



Comparative study of 2,4,6-trichlorophenol adsorption by montmorillonites functionalized with surfactants differing in the number of head group and alkyl chain



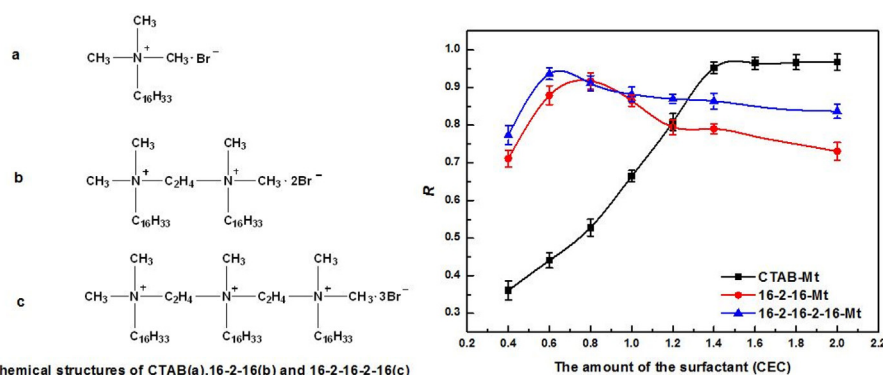
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HIGHLIGHTS

- Organoclays modified by the novel trimeric quaternary ammonium surfactant were prepared.
- 16-2-16-2-16-Mt presented highest adsorption capacity at the lower modifier dosage for 2,4,6-TCP.
- 2,4,6-TCP adsorption is related to the number of alkyl chain and loaded amount of surfactant.
- Hydrophobic interactions are responsible for 2,4,6-TCP adsorption.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 19 October 2016
 Received in revised form 20 February 2017
 Accepted 22 February 2017
 Available online 24 February 2017

Keywords:

Comparative study
 Montmorillonite
 Quaternary ammonium salts
 Head group
 2,4,6-Trichlorophenol
 Adsorption

ABSTRACT

Understanding the structures and characteristics of surfactants used to modify montmorillonites is crucial to predict the adsorption capacity of the resultant organo-montmorillonites in the aquatic environment. Herein, organo-montmorillonites modified by surfactants containing various amounts of head groups and hexadecyl chains were prepared. A general comparison was conducted of organo-montmorillonites modified by methyl hexadecyl bis[3-(dimethylhexadecylammonio)ethyl] ammonium tribromide (16-2-16-2-16), dimeric surfactants (1, 2-bis (hexadecyldimethylammonio) ethane dibromide, 16-2-16) and cetyl trimethyl ammonium bromide (CTAB) for their adsorption performance on 2,4,6-trichlorophenol (2,4,6-TCP) from aqueous solution. The resultant organo-montmorillonites were characterized by XRD, TGA and FT-IR spectroscopy. Batch studies were performed to evaluate the influences of various parameters like the amount of modifiers, the number of alkyl chain, contact time and solution pH on the removal of 2,4,6-TCP. Results indicated that the removal efficiency follows the order of CTAB-Mt < 16-2-16-Mt < 16-2-16-2-16-Mt from 0.4 CEC to 1.2 CEC, which may be due to increasing hydrophobicity with the increase in hexadecyl chain number. However, the adsorption capacity is on the rise in the order 16-2-16-Mt > 16-2-16-2-16-Mt > CTAB-Mt beyond 1.2 CEC. This might be interpreted in terms of the combined contribution of packing density of hexadecyl chains in the interlayer of montmorillonites and ion-dipole interaction between the head group of intercalated surfactants and 2,4,6-TCP. Full kinetics, equilibrium and thermodynamics were also undertaken. Moreover, the maximum adsorption capacities of 2,4,6-TCP were 328.9 mg/g at 1.6 CEC for CTAB-Mt and 306.7 mg/g at 0.8 CEC for 16-2-16-Mt, respectively,

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whereas as high as 322.6 mg/g for 16-2-16-2-16-Mt even at the modifier amount as low as 0.6 CEC. This study suggests that 16-2-16-2-16-Mt with three head groups and hexadecyl chains can serve as a more high-efficiency and cost-effective adsorbent for removal of 2,4,6-TCP from aqueous solution.

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1. Introduction

Chlorophenols, which have extensively existed in the environmental wastewaters from chemical industries, such as pharmaceuticals, defoliants, fungicides, preservatives, insecticides, herbicides, petroleum refineries, water disinfecting process and as intermediates in chemical synthesis, can exert negative impact on different biological processes [1–4]. Particularly, 2,4,6-trichlorophenol (2,4,6-TCP), a representative chlorophenol pollutant, has been listed as a high-priority pollutant by the US Environmental Protection Agency (EPA) and European Regulatory Authorities because of dramatically toxicological effects and potential carcinogenicity and mutagenicity [5,6]. Therefore, there has grown up an urgent need to address the problem of environmental contamination.

