



## Research paper

## Novel multi amine-containing Gemini surfactant modified montmorillonite as adsorbents for removal of phenols

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## ABSTRACT

A novel multi amine-containing Gemini surfactant (including four positively charged N) modified organo-montmorillonite (GMt) was prepared and served as adsorbents of phenol, o-chlorophenol (2-CP) and 2,4,6-trichlorophenol (2,4,6-TCP). The structure and morphology of GMt were studied by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), N<sub>2</sub> adsorption/desorption isotherms (BET) and thermo gravimetric analysis (TGA). A batch technique was applied to investigate the influence of various factors, and the results illustrated that the saturated intercalation concentration of the modifier was 0.8 times to the cation exchange capacity (CEC) of the original Na-Mt and the adsorption was pH dependent, the optimum adsorption occurred at pH = 10, 7, 5 for phenol, 2-CP and 2,4,6-TCP, respectively. At the same conditions, the adsorption capacities of original Na-Mt were only 8.29 mg/g, 26.20 mg/g and 39.13 mg/g for three phenolic pollutants, while the maximum equilibrium adsorption amounts were 81.68 mg/g, 336.59 mg/g and 535.49 mg/g for phenol, 2-CP and 2,4,6-TCP, respectively. The adsorption kinetics of all the three phenols was in good agreement with the pseudo-second order kinetics model. The adsorption isotherm of 2,4,6-TCP was abided by Langmuir and Freundlich isotherm, however, phenol and 2-CP were better modeled by Freundlich isotherm. The negative values of  $\Delta G^\circ$  and positive values of  $\Delta H^\circ$  got from thermodynamic study confirmed that the adsorption of 2-CP and 2,4,6-TCP on GMt was a physical, spontaneous and endothermic process. The adsorption process of phenol was an exothermic process. Both adsorption and partition contributed to the adsorption of these three phenols to organo-montmorillonite.

## 1. Introduction

Phenolic effluent is one of the most harmful industrial wastewaters in the world, which is also an important source of water pollution. The discharge of phenolic compounds, contaminate water that produce unfavorable taste and odor even at very low concentrations (Păcurariu et al., 2013; Luo et al., 2015). Phenol and its derivatives can not only degrade the quality of the environmental, but also can affect animal and human health via food chains (Sparks, 2005; Ma et al., 2016b; Khan et al., 2017). Chlorinated phenol is one of the most common phenol derivatives in the wastewaters, which is a persistent organic pollutant with high toxic and potential bioaccumulation (Molina et al., 2009; Khan et al., 2018). 2-chlorophenol (2-CP) and 2,4,6-trichlorophenol (2,4,6-TCP) are typical chlorinated phenol which are widely used in the preservation of wood, vegetables and paint relying on its bactericidal properties. They are also intermediate products in the production process of herbicides, pesticides and dyes. The US Environmental Protection Agency (EPA) has listed phenol and chlorinated phenol as the

priority pollutants owing to their carcinogenicity and considerable persistence (Zhao et al., 2015; Zheng et al., 2015; Yang et al., 2017). They have also been reported to cause bad effects on the human nervous system, and can lead to lymphomas, leukemia, and liver cancer via oral exposure (Wang et al., 2005; Senturk et al., 2009; Zango et al., 2016).

Nowadays, various technologies have been proposed to handle the phenolic effluents including biological degradation (Scully et al., 2006), chemical oxidation (Zhou et al., 2014), precipitation (Landis and Keeler, 1997), ion exchange (Dąbrowski et al., 2004; Caetano et al., 2009), solvent extraction (Fan et al., 2008), complexation, membrane separation and adsorption (Chen et al., 2009; Chakrabarty et al., 2010; Fan et al., 2011; Zhu et al., 2011). Among them, adsorption emerges as a feasible process for the treatment of waste from wastewaters. Presently it is also most widely used method due to its low cost, high efficacy, eco-friendly and easy operation.

The public have paid more and more attention to montmorillonite (Mt), which has many good characteristics (Xi et al., 2007; Wang et al.,

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2008; Lu et al., 2014). However, high surface energy and hydrophilicity make it hard to disperse in the organic phase which has a negative effect on its application in the adsorption of organic contaminants (Ren et al., 2018). So it is needful to modify Mt with organic compound to change the hydrophilicity surface to hydrophobic to improve its affinity towards organic contaminants (Li and Wu, 2010).

Montmorillonite is a 2:1 type of layered clay, which has an aluminum octahedral sheet sandwiched by two siloxane tetrahedral sheets. The isomorphous substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  and  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$  in the octahedral layer produces a negative charged surface. While the negative surface can be counterbalanced by interlayer cations (Liu et al., 2008; Long et al., 2013). The most widely used organic modifiers are cation surfactants especially quaternary ammonium salts, such as cetyltrimethyl ammonium bromide (CTAB) (Du et al., 2016), octadecyltrimethylammonium bromide (ODTMA) (Tong et al., 2010), tetramethylammonium bromide (TMA) (Huang and Zhu, 2011). The majority of the published reports were dedicated to the conventional cation surfactants, which are monomeric surfactants, while Gemini surfactants are recognized as a new generation of surfactant (Tian et al., 2012; Liu et al., 2016). Comparing with monomeric surfactants, dimeric quaternary ammonium (two positively charged N) and trimeric quaternary ammonium (three positively charged N) or multi amine-containing Gemini surfactant (four or more positively charged N) possess more positively ammonium head groups which exhibit excellent characteristics, for instance, remarkably lower critical micelle concentration (CMC) and higher capacity to lower the oil/water interfacial tension (Liu et al., 2011; Wang et al., 2013; Xue et al., 2013). Moreover, several reports have illustrated that the Mt modified by dimeric Gemini surfactant showed better performance than monomeric surfactant modified Mt in getting rid of organic contaminants from the effluent (Liu et al., 2014; Yang et al., 2014; Yang et al., 2015). However, to the best of our knowledge, less information about the application of organoclays modified by multi amine-containing Gemini surfactant containing four positive charge and two hydroxyl groups has been published.

