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Research paper

Optimization of hexadecylpyridinium-modified montmorillonite for removal of perchlorate based on adsorption mechanisms

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Adsorption of perchlorate (ClO_4^-) onto hexadecylpyridinium-modified montmorillonite (OMt) was investigated by *in situ* and *ex situ* methods. For the *in situ* method, ClO_4^- was initially bound by hexadecylpyridinium ($HDPy^+$) in the form of HDPy-ClO_4 which together with the excess $HDPy^+$ were simultaneously captured by Mt. The *ex situ* strategy was performed by adding synthesized OMt into ClO_4^--bearing solution, where conventionally dried OMt (II-OMt) and innovative OMt (I-OMt) without drying and washing procedure were compared as adsorbents. The adsorption capacity of ClO_4^- and amount of HDPy released into equilibrium solution were evaluated, where surfactant release was rarely addressed in previous publications. I-OMt showed relatively high adsorption capacity of ClO_4^- and negligible release of HDPy. The lower adsorption capacity of ClO_4^- onto II-OMt was caused by the washing procedure which removed the unstably anchored HDPy. Inhibition of HDPy release of I-OMt was explained by reconfiguration of HDPy after ClO_4^- adsorption as supported by results of X-ray diffraction and attenuated total reflection Fourier transform infrared spectroscopy. In addition, for anion adsorption onto conventionally synthesized OMt, the difference between the amounts of released counter ion and that of entrapped target anion is generally ignored. Such phenomenon was critically considered in this study, and the results showed that the difference between adsorbed ClO_4^- and released Cl^- decreased with an increase of HDPy loading and was more significant in I-OMt. This is rationalized by the desorption of $HDPy^+$ and formation of HDPy-ClO_4 according to the results of ^{13}C nuclear magnetic resonance spectra and the adsorption energy evaluated by the Dubinin–Radushkevich model.

1. Introduction

Montmorillonite (Mt) is one of the most abundant naturally occurring clay minerals, and has been widely used as a scavenger of metal ions (Gupta and Bhattacharyya, 2012) and cationic dyes (Almeida et al., 2009). This application is because of the negative charges of Mt layer that are derived from isomorphic substitutions in octahedral (Mg^{2+} and/or Fe^{2+} replace Al^{3+}) and tetrahedral (Al^{3+} replaces Si^{4+}) sheets (Bergaya and Lagaly, 2013). Generally, Mt can be readily modified with alkylammonium salts to give organo-Mt (OMt), which can be used in other applications, including sequestration of hazardous anions and organics (Bajda and Kłapyta, 2013; Park et al., 2013; Choung et al., 2014; Luo et al., 2015a). Compared with other adsorbents, OMt shows superior performance in terms of removal capacity and stability (Johnston et al., 2012; Zheng et al., 2013; Luo et al., 2015b). Perchlorate (ClO_4^-) is an emerging contaminant that has attracted worldwide attention in recent years (Ye et al., 2012). Because of the detrimental effects of ClO_4^- on public health and the low costs of physical transfer treatments, a number of adsorbents have been explored for sequestration of ClO_4^- (Komarneni et al., 2010; Baidas et al., 2011; Chitrakar et al., 2012; Fang et al., 2013; Komarneni et al., 2013; Xu et al., 2013; Lin et al., 2014; Li et al., 2015; Luo et al., 2015b).

OMt has been investigated as a remedy for ClO_4^- pollution in several studies because of the high stability and efficiency of OMt (Kim et al., 2011; Chitrakar et al., 2012; Fang et al., 2013; Seliem et al., 2013), whereas the drawback of alkylammonium release from OMt has been rarely considered. In conventional synthesis of dry OMt adsorbent, a washing step removes inorganic salts (ion-exchanged by alkylammonium) and unstably anchored alkylammonium to diminish the release of alkylammonium into treated solutions. However, the release of alkylammonium from OMt is still observed despite intense washing used in preparation of the adsorbent (Luo et al., 2015b). This characteristic introduces a new pollutant into the treatment medium, and impairs some applications of OMt, such as the treatment of drinking water.

