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The characterization of organo-montmorillonite modified with a novel aromatic-containing gemini surfactant and its comparative adsorption for 2-naphthol and phenol

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HIGHLIGHTS

- Organo-clays were prepared by a novel aromatic-containing gemini surfactant (BHPD).
- The novel gemini surfactant can effectively modify Na-montmorillonite at low concentration.
- The adsorption capacity of 2-naphthol was larger than phenol under the same conditions.
- The aromatic group and hydrophobicity of adsorbate had great impacts on the removal efficiency.
- BHPD-Mt was a more highly efficient adsorbent for removing 2-naphthol from wastewater than phenol.

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ABSTRACT

A novel aromatic-containing gemini surfactant, bis-N,N,N,-hexadecyldimethyl-*p*-phenylenediammonium dibromide (BHPD) was used to modify Na-montmorillonite for the first time. The surface and structure of the resultant organoclays were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TG), elemental analysis (EA) and Zeta potential. The results showed that interlayer space of the Na-montmorillonite was significantly expanded at relatively low concentration of BHPD. The comparative study for the adsorption of 2-naphthol and phenol from aqueous solution was performed on the resultant organo-montmorillonites. The results suggested that the adsorption amount of 2-naphthnol was much higher than that of phenol under the same condition, which may be attributed to the stronger hydrophobicity of 2-naphthol and its higher delocalized π-electron density. The important factors, such as the amount of modifier, contact time, temperature and pH in the solution, were also taken into consideration. Additionally, the kinetics and thermodynamics parameters were investigated, it was found that the reaction process was completed in a short time, the experimental data fitted very well with the pseudo-second-order kinetic model, and the equilibrium adsorption data were proved to be in good agreement with the Freundlich isotherm model. Thermodynamic parameters Gibbs free energy (ΔG°), the enthalpy (ΔH°) and the entropy change of sorption (ΔS°) demonstrated that the adsorption of 2-naphthol and phenol was a spontaneous and exothermic process.

1. Introduction

Exposure to organic pollutants and contamination of ground water are believed to be a risk for human beings. Thus, how to effectively and deeply remove undesirable organic pollutants from water system is a very important but still challenging task for environmental engineers. In recent years, the gemini surfactants have drawn much attention in modifying clay minerals through ion exchange because of their superior characteristics compared with conventional surfactants [1–6]. Moreover, several researches proved that gemini-modified clays exhibited better efficacy than its monomer-modified clay in the removal of organic contaminants from wastewater [7,4,8]. Li and Rosen had investigated the adsorption of a series of gemini surfactants on Na-montmorillonite from aqueous solution and the effect of the surfactant modified clay on the removal of 2-naphthol and 4-chlorophenol, the results indicated the organoclays prepared from the gemini surfactants were both more efficient and effective than conventional surfactant modified clays in terms of adsorbing the pollutants [7]. Wang and his colleagues reported the gemini surfactant N_G was more effective than the monomer N_S at expanding the interlayer space

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of Na-Bt and the corresponding modified clays N_G-Mt showed better performance than Ns-Mt in removing MO from aqueous phase [4]. Therefore, the organoclays modified with gemini surfactants will become potential adsorbents for treating waste water in the future.

It is well known that the adsorption capacity and mechanism of organoclays are substantially influenced by the molecular structure of the exchanged organic cations, the extent of cation exchange and the molecular structure of solute [9–13]. Recently, the contribution of specific molecular interaction between the functional groups of the organic pollutants and the organoclays in the process has gathered increasing attention and provided some insights into adsorption mechanism. Qu found that cation–π interaction between ammonium cations and PAHs could enhance the PAHs adsorption to organoclays modified with quaternary ammonium cations in relative to chlorobenzenes that are incapable of such interaction [14]. Xu reported that the π–π interaction contributed the adsorption–desorption behavior of naphthalene onto CDMBA-modified bentonite [15]. Xue et al. [16] had prepared two gemini surfactants (BDP and BDHP) modified montmorillonites and were used to treat *p*-nitrophenol solution. As a consequence, the organoclays modified by gemini surfactant containing a hydroxyl spacer (BDHP-Mts) showed better performance than that without the hydroxyl spacer (BDP-Mts). Therefore, developing and designing gemini surfactants with special functional group are necessary to remove the organic pollutant molecule effectively.

The main objective of the current study is to prepare organoclay adsorbents modified with a novel aromatic-containing gemini surfactant and do the comparative study for the adsorption of 2-naphthol and phenol on the organo-montmorillonites. Thus, a novel aromatic-containing gemini surfactant bis-N,N,N,-hexadecyldimethyl-*p*-phenylenediammonium dibromide (BHPD) was synthesized in this work and used to modify Na-montmorillonite for the first time. The various methods were applied to characterize the obtained organoclays, including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TG), elemental analysis and Zeta potential. Some important influencing factors, such as the concentration of modifier, contact time, pH and temperature were studied in detail. Furthermore, kinetics and thermodynamics parameters of 2-naphthol and phenol adsorption to organo-montmorillonites were discussed. The obtained results brought new lights into the adsorption mechanisms of organoclays modified by a novel gemini surfactant, and paved the way to develop and design the new modifier molecule, it will have profound influence on wider application of organoclays as adsorbents.