The goal of this work is to investigate the adsorption behavior of the phenol, 2-CP and 2,4,6-TCP from water solution onto the novel multi amine and two hydroxyl-containing Gemini surfactant (Didodecyl dimethyl hydroxypropyl-multi amine bis quaternary ammonium salt) modified montmorillonite (GMt). Fig. 1 displays the structure of the novel Gemini surfactant molecule. The intercalation and surface properties of montmorillonite samples before and after modification were characterized by XRD, FTIR, BET and TGA. Meanwhile, so as to investigate the adsorption capacity of the GMt towards phenol, 2-CP and 2,4,6-TCP, a series of batch experiments were carried out as a function of the amount of modifier, initial adsorbate concentration, reaction time, temperature and solution pH. Additionally, we also studied the adsorption mechanism of phenolic compounds onto the modified montmorillonite by kinetics, isotherm and thermodynamics.

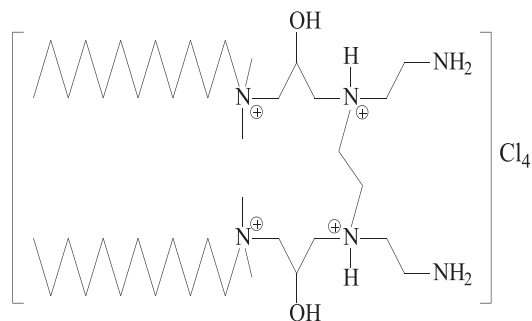


Fig. 1. Chemical structure of novel Gemini surfactant molecule and cation.

## 2. Materials and methods

### 2.1. Materials

The sodium-montmorillonite (Na-Mt) used in the study was supplied by Wancheng bentonite Co. Ltd. (Heishan, Liaoning, China) with the cation exchange capacity (CEC) value of 90 mmol/100 g which was measured by the method of ammonium acetate procedure (Doğan et al., 2000). Gemini surfactant with multi-amine and two hydroxyl-groups is the patented product provided by Simo Institute of Organic Chemistry (Shangyu, Zhejiang, China). They were used as delivered without further purification. Phenol, 2-chlorophenol and 2,4,6-Trichlorophenol with purity of 98% were supplied by Aladdin Chemistry Co. Ltd. (Shanghai, China). All other reagents were of analytical grade. Distilled water was used in all experiments.

### 2.2. Preparation of GMt

A series of organic modified montmorillonites were prepared by taking different amount of multi amine and two hydroxyl-containing Gemini surfactant as modifiers. And the detailed procedures were carried out: 2 g Na-Mt power was put into 100 mL of distilled water and kept stirring until well dispersed. Desired amounts of Gemini surfactant were dissolved in 100 mL of distilled water and then slowly added to the montmorillonite dispersion. The amounts of surfactant were equivalent to 0.4, 0.6, 0.8, 1.0, 1.2 and 1.5 times as the CEC of Mt. Then the mixtures kept stirring for 24 h at room temperature. Thereafter, the precipitates were separated by filtration and rinsed by distilled water for several times until no chloride anions were detected by  $\text{Ag}^+$ . Finally, the products were dried in a vacuum oven at 80 °C for 24 h, grounded with a mortar into powder and sieved through a 200-mesh sieve. They were designated by GMt-0.4, GMt-0.6, GMt-0.8, GMt-1.0, GMt-1.2 and GMt-1.5, respectively.

### 2.3. Characterization methods

A Bruker D8 X-ray (Bruker Corporation, Germany) was used to get X-ray diffraction patterns of power samples. Fourier transformed infrared spectroscopy (FTIR) spectra of the adsorbent samples were recorded by using a Nicolet IS-10 FTIR spectroscopy (Thermo Fisher Scientific, USA). The specific surface area of the original Na-Mt and GMt were characterized by  $\text{N}_2$  adsorption-desorption measurements using an Autosorb-iQ-MP specific surface area and pore size analyzer (Quantachrome Instruments, USA). Thermo gravimetric analysis (TGA) was performed on a STA 449 F3 Jupiter thermo gravimetric analyzer (Netzsch, Germany).

### 2.4. Adsorption experiments

The adsorption capacities of GMts for phenols were carried out by a series adsorption experiments. The influence of varying factors including the concentration of surfactant, initial adsorbate concentration, reaction time, solution pH, and temperature on the uptake of these three phenolic compounds onto organic modified montmorillonites were investigated in detail. To determine the concentration of surfactant, by mixing 0.04 g of GMt samples with 100 mL of phenols when their initial concentrations of 100 mg/L in a 250 mL beaker without controlling the pH and temperature. The dispersions were agitated in the room temperature for 12 h and then the dispersions were filtered through a 0.45  $\mu\text{m}$  membrane filter. After that, the concentrations of residual phenols were determined by using the UV1800 UV-Vis spectrophotometer (Shanghai Jinghua Instrument Corporation, China) with the analytical wavelength of 270 nm for phenol, 274 nm for 2-CP and 293 nm for 2,4,6-TCP. The phenol and its derivatives adsorption capacities on GMt were calculated by the following equation:

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