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Research paper

Effective removal of emulsified oil from oily wastewater using surfactant-modified sepiolite

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ABSTRACT

In this study, tetradecyl trimethylammonium bromide (TTAB), cetyl trimethylammonium bromide (CTAB), and octadecyl trimethylammonium bromide (OTAB) were used to modify natural sepiolite via an ion exchange reaction to form organic sepiolite (organo-Sep) hybrids. This modification is particularly critical in order to obtain good affinity between organo-Sep hybrids and emulsified oil droplets (EOs). The loading surfactants changed the surface wettability from highly hydrophilic to increasingly hydrophobic, and a charge inversion from negative to positive occurred. Organo-Sep hybrids were investigated as adsorbents for removing emulsified oil from simulated oily wastewater. The morphology, texture, and surface properties of Sep and organo-Sep hybrids were characterized by various characteristic techniques, including SEM, XRD, FT-IR, contact angle analyzer, surface area analyzer, and ζ -potential analyzer. After modification, the BET surface area of Sep significantly increased from 297.8 to 698.6 m²/g, while the total pore volume of Sep raised from 0.840 to 3.080 cm³/g with an increase in alkyl chain length of surfactants. Experimental data showed that initial pH and temperature were two key factors affecting adsorption efficiency. It was observed that 98–99% of EOs was successfully removed by organo-Sep hybrids at 60 °C. The maximum adsorption capacities of TTAB-Sep, CTAB-Sep, and OTAB-Sep for EOs were determined from Langmuir isotherm at pH 6 and 60 °C as 434.7, 448.3 and 454.9 mg/g, respectively, along with good recyclability of more than 5 cycles. Thermodynamic data suggested that the adsorption process was physical, spontaneous, and endothermic in nature. Results showed that the organo-Sep hybrids were promising adsorbent materials for the preconcentration and separation of EOs from oily wastewater.

1. Introduction

Wastewater that contains emulsified oil-in-water (O/W) emulsion stems from our daily life and various industrial processes (Syed et al., 2011; Zhu et al., 2011; Li et al., 2016; Gao et al., 2017). Specifically, due to the increasing demand for energy and diminishing amount of conventional oil, increasing numbers of enhanced oil recovery (EOR) technologies have been carried out to improve displacement fluid properties and stabilize crude oil production (Dong et al., 2017). Alkali, surfactants, and polymers are extensively used for this purpose, and are often injected into displacement fluid for enhancing oil recovery efficiency. Oil recovery efficiency can be further enhanced by using a combination of alkali, surfactants, and polymers, which is termed alkali/surfactant/polymer (ASP) flooding. With the rapid growth of oil and gas (O&G) drilling processes, an enormous amount of liquid waste

is generated. Such liquid waste is called produced water or oily wastewater (Dong et al., 2017; Gao et al., 2017). Especially, the discharge amount of produced water increases rapidly as the demands of global energy and innovative O&G drilling techniques continuously rise (Ibrahim et al., 2010; Dong et al., 2017). The direct discharge of such oily wastewater is prohibited by government regulations since it will cause severe and long-term damage to environment and human health. Simple, rapid and efficient methods for treating oily wastewater, especially emulsified O/W emulsion, have received considerable attention. Produced water contains dispersed oil droplets, suspended solid particles, and various dissolved inorganic and organic components (Choi and Cloud, 1992). Among them, oil droplets are finely stabilized by ASP, emulsified in the water, and have a mean size of < 10 μ m, making them very difficult to remove. Therefore, produced water or oily wastewater from ASP flooding pose major difficulties for treatment

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due to the presence of ASP, which contributes to emulsion stabilization (Ibrahim et al., 2010; Dong et al., 2017; Gao et al., 2017). Simultaneously, due to rapid industrialization and population growth, freshwater scarcity constitutes one of the most severe problems in the world, especially in underdeveloped regions (Choi and Cloud, 1992). Furthermore, water standards are continuously improving and becoming stricter. Therefore, much attention has been paid to developing facile means for rapid and effective separation of emulsified oil from produced water or oily wastewater prior to being discharged into above-ground receiver facilities for recycling. In particular, effectively recovering a large portion of water for reuse can greatly improve the efficiency of freshwater utilization (Oki and Kanae, 2006; Ye et al., 2016).

