



Research article

Adsorption kinetics and isotherms of arsenite and arsenate on hematite nanoparticles and aggregates

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ABSTRACT

Iron (Fe) nanoparticles, e.g., zerovalent iron (ZVI) and iron oxide nanoparticles (IONP), have been used for remediation and environmental management of arsenic (As) contamination. These Fe nanoparticles, although originally nanosized, tend to form aggregates, in particular in the environment. The interactions of As with both nanoparticles and micron-sized aggregates should be considered when these Fe nano-materials are used for mitigation of As issue. The objective of this study was to compare the adsorption kinetics and isotherm of arsenite (As(III)) and arsenate (As(V)) on bare hematite nanoparticles and aggregates and how this affects the fate of arsenic in the environment. The adsorption kinetic process was investigated with regards to the aggregation of the nanoparticles and the type of sorbed species. Kinetic data were best described by a pseudo second-order model. Both As species had similar rate constants, ranging from 3.82 to $6.45 \times 10^{-4} \text{ g}/(\mu\text{g}\cdot\text{h})$, as rapid adsorption occurred within the first 8 h regardless of particle size. However, hematite nanoparticles and aggregates showed a higher affinity to adsorb larger amounts of As(V) ($4122 \pm 62.79 \mu\text{g/g}$) than As(III) ($2899 \pm 71.09 \mu\text{g/g}$) at equilibrium. We were able to show that aggregation and sedimentation of hematite nanoparticles occurs during the adsorption process and this might cause the immobilization and reduced bioavailability of arsenic. Isotherm studies were described by the Freundlich model and it confirmed that hematite nanoparticles have a significantly higher adsorption capacity for both As(V) and As(III) than hematite aggregates. This information is useful and can assist in predicting arsenic adsorption behavior and assessing the role of iron oxide nanoparticles in the biogeochemical cycling of arsenic.

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1. Introduction

Contamination of surface and ground water by arsenic (As), a notoriously toxic element to humans and animals, has led to human population exposed to arsenic through drinking water or food, causing global health concerns (Carabante et al., 2009; Mandal and Suzuki, 2002; Zhang et al., 2002). Arsenic in the natural waters is predominantly in the inorganic forms: pentavalent arsenate (As(V)) and the trivalent arsenite (As(III)) (Ko et al., 2004; Zaspalis et al., 2007). The transport and transformation of arsenic in the environment include adsorption, ligand exchange, oxidation–reduction and precipitation (Banerjee et al., 2008). Adsorption to metal oxides

particularly iron oxides to form inner-sphere complexes is one of the most significant factor controlling arsenic mobility in the environment (Al-Abed et al., 2006).

Studies have been conducted to investigate the adsorption of arsenic to bulk iron and iron oxides and their nanoparticles, and it was found that the process can be enhanced using zerovalent iron nanoparticles (NZVI) and iron oxide nanoparticles (IONPs) (Dixit and Hering, 2003). Iron oxides in general, whether in the bulk form or nanoparticulate form, have strong binding affinity for both arsenite and arsenate. The application of IONPs in contaminant remediation has enhanced the adsorption process due to the large surface area and its strong adsorption characteristics. These nanoparticles have increased adsorption capacity while maintaining many of the properties of bulk iron oxides. Numerous studies have investigated the adsorption behavior of arsenic with bulk iron oxides (Banerjee et al., 2008; Jain et al., 1999; Jeong et al., 2007; Zhang et al., 2004), as well as with bare/unmodified iron oxide

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nanoparticles (Auffan et al., 2008; Shipley et al., 2010; Turk et al., 2010; Tuutijarvi et al., 2009). Due to the strong binding affinity of iron oxides surface for arsenic and the development of nanotechnology as a potential remediation tool for arsenic contamination, it is of great interest that we evaluate the effects of IONPs on the fate and mobility of arsenate and arsenite in aqueous environment. The adsorption of arsenic and its retention on IONPs should be investigated while considering several factors such as the aggregation of the nanoparticles and the type of sorbed species.

Studies in the literature focusing on arsenic adsorption behavior with IONPs had failed to monitor IONPs particle size during adsorption. From our previous studies (Dickson et al., 2012) and other's (Zhang et al., 2008), IONPs tend to aggregate either at the initial stage of experiments and as time persists. These IONPs can grow to micron size particles during the adsorption process and will eventually sediment. This will influence the adsorptive properties of IONPs and its interaction with arsenic. Hence, previous studies on arsenic adsorption on IONPs in the literature, if not monitoring particle size and the aggregation occurred, might not be representative of the behavior of arsenic adsorption on nanoparticles. The potential aggregation of the nanoparticles can retard adsorption by reducing the surface area consequently decreasing IONPs reactivity and reducing the efficiency of arsenic adsorption (He et al., 2008). However, aggregation can be beneficial in the immobilization of arsenic by trapping the arsenic in the interior portions of the iron oxide aggregates thus reducing its bioavailability (Waychunas et al., 2005). Therefore, it is important to understand and demonstrate the difference of arsenic adsorption between nanoparticles and aggregates of iron oxides.

