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Research paper

Effect of surfactant molecular structure on perchlorate removal by various organo-montmorillonites

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ABSTRACT

A series of organo-montmorillonites (organo-Mt) was synthesized using various cationic surfactants with different alkyl-chain lengths, head groups, and alkyl-chain numbers, which were systematically examined for perchlorate adsorption. The products were characterized by the specific surface area, field-emission scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. In addition, the surfactant loadings and surface charges were investigated by CHN analysis and zeta potential measurements. The greatest adsorption capacity of 0.95 mmol/g-composite was obtained on benzyloctadecyldimethylammonium-modified Mt. Increasing the alkyl-chain length significantly enhanced the capacity and selectivity for perchlorate adsorption, but resulted in decrease of adsorption rate. Compared with trimethylammonium and pyridinium with the same alkyl-chain length, the benzyldimethylammonium as a head group showed better performance in terms of adsorption capacity and selectivity of perchlorate because of higher hydrophobicity. Moreover, increasing the alkyl-chain number decreased adsorption rate, but enhanced adsorption capacity, because of dense packing of alkyl chains and high driving force for entrapment of counter ion-accompanying surfactant. The perchlorate adsorption performance of organo-Mt was synergistically influenced by the alkyl-chain length, head group and alkyl-chain number of the surfactants used for modification.

1. Introduction

Perchlorate (ClO_4^-) has aroused widespread concern because it interferes with iodide uptake in tissues (e.g., the thyroid gland) (Wolff, 1998). Perchlorate contamination has been widely observed in groundwater and surface water (Logan, 2001; Kannan et al., 2009), and it has also been detected in vegetables (Sanchez et al., 2005), rice, milk, and bottled water (Shi et al., 2007). Therefore, it is important to develop technologies and methods to sequester perchlorate from aqueous media. Currently, physical transference, chemical reduction, and biological degradation are used for perchlorate removal, while physical adsorption is extensively applied because of its high-performance and cost-effective features. A series of regenerable resins has been adapted as adsorbents for perchlorate (Xiong et al., 2007). It is relatively costly and complicated to synthesize resins, and special regenerants, such as $FeCl_3$–HCl, are required to efficiently regenerate highly selective perchlorate exchange resins (Gu et al., 2007). Therefore, ion-exchange resins may not be the best adsorbents for perchlorate removal. Low-cost natural materials can be developed as economical alternatives after facile modification (Baidas et al., 2011; Xu et al., 2013).

Montmorillonite (Mt) is one of the most abundant naturally occurring clay minerals. It has a typical layered structure with one octahedral Al–O(H) sheet sandwiched between two tetrahedral Si–O sheets. Isomorphic substitution occurs in both octahedral and tetrahedral sheets, but mainly in the sandwiched Al–O(H) sheet, resulting in negative charges delocalizing on the surface of Si–O sheets (Droge and Goss, 2013). The hydrated inorganic cations (e.g., Na^+) can be introduced in the interlayer space and readily replaced by cationic surfactants. Functional head groups in the cationic surfactant are responsible for ion exchange with pollutant anions (Behnsen and Riebe, 2008; Fang et al., 2013). The adsorption capacity greatly depends on the entrapped amount of counter ion-accompanying surfactant. Uptake of counter ion-accompanying surfactant by hydrophobic interactions is significantly affected by the molecular structure of the surfactant, mainly the length of alkyl chain (Zhang and Somasundaran, 2006). The selectivity for anions may be affected by the degree of hydration of the functional head group in the surfactants associated with its hydrophobicity (Wolff, 1998). An increase in the head group size makes the surfactant more hydrophobic and reduces the binding force to the counter ion (Lin et al., 2013). More poorly hydrated head groups require lower free energy to displace the hydration shell and bind to the target anions with lower hydration energy (Wolff, 1998; Xiong et al., 2007). In the present work, the influence of the surfactant structure to modify Mt on the removal of perchlorate by modified Mt was examined, because

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of the potential harmfulness, high solubility and persistence of ClO_4^- in aqueous medium.

