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The preparation of organo-bentonite by a new gemini and its monomer surfactants and the application in MO removal: A comparative study

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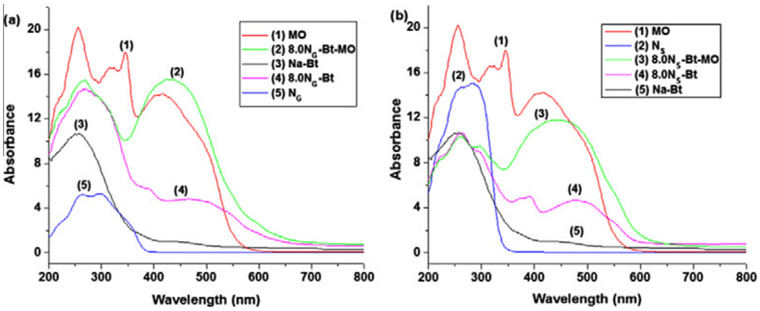
HIGHLIGHTS

- N_G is more effective than N_S in expanding basal space and in removing MO.
- N_S mainly stays in interlayer, however N_G on the clay surface due to its big head.
- MO removal by N_G-Bt/N_S-Bt is pH dependent.
- The complex of MO–N_G-Bt/MO–N_S-Bt forms during MO removal.

GRAPHICAL ABSTRACT

Solid-state UV–vis spectra of the samples employed in this study.



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ABSTRACT

Gemini surfactant, 1,1′-(butane-1,4-diyl)-bis(3-(tetradecyloxycarbonyl)pyridinium) dibromide (designated as N_G), and the corresponding monomer, 1-ethyl-3-(tetradecyloxycarbonyl)pyridinium bromide (N_S), were prepared and utilized to modify sodium bentonite (Na-Bt). The surfactant modified bentonites (N_G-Bt for the gemini modified bentonite and N_S-Bt for the monomer modified one) were then used for methyl orange (MO) removal from the wastewater. The results indicated that the gemini surfactant N_G was more effective than the monomer N_S at expanding the interlayer space of Na-Bt and in removing MO from wastewater. The maximum basal spacing of N_G-Bt (4.02 nm) was almost twice as that of N_S-Bt (2.63 nm). MO removal efficiency was 9.68% for 4.0N_S-Bt and 99.88% for 4.0N_G-Bt at a dosage of 0.06 g, respectively. N_S easily intercalated into the interlayer of Na-Bt, however more N_G mainly stayed on the solid surface owing to its bigger head. The adsorption of both N_G and N_S on Na-Bt obeyed the pseudo-second-order kinetic model and Langmuir isotherms. The solid-state UV–vis spectrometry evidenced the formed complex of N_G/N_S with MO on Na-Bt, and the stronger interaction of N_G-Bt with MO.

1. Introduction

Dyes are used widely as coloring agents in textile, cosmetic, leather, printing, food, plastic and so on. Due to their resistance to degradation, they remain in wastewater. Dyes and their metabolic products might be cancerogenic and mutagenic [1,2]. Several conventional methods, for instance, coagulation and flocculation, membrane filtration, biological treatments, adsorption and advanced oxidation processes, are available for the treatment of dye wastewater, in which the adsorption is the most effective and convenient one [3–7]. Clay minerals are potential absorbents.

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Because of their hydrophilicity the uptake capacity of clays for organic contaminants is quite low. The modification of clay minerals by surfactants is a convenient method to convert the mineral surface from hydrophilic to hydrophobic, and therefore to enhance their adsorption capacity towards organic pollutants [8–11]. Selecting modifiers is a key factor in order to obtain suitable organo-clays of high efficiency.

In recent years, gemini surfactant modified clay has captured much interest [12–14]. Rosen et al. have studied the adsorption of a series of gemini surfactants on Na-montmorillonite from their aqueous solution in 0.01 M KBr and the effect of the surfactant modified clay on the removal of 2-naphthol and 4-chlorophenol [15]. Compared to those of conventional cationic surfactants, only one of the hydrophilic groups in the gemini molecule is adsorbed onto the clay and the other is presumably oriented toward the aqueous phase. The adsorption of the pollutants onto the clay treated by either the gemini or the conventional surfactant shows that the former is both more efficient and more effective at removing the pollutant from aqueous phase. The adsorption on silica of monomeric (dodecyltrimethyl ammonium bromide), dimeric (1,2-bis (dodecyldimethylammonio) ethane dibromide) and trimeric (methyldodecyl bis[2-dimethyldodecylammonio)ethyl] ammonium tribromide) and the effect on the removal of 2-naphthol are investigated [16]. The amounts adsorbed at saturation decrease with increasing dodecyl chain number of the surfactants. The ratio of maximum amount of 2-naphthol solubilized to the adsorbed amount of surfactant on silica increases with an increase in the dodecyl chain number of the surfactants. Liu and his colleagues had investigated the modified montmorillonite by three gemini surfactants. The author pointed out that the chain length and the amount of gemini surfactant had a significant effect on the arrangement of the intercalary surfactant. The adsorption capacity of the organo-MMTs for MO was improved by increasing the amount or the chain length of gemini surfactants [17].

