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Competitive adsorption of humic acid and arsenate on nanoscale iron–manganese binary oxide-loaded zeolite in groundwater

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ABSTRACT

Arsenic contamination in groundwater is widespread around the world. The identification and implementation of inexpensive and effective sorbent for arsenic removal are of great importance, and this topic has been intensively studied recently. The sorbent efficiency can be affected by groundwater containing natural organic matter. In this study, a new nanoscale iron–manganese binary oxide-loaded zeolite (NIMZ) sorbent was prepared to evaluate its efficiency for arsenate removal in the presence of natural organic matter. This new sorbent has shown an excellent capacity for arsenate removal, which was investigated by considering the interaction of humic acid (HA) that was before, after and simultaneously adsorbed on NIMZ under different pH values. Results of kinetic studies showed that the removal of arsenate on NIMZ was not affected by the presence of HA at the tested levels up to 10 mg/L. Affinity of arsenate, at the application level of 2 mg/L, on NIMZ surface was found to be much stronger than HA in terms of adsorption removal. For the pre-equilibrium study of HA adsorption onto NIMZ, the added arsenate could replace HA which was released into the solution, while arsenate was adsorbed on NIMZ. On the contrary, in the study of NIMZ pre-equilibrated with arsenate adsorption, the added HA hardly affected the adsorbed arsenate. In the test of simultaneous adsorption of arsenate and HA on NIMZ, the competition of arsenate on adsorption sites of NIMZ was much stronger than HA. These three cases indicated that NIMZ adsorbent was effective for arsenate removal even when the natural organic matter was present. Zeta potential measurements showed that arsenate and HA can be adsorbed on NIMZ despite the electrostatic repulsion. Arsenate removal in the presence of HA on NIMZ mainly induced by ligand exchange from FTIR analyses of their surfaces, and phenolic OH and COOH groups of HA were responsible for ligand exchange with NIMZ.

1. Introduction

Arsenic is a widespread contaminant in freshwater around the world, and its chronic accumulation can cause serious, and often fatal, diseases in human body. Inorganic arsenic is more toxic than organic arsenic (Smedley and Kinniburgh, 2002). Proven to be an effective, low-cost and easily-operative technology for removing arsenic from groundwater, the permeable reactive barriers (PRBs) packed with an arsenic-removal adsorbent is the most popular technique (Mohan and Pittman, 2007). Common sorbents include activated carbons, natural minerals, metal-based methods such as zero-valent iron, bimetallic sorbent and metal oxides or hydroxides (Mohan and Pittman, 2007). Iron–manganese binary oxides receive special attention as they have unique characteristics favoring arsenic removal (Manning et al., 2002; Zhang et al., 2007a, 2007b). Furthermore, nanoscale sorbents have large specific surface areas, and zeolite is widespread and commonly used as an adsorbent because of its unique three-dimensional porous structures (Jeon et al., 2009; Li et al., 2007, 2011). Nanoscale iron–manganese binary oxides loaded onto zeolite (NIMZ) can prevent agglomeration phenomenon and greatly enhance contaminant removal.

Natural organic matter (NOM) is ubiquitous in natural aquatic systems, and it affects arsenic adsorption on the surfaces of minerals. Humic acid (HA), as a typical NOM substance, is present as dissolved organic matter in water (Saito et al., 2003). Previous studies of HA removal by Fe^0, and its effect on arsenic, confirmed that Fe–HA formed an inner-sphere surface complex (Giasuddin et al., 2007). As HA and arsenate can both bind directly to the Fe oxide surface, their competitive adsorption occurs when similar adsorption sites are involved. In addition, the formation of organically-complexed As by bridging metals and ligand exchange has been postulated. The formation of

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HA–As–surface complexes, as adsorption (Thanabalasingam and Pickering, 1986) and As complexation with HA, is also favorable as HA–As complex and ligand exchange reactions are possible (Ko et al., 2007).

The adsorption study of HA by nano-oxides finds that HA adsorption is mainly induced by electrostatic attraction and ligand exchange between HA and nano-oxide surfaces (Yang et al., 2009). The surface hydrophilicity and negative charges of nano-oxides affect their adsorption of HA. The phenolic OH and COOH groups of HA are responsible for ligand exchange. Adsorption of HA reduces the micropore surface area of nano-oxides, but not the external surface area because of the micropore blockage. Adsorption of HA also decreases the zeta potential of nano-oxides, indicating that HA-coated nano-oxides could be more easily dispersed and suspended and more stable in solution than uncoated ones, because of their enhanced electrostatic repulsion (Yang et al., 2009). But the adsorption affinities of arsenate and HA on NIMZ are not clear, and the application efficiency of NIMZ is not studied at their common concentrations observed in groundwaters.

The objective of this study is to investigate the competitive adsorption of HA and arsenate onto NIMZ to develop a new sorbent for arsenate removal in treating groundwaters containing NOM. The following tasks are carried out to achieve the objective. Firstly, we prepare a new NIMZ with an improved co-precipitation method; secondly, we investigate an arsenate adsorption process as affected by NIMZ at different solution pH; thirdly, we study influences of HA on arsenate sorption, and interaction of HA and arsenate removal on NIMZ. Three sets of experiments were designed to investigate the mechanism of interaction between HA and arsenate.