In this study, two strategies for sequestering ClO_4^- with OMt were investigated: (1) *ex situ* entrapment where OMt was first synthesized then applied for removal of ClO_4^-; and (2) *in situ* entrapment where hexadecylpyridinium chloride (HDPy-Cl) was added to ClO_4^--contaminated solution, followed by an addition of Mt (obtained solid termed III-OMt). For the *ex situ* strategy, an unwashed wet HDPy-modified Mt (I-OMt) was compared with conventionally synthesized

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dry HDPy-modified Mt (II-OMt). The performance of the three OMt was investigated in terms of adsorption capacity of ClO_4^- and release of HDPy. To investigate the release of HDPy, X-ray diffraction (XRD) and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) were used to characterize OMt.

In previous studies using alkylammonium-modified substrates as adsorbents *via* the *ex situ* strategy (Behnsen and Reie, 2008; Lin et al., 2013; Luo et al., 2015b), there have been discrepancies between the amount of removed target anion and the released counter ion (*e.g.*, Cl^- or Br^-). Based on the principle of ion exchange, the amount of removed target anion should be equal to that of the released counter ion (depending on the ion valence states). This discrepancy suggests the presence of other interactions between adsorbate and adsorbent. Anion entrapment by OMt without anion-exchangeable sites is far less studied than that by OMt with abundant anion-exchangeable sites. To reveal the underlying interactions between ClO_4^- and OMt, solid-state ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy, thermodynamic and kinetic studies were conducted.

2. Materials and methods

2.1. Materials

High-purity sodium-Mt (Kunipia-F) with a median particle size (d_{50}) of 1.9 μm, and a cation exchange capacity (CEC) of 115 meq/100 g was supplied by Kunimine Industries (Tokyo, Japan). HDPy-Cl (99–102%, calculated on anhydrous basis) and sodium perchlorate monohydrate ($NaClO_4 \cdot H_2O$, 98%) were provided by Wako Pure Chemical Industries (Osaka, Japan). Ultrapure water was obtained using a Millipore water purification system (Synergy UV, Merck, Darmstadt, Germany).

2.2. Preparation of OMt and adsorption of perchlorate

A flowchart to prepare OMt and receive the solid residues after adsorption of ClO_4^- is shown in Fig. S1. All abbreviations used are summarized in Table 1. Different I-OMt were prepared by adding 50–120 mg Mt in a 50-mL centrifugation tube containing 10 mL of 11.5 mM HDPy-Cl and 10 mL of deionized water, and mixing for 2 h at room temperature using a shaker (MMS-5010, EYELA, Tokyo, Japan). The solid was collected by centrifugation (19,650*g*), and the supernatant was filtered through a membrane filter (0.45-μm cellulose acetate). The filtrate was provided for determination of residual HDPy by UV–vis spectroscopy (UV-2450, Shimadzu, Japan) and Cl^- by ion chromatography (ICS-2100, Dionex, USA), respectively. Notably, no HDPy or Cl^- was sequestered by filtration. Unwashed wet solid (I-OMt) was re-dispersed in 10 mL deionized water with vortex mixing (Vortex-Genie®2, Scientific Industries, USA), then 10 mL of 5.0 mM ClO_4^- was added and the mixture was shaken for 2 h at room temperature. The released HDPy and Cl^-, and residual ClO_4^- concentration (ion chromatography, ICS-2100) were determined after centrifugation under the same conditions as above. A portion of I-OMt-ClO_4^- was lyophilized (FD-5N, EYELA, Tokyo, Japan) and renamed as I-OMt-ClO_4^-(D).

The synthetic procedure for II-OMt was similar to I-OMt, except for three times of washing with 20 mL deionized water after I-OMt. All washing supernatants were collected (*ca.* 80 mL) for determination of HDPy-Cl and Cl^-. After washing, the final wet solid (II-OMt) was lyophilized and then provided for adsorption of ClO_4^- by adding 20 mL of 2.5 mM $NaClO_4$ with shaking as described above. The wet solid (II-OMt-ClO_4^-) was separated after the equilibrium, and the liquid phase was supplied to determine the concentrations of released HDPy and Cl^-, and remaining ClO_4^-. A part of II-OMt-ClO_4^- was lyophilized and named as II-OMt-ClO_4^-(D).