To date, various methods, including electrochemical treatment, dissolved air floatation, gravity separation, membrane separation, coagulation, and flocculation have been utilized to treat oily wastewater (Oldham, 1978; Cheryan and Rajagopalan, 1998; Zouboulis and Avranas, 2000; Yang, 2007; Zeng et al., 2007; Al-Yaari et al., 2014). Nevertheless, these conventional methods are mainly useful for free oil and dispersed oil. When oil droplets are finely emulsified and oil droplet size < 10 μm, these techniques are found to be ineffective (Cheryan and Rajagopalan, 1998; Al-Yaari et al., 2014). An economical and effective approach for removing emulsified oil from industrial wastewater, especially in the presence of ASP, remains highly desired. Adsorption has been considered to be an advantageous technique for the removal of emulsified oil due to acceptable discharge quantity, relative simplicity, and low operation cost. The addition of adsorbent materials in oily wastewater facilitates a change from liquid phase to semi-solid phase and once this change is achieved, the removal of emulsified oil by removal of the adsorbent structure then becomes much easier (Reynolds et al., 2001; Teas et al., 2001; Adebajo et al., 2003). To meet the fast-developing water treatment requirements, some properties that are necessary for ideal oil-adsorbent materials, such as hydrophobicity and oleophilicity, environmental friendliness, large surface area, high adsorption capacity, good recyclability, biodegradability, recovery of oil from adsorbent materials, etc. (Zeng et al., 2007). Oil-adsorbent materials are mainly classified into three major types: natural inorganic mineral products, oleophilic vegetable products, and synthetic organophilic products (Adebajo et al., 2003; Lin et al., 2014). Among these oil-adsorbent materials, the most widely used materials are natural inorganic mineral products due to their high ion exchange capacity, large surface area, swelling properties, and strong adsorption capacities (Delacailierie et al., 1995; Xi et al., 2005).

Sepiolite (Sep) is a natural clay mineral with an ideal formula of magnesium silicate $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$ (Dentel et al., 1995; Cheng et al., 2011; Özcan and Gök, 2012). The Sep structure is constituted by two silica-oxygen tetrahedral sheets sandwiching a magnesium-oxygen octahedral sheet. Similar to other types of silicate minerals, it contains a continuous tetrahedral sheet, however, it also differs from other layered silicates while it lacks a continuous octahedral sheet. The surface of Sep can be considered to be derived from talc-like T-O-T ribbons that grew up in the fibre direction. Each ribbon being linked to the next through an inversion of Si–O–Si bond (Özcan et al., 2005; Tartaglione et al., 2008). Because of the discontinuous octahedral sheets, many fine microporous tunnels and channels occur in the Sep structure with dimensions of $3.7 \times 10.6 \text{ \AA}$ (Galan, 1996; Alvarez et al., 2011; Zhuang et al., 2018a). The presence of nanostructured tunnels and channels allow the access of more voluminous gases, oils, and organic components into the structure of Sep, giving rise to important environmental applications (Alkan et al., 2007; Moreira et al., 2017). Nevertheless, the hydration of inorganic cations (i.e., K^+ , Na^+ , and Ca^{2+}) on the exchange sites results in hydrophilic environment at the Sep surface (González-Pradas et al., 2005; Franco et al., 2014). Thus, naturally occurring Sep shows relatively ineffective as an adsorbent for low-polarity of EOs. Nevertheless, such a difficulty can be overcome by ion exchange of inorganic cations with quaternary ammonium salts,

which may be represented as $[(\text{CH}_3)_3\text{NR}]^+$, where R is a hydrocarbon group (Ruiz-Hitzky, 2001; Li et al., 2009; Suárez and García-Romero, 2012). It has been confirmed that replacement of the exchange inorganic ions by organic cationic surfactants can provide a hydrophobic and oleophilic environment at the surface (Booij et al., 1996; Klopogge et al., 2002; Kuleyin, 2007; Marjanović et al., 2011). Furthermore, surface modification of Sep with specifically designed organic surfactants can enhance Sep compatibility with organic contaminants. This type of Sep is called as organo-Sep.

