



Research paper

Influence of the pre-dispersion of montmorillonite on organic modification and the adsorption of perchlorate and methyl red anions

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ARTICLE INFO

Keywords:

Montmorillonite
Modification
Dispersion
Configuration
Adsorption

ABSTRACT

In this study, hexadecyl pyridinium chloride (HDPy-Cl) was applied to modify powdery and dispersed montmorillonite (pMt and dMt, respectively). Then, perchlorate (ClO_4^-) and methyl red (MR) were selected as representatives of hazardous inorganic and organic pollutants, respectively, to investigate the influence of the dispersion of Mt on their adsorption using the obtained composites (pMt/HDPy and dMt/HDPy). Based on the X-ray diffraction patterns and water chemistry results, pre-dispersion of Mt resulted in a lower crystallinity of the obtained composite with slightly higher contents of HDPy⁺ (0.93 mmol/g-Mt) and HDPy-Cl (1.41 mmol/g-Mt) compared to the original powdery Mt (0.85 and 1.36 mmol/g-Mt). Moreover, as supported by thermogravimetry results, the amount of HDPy distributed on the external surface of dMt/HDPy was greater than that on pMt/HDPy, which was opposite of the HDPy content in the interlayer space. The adsorption kinetic of ClO_4^- and MR on two composites was studied and the results were fitted by three models, where the intra-particle diffusion model fitted the experimental data best. Similar adsorption capacities were obtained, and the slight differences in the adsorption kinetics as supported by the intra-particle diffusion model were ascribed to the differences in the HDPy contents and configuration. The pre-dispersion of Mt is not necessary when a modified composite is planned for use as an adsorbent of pollutants, but it would be beneficial to the synthesis of clay/polymer nanocomposites.

1. Introduction

Environmental remediation and the manufacturing of clay/polymer nanocomposites (CPN) are two main applications of organoclays. The structures of organoclays are associated with modifier species that determine the properties of CPN (Fornes et al., 2002; Lee and Han, 2003; Shah et al., 2016). The homogeneous dispersion of a completely exfoliated individual layer in a polymer matrix is the desired goal for synthesizing CPN. The configuration and distribution of organic modifiers in organoclays influence not only the exfoliation degree of clay particles but also the compatibility or affinity between separated layers and the polymer (Lee and Han, 2003; Paul and Robeson, 2008). However, in terms of adsorbing organic or inorganic contaminants using organoclays, the configuration of the modifier in the organoclay determines the adsorption performance because the major adsorption mechanisms of partition and/or ion exchange are closely related to the modifier configuration (He et al., 2006b; Luo et al., 2016).

Quaternary ammonium compounds (QAC) are the most typical organic modifiers used for the synthesis of organo-montmorillonite

(OMt). The configuration and distribution of QAC in OMt can be regulated by changing the synthetic methods. A comparison between ultrasonic and hydrothermal methods indicated that ultrasonic preparation resulted in a higher QAC concentration within the Mt interlayer space (Xi et al., 2005). Baldassari et al. (2006) investigated the differences between using conventional and microwave hydrothermal methods for the preparation of organoclays, and they found that microwave heating resulted in a complete replacement of the inorganic cations, whereas partial intercalation was observed for the conventional hydrothermal method in many cases. With respect to other synthetic protocols, the conventional hydrothermal method is still the most extensively used for OMt synthesis because it is more flexible and cost-effective, but the powdery Mt is sometimes first dispersed in an aqueous solution to swell or delaminate the silicate layers and is then mixed with a surfactant-bearing solution (Chen et al., 2014; Fatimah and Huda, 2013; Luo et al., 2017; Yang et al., 2015). In contrast, adding powdery Mt without pre-dispersion has been applied in many studies (Ma et al., 2016; Parolo et al., 2014; Peng et al., 2017). This inspired researchers in this field to consider the necessity of pre-dispersion for

