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Immobilization of phenanthrene onto gemini surfactant modified sepiolite at solid/aqueous interface: Equilibrium, thermodynamic and kinetic studies

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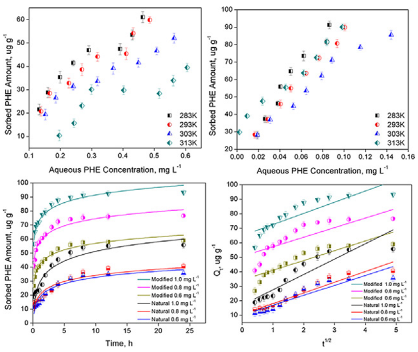
HIGHLIGHTS

- The PHE immobilization on gemini surfactant modified sepiolite was greatly enhanced.
- FT-IR, SEM and TGA indicated that the modification of sepiolite was successful.
- Partitioning into sepiolite-sorbed gemini surfactants greatly increased PHE sorption.
- Freundlich and Elovich models well described the thermodynamic and kinetic data.
- PHE immobilization onto modified sepiolite was spontaneous and exothermic in nature.

GRAPHIC ABSTRACT



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ABSTRACT

The immobilization of phenanthrene from aqueous phase onto natural and gemini surfactant modified sepiolite was investigated with respect to contact time, pH, ionic strength and temperature. The surface modification was examined through FT-IR characterization, SEM technique, and the thermogravimetric analysis. The maximum sorption capacity of phenanthrene on modified sepiolite was 95.15 μg g^{-1} with initial PHE concentration 1.0 mg L^{-1}, temperature 293 K, pH 7, and ionic strength 1 M. The corresponding PHE removal efficiency was higher than 95%. The Langmuir, Freundlich and Temkin isotherm models were applied to describe the phenanthrene sorption behavior and the Freundlich equation agreed well with the experimental data. The evaluation of the thermodynamic parameters indicated that the immobilization of phenanthrene onto gemini surfactant modified sepiolite was a spontaneous and exothermic process from 283 to 313 K. The pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models were used to evaluate the kinetic data. According to the calculated kinetic parameters, the immobilization process of phenanthrene followed the Elovich kinetic model with the highest correlation coefficients. The obtained results show that gemini surfactant modified sepiolite could be effectively utilized as one type of low-cost clay material to remove polycyclic aromatic hydrocarbons from water effluents.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a typical species of persistent organic compounds, which exist in environment from natural sources such as forest fires or from human activities (Yang et al., 2017). Immobilization of PAHs plays an important role in the fate, transport, and bioavailability of these compounds in natural environment (Zhao et al., 2015a). For the immobilization process, the most popular sorbent is activated carbon. However, there is a need for alternative low-cost sorbents because the regeneration of activated carbon is too expensive (Montanher et al., 2005). Sepiolite is a type of low-cost, abundant and safe solid sorbent which is often found associated with other clay and non-clay minerals (Özdemir et al., 2007; Sturini et al., 2016). The abundance and availability of sepiolite clay, together with its relatively low price, guarantee its extensive applications (Kim et al., 2008). Sepiolite is used as a powerful sorbent to remove heavy metals from aqueous solutions (Álvarez-Ayuso and García-Sánchez, 2003; Marjanović et al., 2013). However, to the best of our knowledge, less data has been reported on the removal of organic contaminants through sepiolite.

Natural clays can be modified to significantly improve the immobilization capacity for organic contaminants (Bouras et al., 2007; Cheng et al., 2011). The unique characteristics of gemini surfactants have been reported and the sorption of organic compounds (such as p-nitrophenol and 2-naphthol) can be largely improved through the modification of clay sorbents with gemini surfactants (Xue et al., 2013; Yang et al., 2015). In addition, the excellent solubilization of gemini surfactants towards phenanthrene (PHE) has been proved due to its more micellar core solubilization and intense attraction with PHE at the micelle-water interface (Wei et al., 2011; Wei et al., 2012). The enhanced soil retention for PHE with the addition of gemini surfactants has also been demonstrated (Zhao et al., 2015b). In previous studies, the modification of sepiolite with conventional surfactants could enhance the sorption capacity for dyes (Moreira et al., 2017), pesticides (Sanchez-Martin et al., 2006), and fungicides (Rodríguez-Cruz et al., 2008). However, little information exists about the modification of sepiolite with gemini surfactants, and limited data is available about the removal of PAHs using gemini surfactant modified sepiolite.

The environmental factors (temperature, contact time, ionic strength, pH, etc.) play an important role on the immobilization process of PAHs at the solid/water interface (El-Nahhal and Safi, 2004; Gök et al., 2008; Zeng et al., 2014; Zhao et al., 2015a). Though the effects of environmental parameters on PAHs sorption to various sorbents were reported, the specific mechanisms regarding immobilization of PAHs on modified sepiolite under the influences of various factors are rarely reported.

