrasonic bath with 120 Hz and then stirred for 24 h at room temperature with a Kexi magnetic stirrer. In the following step, the prepared OMts were washed with deionized water several times, and then dried in an oven at 60 °C for 12 h. The OP-10 modified Mt prepared at a concentration of 0.25 CEC were denoted as “0.25 OP-10Mt” and the others were denoted in the similar way.

2.3. Characterizations

Powder X-ray diffraction (XRD) patterns were recorded between 1° and 40° on a Bruker D8 diffractometer with Cu K α radiation

($\lambda = 0.15406$ nm) operating at 40 kV and 40 mA at a step size of 0.02. Thermogravimetric analysis was obtained using a Mettler TGA instrument with heating rate at 10 °C/min from room temperature to 1000 °C in a high-purity nitrogen atmosphere (50 mL/min). Elemental analysis of C and H was conducted on a Germany Vario Elementar cube. Fourier transform infrared (FT-IR) spectroscopy was observed in the wave-number region of 4000–500 cm⁻¹ with a Nicolet IS10 spectrometer using KBr pellets. Pore structure parameters such as surface area, pore volume and average pore size were measured from N₂ adsorption–desorption isotherms using a Micromeritics ASAP2020 instrument. The samples were firstly ground in an agate mortar to pass through a 200 mesh standard screen (74 μ m), and then degassed at 105 °C for 12 h prior to N₂ adsorption.

2.4. Batch adsorption experiments

The batch adsorption experiments were carried out to determine the adsorption behaviors of the prepared OMts for MB from aqueous solutions. The adsorption experiments were operated in conical flasks mounted on a shaker at 260 rpm for a specified time. The concentration of MB was determined from the calibration curve prepared by measuring the absorbance of different predetermined concentrations of MB solutions at 664 nm using a UV–vis spectrophotometer (UV-9000S, Shanghai Metash, China). The adsorption amounts of MB on per unit mass of the sample, Q_e (mg g⁻¹), were calculated according to the following Eq. (1):

$$Q_e = \frac{(C_i - C_e)V}{M} \quad (1)$$

where the C_i is the initial concentration of MB (mg L⁻¹), C_e is the equilibrium concentration of MB (mg L⁻¹), M is the mass of the sample (g), and V is the volume of the MB solution (L).

For adsorption kinetic studies, 25 mg of adsorbents were dispersed in 200 mL of MB (100 mg/L, pH 8.0) aqueous solutions and agitated. The concentrations of MB were measured at different time intervals from 0 to 180 min. To evaluate the thermodynamic properties, 25 mg of sample was added into 40 mL of MB solution with different concentrations under temperatures of 298.15 K, 308.15 K and 318.15 K, respectively. Similarly, the effect of solution pH on the adsorption of MB was studied by adjusting the pH of MB solution (using either 0.1 M HCl or NaOH). All adsorption experiments in this paper were carried out at least 3 times and the averaged values were presented.

3. Results and discussion

3.1. Characterizations

3.1.1. XRD analysis

XRD patterns of raw Mt and OMts at different OP-10 loadings are presented in Fig. 1. The untreated Mt has a d-spacing of 1.41 nm. With increasing surfactant loading, the expansion of layers was observed according to the d001 values, which is an indication that surfactant has been intercalated within the interlayer of OMts. The interlayer spacings, calculated by subtracting the thickness of Mt unit (0.96 nm) from the d-spacings are 0.57, 0.60, 0.73, 0.88 and 0.90 nm, respectively. On the other hand, it is also obvious that the width of d001 reflection becomes boarder but the intensity weakens after the surfactant loadings exceed 0.75 CEC, which suggests the structural destabilization of organoclays with increasing the surfactant loadings (Dellisanti and Valdre, 2005; Jana et al., 2007).

In Fig. 2a, the molecular structure of OP-10 displays zigzag arrangement. However, when it is intercalated into the interlayer of Mt, the oxygen atoms in the polyoxyethylene ether chain are inclined and attached on the clay mineral surface of Mt through hydrogen bonding (Huang et al., 1996; Mathur and Moudgil, 1998; Postmus et al., 2007; Shen, 2001; Somasundaran et al., 1991). As a result, the structure of

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