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OMt synthesis and the associated influence on the application of OMt. In addition, in some studies, the time for Mt dispersion and/or subsequent mixing has been selected arbitrarily without clear explanation, such as 1 h (Yang et al., 2015) or 2 h (Luo et al., 2017) for pre-dispersion, and 30 min (Peng et al., 2017), 1 h (Chen et al., 2014), 2 h (Luo et al., 2016), 3 h (Yang et al., 2015), 4 h (Parolo et al., 2014), 12 h (Ma et al., 2016) or 24 h (Fatimah and Huda, 2013; Luo et al., 2017) for mixing. Reducing the synthesis time in an expeditious manner will decrease the consumption of energy and likely not significantly affect the efficiency. Although adsorption of cationic organics analogous to QAC on clay minerals have been extensively studied (Auta and Hameed, 2012; Grauer et al., 1987; Gürses et al., 2006), there are few reports on the necessity for dispersion of Mt and appropriate time for synthesis of OMt (Xu and Boyd, 1995).

Based on the aforementioned background and considering the wide applications of OMt in environmental remediation as adsorbents, an adsorption experiment was designed to determine the necessity of Mt pre-dispersion. Hexadecyl pyridinium chloride (HDPy-Cl) is one of the most extensively used QAC for Mt modification, conferring Mt/HDPy favorable adsorption performance such as for iodide (Riebe et al., 2005). In this study, a stoichiometric amount of HDPy-Cl over than 1.0 times CEC of Mt was used in modification, resulting in the presence of organic salt in the composites behaving as ion-exchanging sites for anions. Perchlorate (ClO_4^-) and methyl red (MR) anions with different molecular sizes and chemical structures were considered and selected as probes of the accessibility of these ion-exchanging sites. Some sites located in the interlayer space are generally unavailable for large diffusive molecules considering the steric hindrance due to the negligible swelling property of the compact interlayer space. Adsorption performances of two adsorbates can be used to illustrate indirectly the configuration and distribution of QAC in composites. Understanding the influence of pre-dispersion and reaction time on the configuration and distribution of QAC will provide guidance for the synthesis of OMt.

2. Materials and methods

2.1. Chemicals

High-purity sodium montmorillonite (Mt, Kunipia-F) was provided by Kunimine Industries Co., Ltd. (Tokyo, Japan) in which the cation exchange capacity (CEC) was measured to be 1.114 mmol/g using the method by Bergaya and Vayer (1997). Chemical formula of Mt can be expressed as $(\text{Na}_{1.0}\text{Ca}_{0.1})(\text{Si}_{7.7}\text{Al}_{0.3})(\text{Al}_{3.1}\text{Fe}_{0.27}\text{Mg}_{0.63})\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ based on the chemical analysis (method of ME-ICP61, ALS Global Ltd., North Vancouver, Canada). The particle size distribution of original Mt is shown in Fig. S1, and its Brunauer-Emmett-Teller surface area (S_{BET}) was 30.6 m²/g. Hexadecyl pyridinium chloride monohydrate (HDPy-Cl·H₂O) (anhydrous basis, 99.0–102%), sodium perchlorate monohydrate ($\text{NaClO}_4 \cdot \text{H}_2\text{O}$, 98.0%) and methyl red (MR) in analytic grade were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The chemical structure of MR is shown in Fig. S2. Ultrapure water was produced by a Millipore water purification system (Synergy UV, Merck, Darmstadt, Germany).

2.2. Preparation of Mt/HDPy using powdery and dispersed montmorillonite (Mt)

In total, 10 g of powdery Mt was dispersed in 500 mL of deionized water using magnetic stirring at room temperature overnight to ensure full swelling of the Mt particles. A stoichiometric amount of HDPy-Cl corresponding to 4.0 times the CEC of Mt was dissolved in 500 mL or 1000 mL of ultrapure water. The same amount of HDPy-Cl was also used for Mt modification in previous studies (Bagherifam et al., 2014; Chitrakar et al., 2012). Although increasing the dosage of modifier leveled up the adsorption capacity to target anionic pollutant, the amount of loaded organic modifier with respect to the originally added on Mt

