Chemical Engineering Journal 349 (2018) 388–396

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Comparative study of organo-vermiculite, organo-montmorillonite and organo-silica nanosheets functionalized by an ether-spacer-containing Gemini surfactant: Congo red adsorption and wettability

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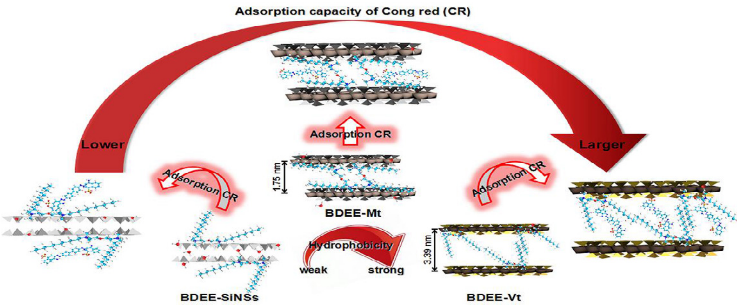
HIGHLIGHTS

- An ether-spacer-containing Gemini surfactant was used as modifier for three organo-clays.
- Modifier structure and wettability have significant influence on the adsorption performance of organo-clays.
- The adsorption capacity of organo-vermiculite (BDEE-Vt) towards CR is up to 298 mg g^{-1} at 55 °C.
- The larger layer charge of the clay, the more hydrophobic of the particle, the more CR adsorbed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Organo-vermiculite
Organo-montmorillonite
Organo-silica nanosheets
Gemini surfactant
Congo red
Wettability

ABSTRACT

Clay minerals (vermiculite, montmorillonite and silica nanosheets) with diminishing layer charge were modified by a novel Gemini surfactant, 2,2′-bis(dodecyldimethylammonio)-ethyl ether dichloride (BDEE) for the first time. The resultant products were certified by FT-IR, Elemental analysis (EA), TG, SEM and XRD, which indicated that the BDEE in vermiculite (Vt), montmorillonite (Mt) and silica nanosheets (SiNSs) adopted different arrangements. Adsorption capacities as a function of contact time, concentration of the Congo red (CR) and temperature were explored in detail. The results showed that the saturated sorption amount of BDEE-Vt, BDEE-Mt and BDEE-SiNSs up to 298, 154 and 64 mg g^{-1} at 55 °C within 120 min, respectively. Interestingly, the order of adsorption capacities of these organo-clays were agreed with the sequences of the layer charge and the hydrophobicity of particles characterized by Lipophilic to Hydrophilic Ratio (*LHR*), which further proved the importance of hydrophobic interaction to CR adsorption onto organo-clays. The pseudo-second-order and Redlich-Peterson models were more suitable for the adsorption data of each adsorbent. Thermodynamic parameters showed that the processes of absorbed CR on BDEE-Vt and BDEE-Mt were endothermic and spontaneous, while BDEE-SiNSs was endothermic and non-spontaneous converted to spontaneous with temperature increasing. This work provides theoretical guidance for further design of highly efficient modifiers and high-performance organo-clay adsorbents.

1. Introduction

With the problem of water pollution intensified, several approaches have been developed to solve this problem, and adsorption cut a figure by virtue of the simple operation, low maintenance and high removal efficiency [1–3]. Considering the cost-effective, the budget clay-based

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https://doi.org/10.1016/j.cej.2018.05.095
Received 8 May 2018; Accepted 16 May 2018

adsorbents come into scholar's views. The vermiculite and montmorillonite, typical layered phyllosilicates that have sandwiched structure of two tetrahedral coupled with one octahedral sheets, are widely used in industrial, dye and pharmaceutical wastewater on account of their remarkable features [4–9]. What's more, a neotype material, silica nanosheets that stems from vermiculite [10], also arouses researchers' concern on biological as well as adsorption applications [11,12]. Of their superior performance, vermiculite, montmorillonite as well as silica nanosheets seem to be the versatile matrix of promising adsorbents.

Inspired by organo-clays served as an reliable and green adsorbents for removing the persistent pollutant, several attempts have been conducted for dislodging Congo red (CR), whose complex aromatic structure lead to non-biodegradation [13], even environmental and public health risk [14]. Du et al. [15] introduced silica nanoparticles as adsorbents' precursor to get rid of CR from aquatic. Hectorites [16], vermiculite [17] and montmorillonite [18] modified by single chain quaternary ammonium salts such as cetyltrimethyl ammonium bromide (CTAB) used for selective removing of the anionic dye CR were investigated. With the development of organic absorbent, the emerging Gemini surfactant was introduced into modification process of organo-clays for enhancing adsorption efficacy [19]. Several Gemini-modified clays with spacer grafted polar functional group have shown their immense superiority in the removal of organic contaminants [20,21], it is of importance to design novel Gemini surfactant with polar spacer.

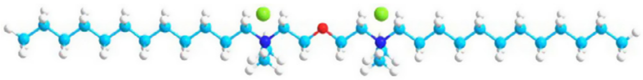
Given that hydrophobic interaction is one of the crucial adsorption mechanisms [22], exploring the hydrophobicity of organo-clay is imperative. In view of the fact that the wettability, an important characteristic of particles surface [23], not only has influence on adsorption, but also biological application and water/oil separation [24,25], capillary rise tests and the Lipophilic to Hydrophilic Ratio (*LHR*) values have developed for evaluating the wettability of the clays [26]. As literature reported, the wetting and adsorption properties of organo-clays varies with layer charge and structure of surfactant [27,28]. The relationship between the adsorption capacity and the hydrophobic character of organo-clays with different layer charge still calls for a further investigation.