The aim of this work is to study the immobilization behavior of PHE on gemini surfactant modified sepiolite. In detail, 1) Prepare and characterize the gemini surfactant modified sepiolite; 2) Investigate the effects of environmental factors (pH, initial PHE concentration, ionic strength, and temperature) on PHE immobilization at the water-modified sepiolite interface; 3) Elucidate the mechanisms regarding how gemini surfactants enhance the PHE immobilization on sepiolite; and 4) Establish the thermodynamic and kinetic models and study the nature of the immobilization process. The conclusions obtained from this study could contribute to the widespread use of gemini surfactant modified sepiolite for PAHs-contaminated water treatment.

2. Materials and methods

2.1. Materials

Sepiolite was purchased from Xinglei Sepiolite Company (Henan, China). The general characteristics and properties are listed in Table S1. The natural sepiolite was characterized with respect to its cation exchange capacity (CEC) by the methylene blue method (Gök et al., 2008). The specific surface area was determined at 77 K with a TriStar II 3020 (Micromeritics, USA) using BET nitrogen gas sorption method. PHE was selected as the representative PAHs, and was purchased from A Johnson Matthey Company (MA, USA) with the purity greater than 98%. Cationic gemini surfactant (N1-dodecyl-N1, N1, N2, N2-tetramethyl-N2-octylethane-1, 2-diaminium bromide, 12-2-12) was obtained from Chengdu Organic Chemicals Co., Ltd. (Sichuan, China), with a purity of 98%. The water solubility of PHE is 1.06 mg L^{-1} at 298 K and the octanol–water coefficients (log K_{ow}) is 4.57. The stock solution of PHE was made by diluting the desired amount of pure PHE into HPLC-grade methanol solution, and was stored in a dark place at 277 K in an amber borosilicate bottle to minimize photodegradation and volatilization.

2.2. Modification

The modification experiments were conducted in a 250 mL conical flask. 10 g of sepiolite and 0.2 g gemini surfactants were first added into the conical flask; after that, 100 mL of deionized water were added into the flask. Then the flask was placed in a reciprocal shaker (SHKE5000, Thermo Scientific, USA) at 293 K and 200 rpm for 24 h to reach the sorption equilibrium. It was then filtered and washed with deionized water until the liquid was bromide free. After dried at 333 K, the modified sepiolite was obtained through mechanically whetted to 100 meshes with a mortar pestle. The sieved solid was homogenized as much as possible and stored in glass containers. Instrumental analyses such as Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA) were conducted to demonstrate the effective modification of sepiolite with gemini surfactants. The FT-IR spectra of natural sepiolite and gemini surfactant modified sepiolite were recorded on a FT-IR spectrophotometer (Tensor 27, Bruker, USA). The morphology of the modified sepiolite was examined by scanning electron microscopy (JSM-7001F, Japan). Thermogravimetric analysis of the modified sample was obtained using a simultaneous thermal analyzer (STA 6000, PerkinElmer, USA) operating at a ramp of 283 K/min from room temperature to 1073 K in a high-purity flowing nitrogen atmosphere (100.0 mL $\min^{-1}$).

2.3. Sorption studies

The batch sorption experiments were conducted in 20 mL glass vials. To investigate the effect of contact time, 0.1 g natural/modified sepiolite and 10 mL solution were placed in a reciprocal shaker at 293 K and 200 rpm for 24 h. The initial PHE concentration was 0.6, 0.8, and 1 mg L^{-1} and the solutions contained 0.01 M NaCl at pH 7. The aqueous concentration of PHE was recorded at 0.17, 0.33, 0.5, 0.67, 1, 1.5, 2, 3, 4, 6, 8, 12, and 24 h, respectively. Preliminary experiments showed that 24 h was sufficient for the sorption process to reach equilibrium and the experimental loss of PHE was negligible (Asztalos and Kim, 2015; Ben-Awuah et al., 2015; Forsythe et al., 2015). Before testing, the samples was placed for 10 min to separate sepiolite from solution. (Preliminary experiments demonstrated that 10 min was enough for the purification of supernatant.) An appropriate aliquot of supernatant was then carefully withdrawn with a volumetric pipette to further determine the residual amount of PHE. Meanwhile, controlled experiments without PHE were conducted and the supernatant of controlled samples were analyzed as the background concentration for PHE. PHE was analyzed using HPLC. The HPLC instrument, an Agilent 1260 Infinity LC System (USA), was equipped with vacuum degasser, binary pump, autosampler, thermostated column compartment (set to 303 K), diode array detector (DAD), and ZORBAX Eclipse PAH column (3.5 μm particle size, 4.6 mm × 150 mm ID). A mobile phase consisting of acetonitrile/water (75:25, v/v) was used at a flowrate of 1.0 mL/min. PHE was monitored with DAD at 250 nm. The amounts of PHE sorbed to the sample were the difference between the initial amount added and the amount remaining in the solution.