In this study, the adsorption/desorption process of arsenic on nanoparticulate iron oxides and iron oxides aggregates was investigated with unmodified hematite (α -Fe₂O₃). Hematite is one of the most thermodynamically stable iron oxides and is usually the final stage of iron oxide phase transformations (Zaspalis et al., 2007). Phase transformation can be detrimental to adsorption since adsorbates can be desorbed and become bioavailable during the process. Therefore hematite has a greater potential for contaminant adsorption due to its stability. These hematite nanoparticles will have no surface modifications as modifiers could affect the sorption and desorption of contaminants on the nanoparticle surface, introduce additional mass transfer limitations of contaminants to active surface sites, and could decrease the reaction rate of the reactions that could be taking place at the surface (Phenrat et al., 2009). Therefore, we investigated and compared the adsorption process of As(V) and As(III) with hematite nanoparticles and larger aggregates. In this study, we utilized a probe ultrasonication dispersion method to produce IONPs from commercially bought nanoparticle powder and a conventional method to mimic IONPs that may be aggregated at the early stage of experiments. Our goal is to understand the kinetics and thermodynamics of arsenic-IONPs interactions, focusing on the size effect of nanoparticles on arsenic adsorption. In doing so, we will determine kinetic parameters, adsorption isotherms and adsorption capacities, thus evaluating the role of hematite nanoparticles and aggregates in the fate, mobility and bioavailability of arsenic in the environment.

2. Procedures and methods

2.1. Materials and chemicals

Commercial iron oxide nanoparticles (α -Fe₂O₃, 98% purity and 50 m²/g specific surface area) were purchased from Nanostructured and Amorphous Materials (Houston, Texas). Stock solutions of 1000 mg/L and 10 mg/L As (III) and As (V) were prepared by dissolving sodium (meta)arsenite (NaAsO₂, 98% purity) and sodium

arsenate dibasic heptahydrate (Na₂HAsO₄·7H₂O, 99% purity), respectively in 18.2 MΩ water produced from a Nanopure Diamond lab water system (Barnstead Thermolyne Corporation, Dubuque, IA). The arsenic standards were reagent grade and obtained from Aldrich Chemical Company (Milwaukee, WI).

2.2. Instrumentation

Iron oxide nanoparticles were dispersed by probe ultrasonication using a Fisher Scientific sonic dismembrator model 100 (Pittsburg, PA) to prepare hematite nanoparticles. The IONPs were dispersed by vortex using a Fisher Scientific touch mixer model 232 (Pittsburgh, PA) to prepare micrometer size particles. Dynamic Light Scattering (DLS), a Malvern Zetasizer Nano-ZS (Westborough, MA.), was employed for particle size monitoring through measurement of hydrodynamic diameters of particles, representing the average particle diameter “z-average” intensity peak as a function of size. Total iron concentration was monitored using a graphite furnace atomic absorption spectrometer (GFAAS) (Perkin Elmer, model Analyst 600). The pH measurements were made using a Fisher Scientific Accumet Research AR15 pH/mV/°C Meter. Quantitative determination of arsenic concentration was conducted using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Perkin Elmer, Elan DRce). Prior to arsenic analysis by ICP-MS, samples were centrifuged with a Fisher Marathon 21000R centrifuge (Needham Heights, MA).

2.3. Experimental procedures

2.3.1. Adsorption kinetics experiments

Adsorption studies were performed by mixing 10 mg/L hematite particles with 200 μg/L of As(V) or As(III) in 50 mL polypropylene centrifuge tubes. For nanoparticle experiments, IONPs were dispersed using probe ultrasonication for 20 min at power level 6 to generate hematite nanoparticles and the suspension was spiked with 200 μg/L of arsenic standard (10 mg/L). All samples were prepared in nanopure 18.2 MΩ water and the pH ranged from 6.8 to 8 as the suspensions were not buffered. Samples were agitated by pulsing with probe ultrasonicator regularly. Aliquots of samples (2 mL) were collected from 3 tubes for each sampling point at definite time intervals (0–168 h, t_{0h}–t_{168h}) and the arsenic concentration in solution was monitored as a function of time.

The aliquots collected at the different time intervals (0–168 h) during the adsorption experiments were centrifuged for 60 min at 10 000 rpm for separation of particles from solution (See Supplementary Materials for selection of separation methods). The supernatant was analyzed for arsenic concentrations using ICP-MS. The amount of arsenic adsorbed was calculated from the difference between the initial and supernatant arsenic concentrations. The IONPs particle size was monitored during the adsorption experiment. IONPs concentration was also determined by measuring the total iron concentration in the suspensions using GFAAS in order to monitor the sedimentation of IONPs over time. Before iron analysis, IONPs suspension underwent acid digestion in 50% nitric acid for 20 min at 95 ± 5 °C.

For hematite aggregate experiments, adsorption was performed with similar procedures as described above except the aggregates were dispersed using vortex for 20 min at level 10. This dispersion method generates particles in the micrometer size range (Dickson et al., 2012). The samples were agitated by shaking on an orbital shaker at 250 rpm for the entire experimental time.

2.3.2. Adsorption isotherms

Hematite nanoparticles were dispersed similarly to procedures in the adsorption kinetics experiment. The hematite nanoparticles

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