



Sequential modification of montmorillonite with dimethyl dioctadecyl ammonium chloride and benzyl octadecyl dimethyl ammonium chloride for removal of perchlorate



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ABSTRACT

A novel method is reported for surfactant modification of montmorillonite (Mt), and then the performance of the surfactant-modified Mt was investigated for the removal of perchlorate (ClO_4^-). Mt was first modified with dimethyl dioctadecyl ammonium chloride (DDAC) under microwave irradiation, which was followed by a second modification with benzyl octadecyl dimethyl ammonium chloride (BODAC). The influence of the added amount of DDAC in terms of ClO_4^- adsorption to the modified Mt was intensively investigated. In addition, sequential and simultaneous-mixing methods were compared for preparation of the modified Mt in terms of ClO_4^- removal performance. Using sequential modification, addition of DDAC corresponding to 0.05 times the cation exchange capacity of Mt significantly increased BODAC uptake, resulting in the highest adsorption capacity for ClO_4^- (1.08 mmol/g). This can be explained by the good balance between the decrease of steric hindrance and the formation of a hydrophobic interface because of adsorbed DDAC. In contrast, for a composite synthesized with the same ratio of DDAC to BODAC, the simultaneous-mixing method resulted in modified Mt with much poorer ClO_4^- removal performance than the sequential modification method because of the negligible contribution of DDAC to BODAC uptake by Mt. Moreover, a high binding affinity of ClO_4^- to the sequentially modified composite was obtained because of hydrophobicity of interlaced alkyl chains.

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1. Introduction

Quaternary ammonium compounds (QACs) are one of the most effective surfactants which are generally used to modify clays such as zeolite [1] and bentonite [2]. Montmorillonite (Mt), a representative type of negatively charged abundant clay, was selected as a substrate for modification by QACs in this study. There are two approaches to incorporate QACs into Mt: ion exchange with inorganic cations (e.g., Na^+) and hydrophobic interactions of QACs molecules. The obtained QACs-modified montmorillonites (SMt) have been extensively used in environmental remediation, including for the adsorption of pesticides [3], phenol [4], chromium (VI) anionic species [5], etc.

Perchlorate (ClO_4^-) is an emergent contaminant and has been widely detected in aqueous environment [6–8]. Because of the adverse health effects of ClO_4^- [9], development of cost-effective

remediation technologies for contaminated media has aroused extensive interest. A series of adsorbents, such as functionalized SBA-15 [10], MCM-41 silica [11], protonated cross-linked chitosan [12], quaternary amine modified reed [13], amine-crosslinked cotton stalk [14], wood-derived biochar [15], and calcined layered double hydroxides [16], have been investigated for ClO_4^- removal, and SMt have also recently been investigated for this purpose [17–19]. Anions with low hydration energies such as ClO_4^- and perchlorate (TcO_4^-) would be removed through ion-exchanging with counter ion (e.g., Cl^-) in SMt because of the high selectivity of quaternary ammonium to those anions [18–21]. Increasing the amount of counter ion-accompanying QACs improves the adsorption capacity of such hazardous anions by SMt. QACs with long alkyl-chain length and multiple alkyl-chain numbers significantly increase the content of counter ion-accompanying QACs in final SMt [17,22].

In the present work, Mt was initially modified with different amounts of dimethyl dioctadecyl ammonium chloride (DDAC), and then modified with a constant amount of benzyl octadecyl dimethyl ammonium chloride (BODAC). DDAC is a QAC that

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contains two C18 hydrocarbon chains. BODAC has a long alkyl chain (C18) and a large polar head group with a benzene ring, which would enhance the selectivity for large anions [20,22]. Modification of Mt by single QAC was widely studied, while combination of two or more QACs for modification of Mt is rarely addressed. Such sequential modification of Mt with two different types of surfactant for anion adsorption has not been investigated in previous studies.

A large number of clay-based polymer nanocomposites have been synthesized by introducing a specific surfactant to enhance the compatibility with the polymer [23–26]. Strong hydrophobicity will be developed once Mt is modified with DDAC because of its two long hydrocarbon chains. Therefore, application of a certain amount of DDAC to create a strongly hydrophobic interface may decrease the interfacial energy barrier and enhance the binding affinity for following modifiers by hydrophobic interaction. A greater loading of a second modifier associated with higher adsorption capacity for target anions may be obtained. However, the amount of DDAC used influences the exfoliation degree of Mt particles into thinner or single layers, which may reduce the accessibility of the hydrophobic binding sites for the second modifier [24]. Thus, it is important to optimize the loaded amount of DDAC. Moreover, as a control, the same amounts of DDAC and BODAC were initially mixed and applied to modify Mt to compare with sequentially modified Mt in term of ClO_4^- removal. The influence of the amount of added DDAC on ClO_4^- adsorption was interpreted using multiple techniques.