was gradually decreased (Luo et al., 2015). Taking such issue into account, the amount of HDPy was selected as 4.0 times CEC of Mt for the modification. For the synthesis of dMt/HDPy, a Mt dispersion was quickly added into the 500-mL HDPy-Cl solution and vigorously mixed via mechanical stirring. The pMt/HDPy was synthesized using a similar protocol: 10 g of powdery Mt instead of the dispersed Mt was added into a 1000-mL HDPy-Cl solution. Addition of the powdery Mt should be performed regularly and rapidly to avoid aggregation and reduce a reaction time delay. At pre-determined times of 1.0, 2.5, 4.0, 5.5, 7.0, 9.0, 11, 15, 20, 25, 30, and 40 min, a 4.0-mL suspension was sampled to separate the solid via centrifugation at 10,000 rpm for 1 min using a MiniSpin plus centrifuge (Eppendorf AG, Type 22331, Hamburg, Germany). The obtained wet solids were kept in a refrigerator at 4 °C and labeled as dMt/HDPy-*t* or pMt/HDPy-*t*, where *t* is the sampling time (min). The liquid was filtered using a 0.45- μm cellulose acetate membrane filter to determine the concentrations of HDPy and Cl^- using a UV-Vis spectrophotometer (at wavelength of 258 nm, UV-2450, Shimadzu, Japan) and ion chromatography (ICS-2100, Dionex, USA), respectively. Notably, no HDPy or Cl^- was sequestered by filtration, which was supported by the negligible concentration change before and after filtration.

2.3. Solid characterization

Particle size distribution of the original Mt was obtained through weighing the samples that passed through a series of sieves, and its organic content was determined by CHN analysis (CHN Corder MT-6 Elemental analyzer, Yanaco, Kyoto, Japan). S_{BET} was calculated based on N₂ adsorption-desorption isotherms at -196.15 °C with a BELSORP-max instrument (Osaka, Japan). Prior to measurement, Mt was degassed for 15 h at 105 °C. The preparation of wet samples for X-ray diffraction (XRD) is described in the supplementary information. XRD patterns were collected using Cu K α X-ray radiation on an Ultima IV X-ray diffraction system at 40 kV and 40 mA with divergence slit of 1.0 mm, antiscatter slit of 10 mm and receiving slit of 0.15 mm from 1.0–10° (2 θ) at a step size of 0.02° and a scan speed of 0.5°/min. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was carried out on a FT/IR-670Plus spectrometer (JASCO, Tokyo, Japan) equipped with a Pike Technologies MIRacle™ accessory (a single reflection HATR universal plate with a silicon crystal). The spectra were recorded with a nominal resolution of 4 cm⁻¹ in the range of 4000–400 cm⁻¹ by averaging data from 128 accumulated scans. Thermal gravimetric analysis (TGA) were performed on 2000SA thermo balance (Bruker, Germany) from room temperature to 900 °C at a heating rate of 10 °C/min in an air atmosphere with a gas flow rate of 100 mL/min. Scanning electron microscopy (SEM) was performed using a VE-9800 scanning electron microscope (Keyence, Osaka, Japan) at an accelerating voltage of 20 kV. After re-dispersing the wet Mt/HDPy in 10 mL ultrapure water under ultrasonic condition for 5 min, zeta potentials of samples were determined on a Zetasizer Nano-ZS (Malvern, Worcester, UK).

2.4. Adsorption of ClO_4^- and MR

The adsorption kinetics of ClO_4^- and MR on pMt/HDPy-40 and dMt/HDPy-40 were performed by mixing 20 mg of solid sample with 400 mL of 0.04 mmol/L ClO_4^- or 0.037 mmol/L of MR using magnetic stirring at 750 rpm and 28 °C. The pH of ClO_4^- and MR solution were 7.3 ± 0.3 and 8.2 ± 0.4, respectively. The pK_a of MR is 5.05 ± 0.05 in the range of 25–30 °C (Tobey, 1958), thus MR existed in anionic form in experimental condition (Fig. S2). Although the equilibrium pH of solution after adsorption were not determined, MR in the solution should still be anionic form due to the poor buffer capacity of Mt/HDPy, which was also supported by the observed maximum absorbance at 427 nm (Tobey, 1958). At different time intervals (2, 5, 7, 10, 15, 20, 30 and 135 min for ClO_4^- , 2.5, 5, 8, 12, 18, 25, 40 and 70 min for MR),

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