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Adsorption of inorganic and organic arsenic from aqueous solutions by polymeric Al/Fe modified montmorillonite

A. Ramesh *, H. Hasegawa, T. Maki, K. Ueda

Department of Chemistry and Chemical Engineering, Graduate School of Natural Science and Technology,
Kanazawa University, Kakuma-Machi, 920-1192 Kanazawa, Japan

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Abstract

Adsorption of arsenite [As(III)], arsenate [As(V)] and dimethylarsinate (DMA) from aqueous solutions onto polymeric Al/Fe modified montmorillonite was studied. Batch adsorption studies were carried out on the adsorption of As(III), As(V) and DMA as a function of contact time, pH, adsorbent dose and initial metal concentration. Fourier transform infrared spectrometry (FT-IR) and scanning electron microscopy (SEM) were used to analyze the functional groups and surface morphology of the montmorillonite or polymeric Al/Fe modified montmorillonite, respectively. SEM images show that modification with polymeric Al/Fe species reduces the clay particle size and aggregation. The results indicate that the maximum adsorption of polymeric Al/Fe modified montmorillonite was obtained in the pH range 3.0–6.0 for As(V), 7.0–9.0 for As(III) and 3.0–7.0 for DMA. The adsorption data was analyzed by both Freundlich and Langmuir isotherm models and the data was well fit by the Freundlich isotherm model. Kinetic data correlated well with the pseudo-second-order kinetic model, suggesting that the adsorption process might be chemical sorption. Thermodynamic studies showed that the adsorption process was endothermic and spontaneous in nature. The presence of phosphate and iron reduced the adsorption efficiency of arsenic, whereas other common coexisting ions had no significant effect on arsenic adsorption. The desorption studies were carried out using dilute NaCl solution.

Keywords: As(III); As(V); DMA; Polymeric Al/Fe modified montmorillonite; Kinetics; Adsorption; Isotherms

1. Introduction

Arsenic is both ubiquitous in the environment and potentially toxic to humans [1]. Arsenic contamination is a worldwide problem, especially in developing countries where a significant percentage of the population depends on groundwater for drinking. Serious arsenic pollution has been observed not only in various mineral and chemical processes but also in groundwater over large areas of Bangladesh, Bengal in India, Inner Mongolia in China, Taiwan, Mexico, Vietnam and Chile [2–5]. Arsenic contamination in groundwater is mainly caused by agricultural activities where arsenic is used for the preparation of insecticides and herbicides. Epidemiological studies have shown a significant increase in the risks of lung, bladder, skin, liver and other cancers associated with high levels of arsenic in drinking water [6,7]. Based on the impact on human health, the world health organization (WHO) has recommended that the arsenic concentration remain bellow 10 μg/l in drinking water [8]. Arsenic is found in natural waters in both organic and inorganic forms. Inorganic arsenic occurs with two main oxidation states in natural waters, as As(V) and As(III). The toxicity of As(III) is much higher and more difficult to remove by the conventionally applied physiochemical methods than As(V). Although inorganic arsenic species dominate in natural waters, the presence of high concentrations of organic arsenic compounds such as monomethylarsonate (MMA) and dimethylarsinate (DMA) have been detected [9,10]. Some reports [11,12] have shown that methyl arsenic species comprise 10–24% of the total arsenic in lake water and groundwater in some places in the USA.

Although, the toxicities of organic arsenic compounds are less than those of inorganic species, the carcinogenic character of methyl arsenic compounds, and especially DMA, has been identified [13]. Yamamoto et al. [14] showed that chronic exposure to DMA enhanced tumor development in the kidney, liver and urinary bladder of F 344 rats. Hence, it is necessary to remove arsenic species from water and wastewater. The conventional

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* Corresponding author. Tel.: +81 76 234 4792; fax: +81 76 234 4792.
E-mail address: attintiram@yahoo.com (A. Ramesh).

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methods used for the removal of arsenic from aqueous solutions are precipitation, coagulation and filtration, reverse osmosis, ion exchange and adsorption. Among the all above methods, adsorption is highly efficient, economical and overall, a promising technique. Several researchers worldwide have used various low cost adsorbents for the removal of inorganic and/or organic arsenic compounds from water and wastewater.