In this work, the comparative adsorption was carried out on the organo-clays (vermiculite, montmorillonite and silica nanosheets, which owned high, middle and low layer charge density accordingly) modified by a novel ether-spacer-containing Gemini surfactant, and the association between adsorption and hydrophobicity was further ascertained. The structure of the resultant organo-clays were detected by X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FT-IR), Elemental analysis (EA) and Thermogravimetric (TG) analysis. And the morphology of the three adsorbents was depicted by Scanning electron microscope (SEM) and Transmission electron microscope (TEM). Adsorption experiments were proceeded on organo-clays for the removal of CR from aqueous solution under different contact time, concentration of solution and temperature in detail. The kinetics, isotherms and thermodynamics of CR adsorption onto organo-clays were further explored. The relevance of adsorption and hydrophobic property were deeply assessed by adsorption capacity coupled with *LHR* values that obtained from capillary rise experiments. The objective of the study is to further comparatively investigate the adsorption behavior of different types of organo-clays, deeply reveal the effect of wettability on adsorption capacity of organo-clays, and pave the way to design and fabrication the new modifier and absorbent.

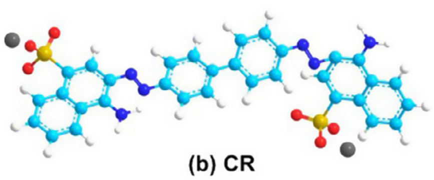
2. Materials and methods

2.1. Materials

The raw vermiculite (Vt, Sigma-Aldrich) and montmorillonite (Mt, Zhejiang Institute of Geology and Mineral Resources, China) were used as matrix of organo-clays, sodium carbonate (Na_2CO_3, Tianjin Guangfu Fine Chemical Research Institute, China) and hydrochloric acid (HCl, Beijing Chemical Works) were served as pretreating agents. Congo red (CR, Tianjin Fuchen Chemical Reagents Factory, China) was chose for exploring the adsorption ability of novel adsorbents. Cyclohexane (Tianjin Fuchen Chemical Reagents Factory, China) and deionized water (18 MΩ cm) were used as testing liquids of capillary rise tests.



(a) BDEE



(b) CR

Fig. 1. The chemical structures of 2,2′-bis(dodecyldimethylammonio)-ethyl ether dichloride (BDEE) and Congo red (CR). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Bis-2-chloroethyl ether (J&K), N,N-dimethyldodecylamine (J&K), 1-propanol (Tianjin Fuchen Chemical Reagents Factory, China) and acetone (Beijing Chemical Works) were used for synthesizing the 2,2′-bis(dodecyldimethylammonio)-ethyl ether dichloride (BDEE), whose synthesis procedures were reported by Kim [29]. The resultant product was characterized by FT-IR, ^{1}H NMR, EA and melting point analysis. The chemical structures of surfactant and Congo red were shown in Fig. 1.

Vermiculite (Vt, 126 mmol $(100\,g)^{-1}$ of cation exchange capacity (CEC)) was pretreated by 1.5 mol L^{-1} Na_2CO_3 solution before use [30]. Moreover, silica nanosheets (SiNSs, 21 mmol $(100\,g)^{-1}$ of CEC) came from the raw Vt leached by 2 mol L^{-1} HCl solution [10,31]. And the CEC of Mt is around 99 mmol $(100\,g)^{-1}$ as reported [32]. Since the CEC is positively correlated with layer charge [33], the layer charge of these clays decreased in the following order: Vt > Mt > SiNSs.

2.2. Preparation of organo-clays

The organo-clays was prepared as follows: 0.126, 0.252, 0.504, 0.756 and 1.008 mmol of 2,2′-bis(dodecyldimethylammonio)-ethyl ether dichloride (BDEE) were dissolved in 100 mL water at 60 °C in a bath for 1 h under intense agitation. Subsequently, 1.0 g of Vt, Mt and SiNSs were put into solutions and reacted at 60 °C for 3 h, respectively. After that, the mixtures were centrifuged and washed by deionized water several times. The wetted products were dried in oven at 80 °C overnight and ground to pass through 200 mush sieves. The three resulting organo-clays were named as BDEE-Vt, BDEE-Mt and BDEE-SiNSs, separately.

2.3. Characterization

Fourier transformed infrared spectroscopy (FT-IR) of BDEE, Vt, Mt, SiNSs and organo-clays were conducted on FT-IR spectrometer (Nicolet Magna 560 E.S.P) in KBr pellets in the scanning range of 4000–400 cm^{-1} with the resolution of 4 cm^{-1}. The X-ray diffraction (XRD) patterns of the samples were obtained by X-ray diffractometer (Shimadzu XRD-6000) with Cu Kα radiation, which operated at 40 kV and 40 mA and scanned from 2 to 10° at 1°/min ($\lambda = 0.15406$ nm). According to the Bragg's law ($\lambda = 2d\sin\theta$), layer spacing of the samples could be calculated. Scanning electron microscope (SEM, SU8010, Japan) and Transmission electron microscope (TEM, Tecnai G^2 F20, America) recorded the structure of the particles. Elemental analysis (EA, EA 3000 organic element analyzer) and thermogravimetric