Large and hazardous anions such as TcO_4^-, ReO_4^- and CrO_4^{2-}, which resemble ClO_4^-, have been efficiently immobilized by surfactant-modified clays. Most studies focused on using one specified surfactant to modify different clays (Haggety and Bowman, 1994; Bors et al., 1999; Behnsen and Riebe, 2008; Xi et al., 2010) and using the obtained organoclays to remove different inorganic anions (Atia, 2008). Although several research groups comparatively studied the influence of surfactant structure (number and length of alkyl chain) on surfactant configuration and distribution in organoclays (Xi et al., 2007; Zhu et al., 2012), the further application and significant discussion in inorganic anion adsorption were not addressed. Thus, it is imperative to investigate the influence of surfactant structure systematically for choosing the optimal modifier. In this study, six surfactants with varying alkyl-chain lengths, head groups, and alkyl-chain numbers were selected as modifiers. All of the organo-Mts were synthesized under the same procedure. The differences in configuration, distribution, and uptake of the surfactants in organo-Mt were thoroughly investigated using multiple techniques. Moreover, the performance of perchlorate removal using these organo-Mt was compared and discussed.

2. Material and methods

2.1. Preparation of organo-Mt

High-purity sodium-Mt (Kunipia-F) with a median particle size (d_{50}) of 1.9 μm, and a cation exchange capacity (CEC) of 1.15 meq/g was used in this study, which was supplied by Kunimine Industries Co., Ltd. (Tokyo, Japan). The chemical formula can be expressed as $(Na_{0.97}Ca_{0.08})^{+1.13}(Si_{7.68}Al_{0.32})(Al_{2.94}Fe^{III}_{0.25}Fe^{II}_{0.03}Mg_{0.78})O_{20}(OH)_4^{-1.13}\cdot nH_2O$ based on chemical analysis (ALS Global Ltd., North Vancouver, Canada). The surfactants were provided by Wako Pure Chemical Industries Ltd. (Osaka, Japan) and Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), as summarized in Table 1.

Modification of Mt was performed by dispersing 0.50 g Mt in 50 mL deionized water under vigorous stirring for 15 min at room temperature, and then adding the surfactant with an amount corresponding to 4.0 times of CEC for Mt. This mixture was decanted into a Teflon vessel, homogeneously blended at 1150 rpm and then ultrasonicated using a Branson 3510 ultrasonicator at 45 kHz for 10 min. After microwave radiation (Milestone Microwave Laboratory System) at 80 °C with keeping at 200 W for 1 h, the suspension was slowly cooled down to room temperature, washed, and separated by centrifugation. The final organo-Mt was lyophilized, ground and sieved (<149 μm), which is abbreviated as surfactant/Mt.

2.2. Characterization

XRD patterns of unmodified Mt and the organo-Mt were recorded using Cu Kα X-ray radiation on an Ultima IV X-ray diffractometer (Rigaku, Japan) at 40 kV and 40 mA with 0.0167° divergence and antiscatter slits from $2\theta = 1.0–10.0°$ at a step size of 0.02°, a scan speed of 0.5°/min and a counting time of 2.4 s.

TG-DTA was performed using 5.0 mg of the sample on a 2000SA thermobalance (Bruker, USA) from room temperature to 1000 °C at a heating rate of 10 °C/min in ambient atmosphere. The organic content in the samples was determined by CHN analysis on a CHN Corder MT-6 Elemental analyzer (Yanaco, Japan).

XPS spectra were collected on a PHI ESCA 5800 system (Ulvac, Japan) using a monochromated Al Kα X-ray source at 200 W with a residual pressure in the analysis chamber lower than 1.33×10^{-6} Pa. Survey scan was performed from 0 to 1200 eV with a pass energy of 187.85 eV at step of 0.8 eV with 1 sweep. Narrow scans of Cl 2p, Si 2p, Al 2p, N 1s and C 1s orbitals were conducted with pass energies of 23.5 or 58.7 eV and steps of 0.1 or 0.125 eV. The binding energy (E_B) was calibrated using the C 1s peak at 284.8 eV, and peak separation was carried out with Casa XPS software (Version 2.3.16 PR 1.6).