Obviously, gemini modified clay exhibits better efficacy in getting rid of organic contaminants from wastewater. However, less information are available for gemini modified clay because only a few gemini of aliphatic quaternary ammonium salts can be commercially supplied due to the difficult in preparation and purification. Therefore the purpose of present work is to investigate the adsorption on bentonite of a new gemini with pyridinium and its corresponding monomer and their removal efficiency for MO in wastewater. The solid-state UV–vis spectroscopy is first employed to probe new evidence for adsorption mechanism of MO by the organo-bentonite. The present work may enrich the understanding of gemini surfactants for future application in wastewater treatment.

2. Materials and methods

2.1. Materials

Nicotinic acid, thionyl chloride, acetone, ethyl acetate and tetradecanol were purchased from Chengdu Kelong Chemical Reagent Co., bromoethane, 1,4-dibromobutane and MO from Sinopharm Chemical Reagent Co., all of the reagents were analytical grade and used as supplied. The Na-bentonite has a cation exchange capacity (CEC) of 66.00 mequiv/100 g. The two surfactants, N_G and N_S were synthesized in our laboratory (Supplementary Material Figs. S1–S9). Distilled water was used in all experiments.

2.2. Standard working curve

The standard working curves used for analysis are depicted in Fig. S10. The corresponding parameters are shown in Table S1.

2.3. Adsorption experiments

Sorption of N_G/N_S on Na-Bt and MO on N_S-Bt and N_G-Bt was done according to that described by Kan et al. [18]. The modified bentonites were designated as *x*NG-Bt or *x*NS-Bt, where *x* is arabic numbers which denotes the initial concentration of N_G/N_S used for the modification.

The amount of adsorbates adsorbed per unit mass of adsorbents was calculated by the mass balance following equation [19,20].

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where q is the amount adsorbed per gram of adsorbent, C_0 and C_t are the concentration of N_G/N_S in the solution at the beginning and t time, respectively, m is the mass of Na-Bt, N_G-Bt or N_S-Bt used, and V is the initial volume of N_G/N_S/MO solution. C_t was obtained from the corresponding standard equation in Table S1.

The decoloration efficiency was given by the following equation [18].

$$\eta = \frac{A_0 - A}{A_0} \times 100\% \tag{2}$$

where η is the decoloration rate, A_0 and A are the absorbance of MO solution untreated and treated by N_G-Bt/N_S-Bt, respectively.

2.4. Characterization

The X-ray diffraction (XRD) patterns and the Fourier transform infrared spectra (FTIR) were obtained according to Kan et al. [18].

Thermogravimetric analyses (TGA) of the samples in a platinum crucible were carried out on STA 449 F3 Jupiter thermal analyzer (Netzsch, Germany), which operated at a ramp of 10 °C/min from room temperature to 800 °C in a high-purity flowing argon atmosphere (20 mL/min) [21].

3. Results and discussion

3.1. Adsorption of the surfactants on the bentonite

3.1.1. The intercalation of N_G/N_S on bentonite

The relationship of adsorption capacity (q_e) of N_G/N_S at equilibrium on Na-Bt with the initial concentration (C_0) is depicted in Fig. 1. It can be seen clearly that the q_e increases linearly with increasing N_G/N_S concentration firstly, and then reaches a platform. This result indicates the existence of strong electrostatic interactions between N_G/N_S and Na-Bt [22]. The q_e of N_G is 2.46 mmol/g, which is twice more than that of N_S (1.06 mmol/g), suggesting that more N_G molecules adsorbs on Na-Bt.

3.1.2. Characterization of N_G-Bt and N_S-Bt

3.1.2.1. The elements in Na-Bt, N_G-Bt and N_S-Bt. The element of C and N in N_S-Bt and N_G-Bt are analyzed by elemental analyzer (EURO-EA3000, Italy). The results in Table S2 unveiled clearly that the content of carbon and nitrogen element has increased in N_S-Bt (20.37%; 1.10%) and N_G-Bt (21.58%; 1.22%) comparing with Na-Bt (0.7%; <0.5%), which confirms that both N_G and N_S exist in the modified bentonite.

3.1.2.2. The basal spacing of N_G-Bt and N_S-Bt. The basal spacing of Na-Bt is 1.39 nm identical to that we have previously reported [18]. Fig. 1 shows that the intercalation of N_G/N_S into Na-Bt results in an expansion of the interlayer space in a stepwise fashion. It increases rapidly with N_S/N_G concentration at the beginning, and then it is up to 3.07 nm for N_G-Bt and 2.13 nm for N_S-Bt at 4.0 mM of N_S/N_G. Then the maximum basal space (2.63 nm) is reached and afterwards it almost unchanged with increasing the