Naturally occurring and modified clay minerals have been widely used for the removal of metal ions, organic pollutants and bacteria from water and wastewater. Because of the high specific surface area, chemical and mechanical stability, high cation exchange capacity and negative character of surfaces, clay minerals have been shown to be good adsorbents. Clays carry a net negative charge due to the broken bonds around the edges of the silica-alumina units that give rise to unpaired charges, which can be balanced by the adsorbed cations. Several reports demonstrated that the adsorption capacities of clays were increased by modification with acids, bases, cationic surfactants and polyoxocations [15–21]. Pillared clays were first tested as catalyst support materials, however in light of their ion exchange properties have been redirected recently as adsorbents for the removal of pollutants. Michot and Pinnavaia [22] reported that polyoxocations are the most applied pillaring agents. Because of the chemical composition, structure and charge, Al-polyoxocation $[Al_{13}O_4 (OH)_{24} (H_2O)_{12}]$ or Al_{13} has been well defined among all the polyoxocations [23]. Jiang et al. [24–26] studied the polymeric species and alkylammonium cationic surfactant mixed polymeric species modified montmorillonite for the adsorption of metal ions and/or organic pollutants. The authors also concluded that the polymeric species modified montmorillonite is the most efficient adsorbent for the removal of metal ions. To date, no report has been identified using polymeric Al/Fe species modified on montmorillonite for the removal of arsenic.

In this study, montmorillonite was modified by polymeric Al and Fe species for the adsorption of inorganic and organic arsenic compounds from aqueous solutions. The study investigated the various adsorption characteristics of arsenic compounds on modified or unmodified montmorillonite in a series of batch experiments. Fourier transform infrared spectrometry (FT-IR) and scanning electron microscopy (SEM) were used to elucidate the structure and surface morphology of modified and unmodified clay, respectively. The effect of coexisting ions on the adsorption of arsenic and desorption process for the regeneration of the adsorbent were also investigated.

2. Experimental

2.1. Chemicals

All the chemicals used were of analytical reagent grade. Deionized doubly distilled water was used throughout the experimental studies. Stock solutions of 1000 mg/l of As(III), As(V) and DMA were prepared by dissolving the required amount of $Na_2HAsO_4·7H_2O$, $NaAsO_2$ and DMA (Sigma–Aldrich) in deionized doubly distilled water. Working standards were prepared by progressive dilution of standard As(III), As(V) and DMA solutions using deionized doubly distilled water. $AlCl_3·6H_2O$, $FeCl_3·6H_2O$ and $NaHCO_3$ (Kanto Chemicals, Japan) were used for modification of montmorillonite. Other chemicals, i.e. HCl, NH_3 solution, $NaNO_3$ and KBr were supplied by Kanto chemicals (Japan). Montmorillonite KSF was purchased from Aldrich.

2.2. Instrumentation and methods of characterization

A graphite furnace atomic absorption spectrophotometer (GF-AAS, Hitachi, Z-8100) with arsenic hollow cathode lamp and argon gas was used to determine the concentration of arsenic. Fourier transform infrared spectrometry (Perkin-Elmer, 1600 series) was used to analyze the functional groups in the adsorbent. The transmission spectrum was acquired at a 64 scans with $4\,cm^{-1}$ resolution and the spectrum was corrected with a KBr background. Scanning electron microscopy (Hitachi, S-4500) was used to analyze the surface morphology of the modified or unmodified montmorillonite. A pH meter (Horiba, F-52) was used for pH measurements. The surface area and pore size distribution were calculated from nitrogen adsorption isotherm data using the Brunauer–Emmett–Teller (BET) and Barret, Joyner and Halenda (BJH) methods on a Belsorp 28 SA apparatus. The chemical compositions of modified and unmodified adsorbents were obtained by energy dispersive X-ray florescence (ED-XRF) analyzer (JEOL, JSX-3201). A temperature controlled bio-shaker (Taitec, BR-30L) was used for agitating the sample solutions. The cation exchange capacity (CEC) was measured using the copper bisethylenediamine complex method [27]. The surface charge and point of zero charge (pH_{ZPC}) of montmorillonite and polymeric Al/Fe modified montmorillonite were calculated by the acid–base titration method [28]. The acid site concentrations of both adsorbents were determined by direct titration with standard NaOH solution [29].

2.3. Preparation of polymeric Al/Fe modified montmorillonite

The preparation of polymeric Al/Fe modified montmorillonite was conducted according to the method described by Jiang and Zeng [26]. The pillaring solution was prepared by adding 0.5 M $NaHCO_3$ to $AlCl_3$ and $FeCl_3$ (10 mg/l, 1:1) solution drop wise with vigorous stirring to obtain the OH/M ratio of 2. Then the pillaring solution was aged for 3 h at 55 °C. After the aging process, the solution was slowly added under vigorous stirring to 15.0 g of montmorillonite clay and allowed to age overnight. Then, the product was collected by filtration and washed with deionized doubly distilled water until free of chlorides, as indicated by the $AgNO_3$ test. The solid was dried at 105 °C for 16 h, ground and sieved.

2.4. Adsorption studies

Batch adsorption experiments were conducted in 100 ml stoppered reagent bottles. A measured amount (0.1 g) of montmorillonite or polymeric Al/Fe modified montmorillonite was placed into the 100 ml reagent bottles, which containing 30 ml of various concentrations of As(III), As(V) and DMA in 0.04 M