2. Materials and methods

2.1. Materials

The pure Na-montmorillonite (Na-Mt) in this study was obtained from Zhejiang Institute of Geology and Mineral Resource, China and used without any treatment. Its cation exchange capacity (CEC) of natural clays is 112 mmol/100 g. Its chemical composition is found to be as follows: 66.80% SiO_2, 20.88% Al_2O_3, 4.18% MgO, 2.88% CaO, 1.97% Fe_2O_3, 2.20% Na_2O, 0.73% K_2O, 0.13% TiO_2 and 0.23% others. N,N-dimethylhexadecylamine (TGI, 98%), α,α′-dibromo-*p*-xylene (Aldrich, 97%) were used without any purification for the synthesis of the novel gemini surfactant. The HCl and NaOH (0.1 mol/L) were employed to adjust the pH of aqueous solution.

A novel gemini surfactant bis-N,N,N,-hexadecyldimethyl-*p*-phenylenediammonium dibromide (BHPD) was synthesized according the procedures reported by Mivehi [17]. The synthesis procedures were listed as follows: α,α′-dibromo-*p*-xylene was dissolved in ethanol in a round-bottomed flask. N,N-dimethylhexadecylamine was added dropwise under stirring. The mixture was refluxed for 48 h, then the solvent was removed under vacuum, and the product was recrystallized from a mixture of ethanol and diethyl ether for several times. The products were dried in a vacuum for 24 h. Its chemical structure was shown in Fig. 1. The synthesized product was further characterized by FT-IR, ^{1}H NMR and elemental analysis.

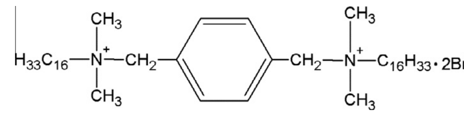

Fig. 1. The chemical structure of BHPD.

The element analysis and ^{1}H NMR results of the novel aromatic-containing gemini surfactant BHPD were listed as follows: the calculated values C: 65.84%, N: 2.49%, H: 10.72%; experimental value, C: 65.85%, N: 3.69%, H: 10.84%. ^{1}H NMR 7.8 (s, 4H), 5.25 (s, 4H), 3.61 (t, 4H), 3.21 (s, 12H), 1.85 (m, 4H), 1.4 (m, 4H), 1.2–1.3 (t, 52H), 0.87 (t, 6H), according to these results, the synthesized material was target product and owned a high purity.

2.2. Synthesis of organo-montmorillonites

The organoclays were prepared according to the following procedures: 5 g of Na-Mt was initially dispersed in 250 mL of deionized water at 60 ± 1 °C for 60 min, into which a stoichiometric amount of the gemini surfactant BHPD (corresponding to 0.4, 0.8, 1.2 and 2.0 CEC, respectively) was added slowly. Subsequently, the mixtures were stirred in waterbathchader at 60 °C for 3 h. All organoclays compounds were washed free from bromide anions as determined by $AgNO_3$, the obtained products were dried in a hot air oven at 80 °C until constant mass. The dried organoclays were ground in an agate and pulverized to pass through 200 mesh sieve, finally stored in a vacuum desiccator until use. The resultant modified Na-montmorillonites were denoted as 0.4, 0.8, 1.2 and 2.0 CEC BHPD-Mt.

2.3. Characterization of organo-montmorillonites

The structures of the organo-montmorillonites and Na-Mt were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TG), and elemental analysis. A Nicolet Magna 560 E.S.P FT-IR spectrometer was used to collect FT-IR spectra from 4000 to 400 cm^{-1} with resolution of 4.0 cm^{-1}. The XRD patterns of the organo-montmorillonite were determined using a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα radiation at 40 kV and 40 mA and collected between 1.5° and 10° (2θ) at a scanning speed of 1°/min. The EA 3000 organic element analyzer was employed to determine elemental composition of Na-Mt and four organoclays. The TG analysis was performed on a TGA/DSC1 STAR system (METLEROLEDO) at a heating rate of 10 °C/min from room temperature to a maximum temperature of 800 °C under argon atmosphere. To evaluate the effect of the pH in the solution on the adsorption capacity of BHPD-Mt, Zeta potentials at different pH values (2, 4, 6, 8, 10) were determined using Zetasizer Nano ZS.

2.4. Adsorption experiments

Adsorption experiments of 2-naphthol and phenol onto organoclays were carried out using batch experimental technique. 0.05 g of organo-montmorillonite (0.4–2.0 CEC) was combined with 50 mL solution containing 60–200 mg/L 2-naphthol (or phe-