It is clear that the use of organo-Sep as an oil-adsorbent may constitute a viable option due to its hydrophobicity and ability to adsorb emulsified oil in the presence of ASP. Therefore, the objective of this study is to elucidate the performance of organo-Sep hybrids for removing EOs from highly stable simulated oily wastewater. Crude oil was chosen as the model oil phase to prepare simulated oily wastewater. Tetradecyl trimethylammonium bromide (TTAB), cetyl trimethylammonium bromide (CTAB), and octadecyl trimethylammonium bromide (OTAB) were utilized as modifying agents for preparing organo-Sep hybrids. This study can make a major contribution to understanding the texture, physico-chemical properties, and potential applications of organo-Sep hybrids, especially in the field of oily wastewater treatment. The morphology, texture, surface properties, and wettability of the surfactant-modified Sep samples before and after adsorption of EOs were characterized by scanning electron microscope, X-ray diffractometer, Fourier transform infrared spectrometer, contact angle analyzer, surface area analyzer, and ζ -potential analyzer. The adsorption of EOs onto organo-Sep hybrids was investigated under various environmental conditions, such as variation of surfactant alkyl chain length, initial pH, contact time, and temperature. The relationship between wettability and adsorption capacity was also studied. In addition, the adsorption process involved in interactions between EOs and active sites on Sep surfaces was discussed.

2. Materials and methods

2.1. Materials

Tetradecyl trimethylammonium bromide (TTAB, $\geq 97\%$), cetyl trimethylammonium bromide (CTAB, $\geq 98\%$), and octadecyl trimethylammonium bromide (OTAB, 98%) were purchased from Sigma-Aldrich Co., Ltd. (U.S.A.). Natural mineral containing > 95% of pure Sep was obtained from the Vallecas-Vicalvaro clay deposits (Madrid, Spain). Crude oil was attained from the Shengli oilfield in China, with a water content of < 0.5%, and a density and a viscosity of 865 kg/m^3 and $60 \text{ mPa}\cdot\text{s}$ at $45 \text{ }^\circ\text{C}$, respectively. Partially hydrolyzed polyacrylamide (HPAM) with an average molar mass of $5.0 \times 10^6 \text{ g/mol}$ and hydrolysis degree of 25% was supplied by the Sumitomo Chemical Company (China). Analytical reagent grade sodium dodecylbenzenesulfonate (SDBS), NaCl, CaCl_2 , NaHCO_3 , Na_2CO_3 , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, Na_2SO_4 , and NaOH were purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were used without further purification.

2.2. Preparation of organo-Sep hybrids

Organo-Sep hybrids were prepared by adding a certain amount of long-chain alkylammonium cations equal to 1–2 times the cation exchange capacity (CEC) of the clay, because previous studies indicated that alkylammonium cations were needed in excess of the CEC to fully saturate exchange sites (Jaynes and Boyd, 1991; Jaynes and Vance, 1999). In this study, we used TTAB, CTAB, and OTAB as modifiers to prepare organo-Sep hybrids. The modification of natural Sep for the preparation of organo-Sep hybrids was performed as follows: 100 g of natural Sep was added to 400 mL mixing solution of deionized water/alcohol (1:1, v/v), and then stirred with a mechanical stirrer for 30 min. A stoichiometric amount of the modifier was dispersed in 100 mL of

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