2. Material and methods

2.1. Synthesis of SMT

High-purity sodium montmorillonite (Na-Mt, Kunipia-F) with a cation exchange capacity (CEC) of 115 meq/100 g was supplied by Kunimine Industries Co., Ltd. (Tokyo, Japan). According to the result of elemental analysis, its chemical formula can be expressed as $(\text{Na}_{0.97}\text{Ca}_{0.08})^{+1.13}(\text{Si}_{7.68}\text{Al}_{0.32}) (\text{Al}_{2.94}\text{Fe}^{\text{III}}_{0.25}\text{Fe}^{\text{II}}_{0.03}\text{Mg}_{0.78}) \text{O}_{20}(\text{OH})_4^{1.13} \cdot n\text{H}_2\text{O}$. DDAC and BODAC (Fig. S1) were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). The synthetic conditions for the preparation of SMT are summarized in Table 1. Briefly, 1.0 g Na-Mt was dispersed in 100 mL deionized

water under stirring for 1 h, and then the dispersion was decanted into suspensions with different amounts of DDAC. The mixtures were then vigorously stirred and transferred to a microwave (ETHOS PLUS, Milestone Microwave Laboratory System) for microwave irradiation. For sequential modification, DDAC was loaded on Mt in the same manner as above as the first step, and BODAC with 4 times the CEC was sequentially added in the second modification step. For comparison with sequential modification, using the same molar ratio of DDAC to BODAC as in the sequential modification, DDAC and BODAC were simultaneously added to Mt, and then microwave irradiated and stirred with mild heat. The final solid product was separated by centrifugation at 10,000 rpm for 10 min, washed several times, lyophilized, ground, sieved to recover samples <149 μm in diameter, and stored in a desiccator. The solid products from one-step, sequential, and simultaneous-mixing modifications are abbreviated as DMt, DBMt, and (D + B) Mt, respectively (Table 1). To facilitate complete ion exchange between inorganic cations and DDAC, microwave irradiation at 80 °C was applied in the first modification step, because DDAC is relatively hydrophobic and difficult to dissolve in water at ambient temperature and only partial intercalation may occur for such a large surfactant using conventional hydrothermal techniques [27].

2.2. Characterization

The organic contents of the obtained solid products were determined by CHN analysis (CHN Corder MT-6 Elemental analyzer, Yanaco, Kyoto, Japan). X-ray diffraction (XRD) patterns of Na-Mt and SMT were recorded using Cu K α radiation on an Ultima IV X-ray diffractometer (Rigaku, Akishima, Japan) at 40 kV and 40 mA from $2\theta = 2.0^\circ - 10.0^\circ$ with a step size of 0.02° . Fourier transform infrared spectroscopy (FTIR) spectra were collected using the KBr method on a 670 Plus Transform Infrared spectrometer (Jasco, Tokyo, Japan) with a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1} , where 5 wt% samples mixed with spectroscopic grade KBr crystals were carefully pressed into a fragile pellet and scanned 100 times. Thermogravimetry–differential thermal analysis (TG–DTA) was performed in air using 5.0 mg samples on a 2000SA thermobalance (Bruker, Billerica, MA, USA) from room temperature to 1000 °C at a heating rate of 10 °C/min. Scanning electron microscopy (SEM) observation of

Table 1
Synthetic conditions and the corresponding notations of the SMTs, and the zeta potential (ζ), CHN content, and water content ($m_{\text{H}_2\text{O}}$) results.

Notation	Surfactant-addition method	Added amount (times the CEC, *CEC)		Physical condition for surfactant modification ^c		ζ (mV) ^d	CHN content (%)			$m_{\text{H}_2\text{O}}$ (%) ^e			
		DDAC	BODAC	First step	Second step		C	H	N				
DMt-0.013	One step	0.013	–	Microwave for DDAC	–	-20.7 ± 6.42 (6.62)	n.d. ^e	n.d.	n.d.	8.30			
DMt-0.05		0.05	–			-23.4 ± 6.18 (6.45)	n.d.	n.d.	n.d.	6.24			
DMt-0.10		0.10	–			-27.9 ± 10.6 (6.41)	n.d.	n.d.	n.d.	7.80			
DMt-0.15		0.15	–			-14.9 ± 5.29 (6.36)	n.d.	n.d.	n.d.	6.35			
DMt-0.25		0.25	–			-23.4 ± 3.15 (6.35)	n.d.	n.d.	n.d.	6.81			
DMt-0.75	0.75	–	-14.3 ± 6.85 (6.18)	27.82	5.33	0.86	2.26						
DMt-4	4	–	39.3 ± 1.93 (5.44)	43.78	8.00	1.37	1.54						
BMt-4	Sequential ^a	0	4	Microwave for DDAC	Magnetic stirring for BODAC	52.8 ± 4.38 (5.80)	37.9	6.22	1.43	2.17			
DBMt-0.013		0.013	4			47.3 ± 7.41 (5.25)	38.21	6.11	1.65	2.97			
DBMt-0.05		0.05	4			72.0 ± 3.86 (5.18)	48.55	7.93	2.08	5.26			
DBMt-0.10		0.10	4			52.0 ± 3.88 (5.68)	41.58	6.82	1.78	3.41			
DBMt-0.15		0.15	4			51.7 ± 2.54 (6.06)	39.18	6.38	1.67	2.20			
DBMt-0.25		0.25	4			52.8 ± 3.92 (4.95)	38.11	6.43	1.53	2.36			
DBMt-0.75		0.75	4			46.4 ± 8.11 (4.80)	41.11	6.95	1.52	2.65			
(D + B)Mt		Simultaneous mixing ^b	0.05			4	Microwave irradiation followed by magnetic stirring		40.5 ± 5.48 (5.60)	38.88	6.28	1.70	2.14

^a Sequential modification, where DDAC was used in the first step and BODAC was added in the second step.

^b Simultaneous-mixing modification, where DDAC, BODAC, and the Mt dispersion were simultaneously mixed in the first step without extra addition in the second step.

^c Microwave irradiation was performed at 80 °C for 90 min, and magnetic stirring was carried out at 45 °C for 24 h in all cases.

^d The zeta potential (ζ) was measured in triplicate, and the number in parenthesis is the corresponding pH value. The ζ of Mt is -35.7 ± 0.7 mV at pH 5.92.

^e n.d. means not determined.

^f Evaluated from the TG results.

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