FTIR spectra were collected by a 670 Plus Transform Infrared spectrometer (Jasco, Japan) with 5% (w/w) of samples in KBr, under the conditions: a nominal resolution of 4 cm^{-1} in the range of 4000–400 cm^{-1}, and by averaging the data from 100 successive scans.

A Zetasizer Nano-ZS (Malvern, UK) was used to determine the zeta potential of the samples which were pre-suspended for 30 min in 1.0 mM NaCl.

FESEM images of Mt and organo-Mt were observed using a SU8000 scanning electron microscope (Hitachi, Japan) at acceleration voltage of 2.0 kV. Measurement of the S_{BET} was performed using 99.99% N_2 gas on a BELSORP-MR6 (BEL Inc., Japan) after the samples were degassed at 120 °C overnight.

2.3. Adsorption experiments

10 mg of organo-Mt was dispersed in 50 mL 0.025–0.23 mmol/L $NaClO_4$ at initial pH = 7.1–7.6, and then the mixture was shaked on a gyratory shaker at 25 °C to reach the equilibrium. The amount of adsorbed ClO_4^- on the adsorbent was calculated by mass balance. Batch kinetic tests were conducted in duplicate with 10 mg of organo-Mt in 50 mL solution of 0.2 mmol/L ClO_4^-. At appropriate intervals, ~1.0 mL of the aqueous mixture was sampled for analysis. To facilitate the comparison of the selectivity for adsorption of ClO_4^- on the organo-Mt, larger concentration of NO_3^- was introduced as a coexisting anion in the ClO_4^- solution. 10 mg of organo-Mt was dispersed in 50 mL

Table 1
Surfactants used for MT modification.

Name	Abbreviation	Chemical formula	Molecular weight (g/mol)		Length × height × thickness (Å × Å × Å)
			Counter ion-accompanying type	Ionized type	
Benzyldimethyltetradecylammonium chloride	C14-BM	$CH_3(CH_2)_{13}N^+(CH_3)_2CH_2C_6H_5Cl^-$	368.04	332.59	23.0 × 10 × 6.0[a]
Benzylcetyldimethylammonium chloride	C16-BM	$CH_3(CH_2)_{15}N^+(CH_3)_2CH_2C_6H_5Cl^-$	397.10	361.65	25.5 × 10 × 6.0[b]
Hexadecylpyridinium chloride monohydrate	C16-PY	$CH_3(CH_2)_{15}N^+C_5H_5Cl^-\cdot H_2O$	358.00	304.54	25.0 × n.d. × 4.3[c]
Trimethylstearylammonium chloride	C18-TM	$CH_3(CH_2)_{17}N^+(CH_3)_3Cl^-$	348.05	312.60	28.1 × 6.7 × 5.1[d]
Benzyloctadecyldimethylammonium chloride	C18-BM	$CH_3(CH_2)_{17}N^+(CH_3)_2CH_2C_6H_5Cl^-$	424.15	388.70	28.1 × 10 × 6.0[b]
Dimethyldioctadecylammonium chloride	2C18-DM	$[CH_3(CH_2)_{17}]_2N^+(CH_3)_2C1^-$	586.50	551.05	$27.0 \times (27.0\cdot\sin\theta) \times$ n.d. [e]

[a] Othmani-Assmann et al. (2007).
[b] Added two or four —CH_2 in the C14-BM alkyl chain (1.27 Å per —CH_2).
[c] Kádár et al. (2006).
[d] With the addition of the length of two —CH_2 (He et al., 2006a).
[e] The θ represents the angle of two C18-alkyl chains (Kádár et al., 2006).