Various treatment technologies including biological degradation [7], photodegradation [8,9], UV/ozone oxidation [10], adsorption [11–14] have been developed for the remediation of 2,4,6-TCP from aquatic systems based on thermal, chemical, physicochemical or biological fundamentals [3]. Of all the known methods, adsorption has been considered to be both feasible and effective for the removal of 2,4,6-TCP from wastewaters because of its simplicity of operation, mild reaction conditions, less secondary pollution and low-cost advantage.

Recently, organo-montmorillonites prepared by the exchange of organic cations (typically quaternary ammonium surfactants) with inorganic ions (e.g., Na^+ , K^+ , Ca^{2+}) in the interlayer galleries of montmorillonites, being low-cost and easily available adsorbents in wastewater treatment, have caused extensive concern. Many studies have been devoted to investigate the environmental behavior of organo-montmorillonites modified by various quaternary ammonium surfactants, such as octadecyltrimethylammonium chloride [15], dodecylpyridinium chloride [16], cetylpyridinium bromide [17], octadecyl dihydroxy ethyl methylammonium bromide [18], 1, 3-bis(octyldimethylammonio)-2-hydroxypropane dichloride [19], glycol bis-N-cetylnicotinate dibromide [20], 1, 3-bis(dodecyldimethylammonio)-propane dibromide [21] for the removal of organic contaminants including chlorophenols. Depending on the structures and characteristics of quaternary ammonium surfactants intercalated, organoclays display distinct adsorptive properties and abilities. Several studies have documented that organoclays modified by the surfactant with longer alkyl chain exhibit higher affinity for organic pollutants because the hydrophobic partition medium resulting from longer alkyl chain within the montmorillonite layer can form and function analogously to a bulk organic phase, thus making it prone to adsorb organic contaminants [22,23]. Reports also suggest that the dimeric surfactant modified organoclays exhibit better efficacy in getting rid of organic contaminants in the aquatic environment in comparison to those modified by the corresponding monomeric surfactant [24,25]. It is noted that the modifiers used to prepare organo-montmorillonites are only limited to monomeric and dimeric surfactants, leaving much space for exploration.

Trimeric surfactants, made up of three amphiphilic moieties connected at the level of, or close to, the headgroups by two spacer groups that may be hydrophilic, hydrophobic, flexible, or rigid, have been developed [26,27]. Compared with the corresponding

monomeric and dimeric surfactants having one or two alkyl chains, trimeric surfactants exhibit excellent and interesting properties, e.g., lower critical micelle concentration (CMC), higher surface activity, stronger hydrophobic microdomains, higher efficiency at reducing the surface tension and better adsorption behavior at the silica-solution interfaces [27–29], especially higher density of positively charged ammonium groups and larger number of hydrophobic alkyl chains, which are expected to be utilized for preparing organo-montmorillonites with remarkable adsorption performance. Nevertheless, studies on 2,4,6-TCP adsorption using trimeric surfactants to modify montmorillonites is still an untapped area.

Inspired by these elegant investigations, montmorillonites functionalized with trimeric quaternary ammonium surfactants containing long alkyl chain were tactfully designed and prepared, then used to remove 2,4,6-TCP from aqueous solution, its adsorptive performance on 2,4,6-TCP were compared with those modified by the corresponding monomeric and dimeric quaternary ammonium surfactants. In this study, the adsorption capacity of the three organo-montmorillonites towards 2,4,6-TCP was investigated through a series of batch experiments as a function of the amount of modifiers, the number of alkyl chain, contact time and solution pH. Additionally, the adsorption mechanism of 2,4,6-TCP onto the three organo-montmorillonites was evaluated in terms of kinetics, equilibrium and thermodynamics. The present work may shed new light on developing novel montmorillonites functionalized with the trimeric surfactants for highly efficient removal of organic contaminants from wastewater.

2. Materials and methods

2.1. Materials

The sodium montmorillonite (Na-Mt), purchased from Zhejiang Institute of Geology and Mineral Resources, China, has a cation exchange capacity (CEC) of 112 meq/100 g. The main chemical composition is listed as follows: 66.80% SiO_2 , 20.88% Al_2O_3 , 4.18% MgO , 2.88% CaO , 1.97% Fe_2O_3 , 2.20% Na_2O , 0.73% K_2O , 0.13% TiO_2 and 0.23% others. Cetyl trimethyl ammonium bromide (CTAB, 99%), 1-Bromohexadecane (98%), N,N,N',N'-tetramethylethylenediamine (99%), N,N,N',N''-pentamethyldiethylenetriamine (>98%), 2,4,6-trichlorophenol (2,4,6-TCP, 98%) were kindly supplied by Sigma-Aldrich.

The monomeric quaternary ammonium surfactant, cetyl trimethyl ammonium bromide (CTAB) was used without further purification. The dimeric quaternary ammonium surfactant, 1, 2-bis(hexadecyldimethylammonio) ethane dibromide (16-2-16) and the trimeric quaternary ammonium surfactant, methylhexadecyl-bis[3-(dimethylhexadecylammonio) ethyl] ammonium tribromide (16-2-16-2-16) were synthesized according to the method as reported in the literature [28]. Their structures are shown in Fig. 1. The purity of the products synthesized were confirmed by means of ^1H NMR, elemental analysis and FT-IR.

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