For *in situ* strategy, adsorption of ClO_4^- was performed by adding 10 mL of 11.5 mM HDPy-Cl into 10 mL of 5.0 mM $NaClO_4$, followed by addition of 50–120 mg Mt. The mixture was stirred at room temperature for 2 h and centrifuged. The obtained solid was dried and named as III-OMt-ClO_4^-(D). The concentrations of HDPy and ClO_4^- in solution were determined.

Adsorption isotherms of I-OMt-120 (unwashed wet OMt when 120 mg Mt was added) were obtained at 25, 35, and 45 °C with initial ClO_4^- concentrations of 0.1–0.6 mM. The stock solution was warmed to predetermined temperature before mixing with I-OMt-120. After shaking for 2 h, the suspension was separated by centrifugation. To establish the equilibrium time for ClO_4^- adsorption onto I-OMt-120, a kinetic study was performed at 25 °C by suspending I-OMt-120 in 20 mL of 2.5 mM ClO_4^-. All tests were conducted in duplicate. Notably, adsorption isotherms and kinetics of ClO_4^- onto I-OMt-120 were studied because there was no HDPy-Cl in the composite (Fig. 1). In this case, the sorption energy of latent interaction rather than ion exchange between ClO_4^- and I-OMt-120 would be obtained and used to elucidate the potential mechanism.

2.3. Solid characterization

XRD patterns of wet and dry OMt were recorded using Cu Kα X-ray radiation on an Ultima IV X-ray diffractometer (Rigaku, Tokyo, Japan) at 40 kV and 40 mA for $2\theta = 1.0–10.0°$ at a step size of 0.02° and a scan speed of 0.5°/min. ATR-FTIR spectra were recorded using a 670 Plus Transform Infrared spectrometer (JASCO, Tokyo, Japan) with a nominal resolution of 4 cm^{-1} in the range of 4000–400 cm^{-1}, averaging the data after 128 successive scans. Solid-state ^{13}C NMR spectra were recorded on an ECA 400 spectrometer ($B_0 = 9.4$ T, JEOL, Akishima, Japan) equipped with a FG-FMAS probe to spin the sample in air at 15 kHz. Spectra were collected by using a single-pulse excitation method with a relaxation delay of 20 s, and the number of scans exceeded 12,000. Chemical shifts were standardized using tetramethylsilane (0 ppm) and hexamethyl benzene (−17.36 ppm). The zeta potential of ClO_4^--loaded I-OMt-120 was measured on a Zetasizer Nano-ZS (Malvern, UK) for supernatant after dispersing the samples in 10 mL of ultrapure water.

3. Results and discussion

3.1. HDPy uptake on Mt

HDPy should be in either ionic form ($HDPy^+$) or counter ion-accompanying form (HDPy-Cl) in OMt. The former is derived from the ion exchange between $HDPy^+$ and Na^+ and the latter is caused by hydrophobic interactions among $HDPy^+$ and HDPy-Cl. Fig. 1 shows the uptake of total HDPy, HDPy-Cl, and $HDPy^+$ onto I-OMt and II-OMt. The uptake of HDPy-Cl on II-OMt is lower than that on I-OMt, because washing removed loosely bound HDPy-Cl, particularly when a relatively

Table 1
Definitions of abbreviations used to describe adsorbents and reagents.

Abbreviation	Definition	Abbreviation	Definition
$HDPy^+$	Hexadecylpyridinium cation	I-OMt-ClO_4^-(D)	I-OMt after ClO_4^- loading in dry condition
HDPy-Cl	Hexadecylpyridinium chloride	I-OMt-120	I-OMt when 120 mg Mt was used
HDPy	Total HDPy including HDPy-Cl and $HDPy^+$	II-OMt	Conventionally synthesized dry OMt with washing
OMt	Organo-montmorillonite	II-OMt-ClO_4^-	II-OMt after ClO_4^- loading in wet condition
I-OMt	Unwashed wet OMt	II-OMt-ClO_4^-(D)	II-OMt after ClO_4^- loading in dry condition
I-OMt-ClO_4^-	I-OMt after ClO_4^- loading in wet condition	III-OMt-ClO_4^-(D)	OMt obtained through *in situ* strategy