2. Materials and methods

2.1. Materials

Most chemicals used for the experiments of this study were purchased, of analytical grades, from Shanghai General Reagent Factory, China. Before use, reaction vessels (glass) were soaked with 5% HNO_3 for 24 h and rinsed several times with ultrapure water. Commercially available sodium salt of HA, purchased from Sigma-Aldrich, Germany of technical grade, was used to represent NOM. A stock solution (1.0 g/L) of As(V) was prepared by dissolving $Na_2HAsO_4 \cdot 7H_2O$ (Sigma-Aldrich) in simulated groundwater with pH value adjusted to become neutral. The simulated groundwater sample in the laboratory, containing 901 mg/L HCO_3^-, 1805 mg/L Cl^-, 96 mg/L SO_4^{2-}, 1029 mg/L Na^+, 173 mg/L Mg^{2+}, and 32 mg/L Ca^{2+}, was used as the background electrolyte. Arsenate working solutions were freshly prepared by diluting the stock arsenate solution with degassed simulated groundwater.

2.2. NIMZ sorbent preparation

The NIMZ sorbent was prepared according to the following procedure: 12.51 g $FeSO_4 \cdot 7H_2O$ and 2.37 g $KMnO_4$ were dissolved in 200 mL of fresh ultrapure water. Then 10 g zeolite was added into the $KMnO_4$ solution. The $FeSO_4$ solution in a sealed sprayer was continuously sprayed into the vigorous magnetic-stirring $KMnO_4$ solution, keeping the droplet as tiny as possible.

The species Fe(III) hydroxide in this system was dependent on the solution pH, and 5 M NaOH solution was simultaneously added to keep the solution pH in the range of 7.0 and 8.0. The formed suspension was continuously stirred for 1 h, aged at room temperature for 12 h, and then washed repeatedly with fresh ultrapure water several times until the pH value becomes neutral. The suspension was then filtrated and dried at 105 °C for 4 h, and calcined at 600 °C for 6 h. The dried sorbent was crushed and stored in a desiccator before use.

2.3. Kinetic experiments

NIMZ was hydrated in groundwater at the desired pH values for 30 min to reach equilibrium before the addition of arsenate and/or HA. In order to understand the competitive adsorption of HA and arsenate on NIMZ, three sets of experiments were designed and conducted as follows:

(I) Pre-adsorption of HA on NIMZ and subsequent adsorption of arsenate (termed as HA Test): The hydrated NIMZ suspension was mixed thoroughly with 10 mg/L HA representing the common concentration in natural groundwaters. Samples were then placed on a shaker at 200 rpm in the dark at 25 °C. After 3 h of mixing, As(V) was added into the solution containing HA, maintaining arsenate as 2 mg/L which represents the typically upper arsenic concentrations observed in contaminated groundwater in Datong District, Shanxi Province in China (Guo and Wang, 2005).

(II) Pre-adsorption of arsenate on NIMZ and subsequent adsorption of HA (Arsenate Test): The hydrated NIMZ suspension was mixed thoroughly with 2 mg/L As(V) in groundwater, and samples were then placed on a shaker at 200 rpm in the dark at 25 °C. After 3 h, HA was added into the solution containing arsenate, keeping the initial concentration of HA at 10 mg/L.

(III) Simultaneous adsorption of As(V) and HA on NIMZ (Arsenate–HA Test): As(V) solution is rapidly mixed with HA in the dark, and pH was adjusted. Initial arsenate and HA concentrations were controlled at 2 mg/L and 10 mg/L, respectively. Then samples were placed on a shaker with the same operational conditions as mentioned above.

Each experiment was carried out in triplicate in the dark. Solutions were regularly sampled to determine the concentrations of As(V), HA and HA–As complex. An aqueous r sample of 15 mL was allowed to pass through a set of silica-based anion-exchange (SAX) cartridges (Supelco, Bellefonte, PA, USA) and 0.45-μm membrane filter connected in series. The flow rate was controlled at 1 ± 0.1 mL/min. The anion-exchange cartridges retained the HA–As complex and As(V). The retained As(V) was subsequently eluted with 1.0 M HCl to be separated from the HA–As complex (Le et al., 2000). For comparison, water samples without passing through the cartridges were also collected under the same conditions for analyses of As(V) and HA.

2.4. Analytical methods

All HA concentrations were measured with a UV–Vis spectrophotometer (Hitachi U-3900, Japan) at 254 nm (Giasuddin et al., 2007). Total aqueous As(V) in comparison water sample, As(V) (extracted using 1.0 M HCl) were determined by an inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Thermo Fisher ICS-1100, USA). The HA–As complex and adsorbed arsenate on NIMZ were calculated from differences of their respective concentrations (Ko et al., 2007).

2.5. Sorbent characterization

The specific surface area and pore-size distribution (PSD) were measured by nitrogen sorption using the Brunauer–Emmett–Teller (BET) method with an ASAP 2020M surface area analyzer (Micrometrics Instrument Corporation, USA). The particle shapes were examined with a scanning electron microscope (SEM-EDX) (FEI Quanta 200, Netherlands) and the elemental contents were analyzed with an energy dispersive X-ray (EDX) detector. The particle size and morphology images were determined by a transmission electron microscope (TEM) (Philips CM12/STEM, Netherlands). Surface zeta potential