



Removal of arsenic from aqueous solution: A study of the effects of pH and interfering ions using iron oxide nanomaterials

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ABSTRACT

Nanophase Fe_3O_4 and Fe_2O_3 were synthesized through a precipitation method and were utilized for the removal of either arsenic (III) or (V) from aqueous solution as a possible method for drinking water treatment. The synthesized nanoparticles were characterized using X-ray diffraction, which showed that the Fe_3O_4 and the Fe_2O_3 nanoparticles had crystal structures of magnetite and hematite, respectively. In addition, Secherrer's equation was used to determine that the grain size nanoparticles were 12 ± 1.0 nm and 17 ± 0.5 nm for the Fe_2O_3 and Fe_3O_4 , respectively. Under a 1 h contact time, batch pH experiments were performed to determine the optimum pH for binding using 300 ppb of either As(III) or (V) and 10 mg of either Fe_3O_4 or Fe_2O_3 . The binding was observed to be pH independent from pH 6 through pH 9 and a significant drop in the binding was observed at pH 10. Furthermore, batch isotherm studies were performed using the Fe_2O_3 and Fe_3O_4 to determine the binding capacity of As(III) and As(V) to the iron oxide nanomaterials. The binding was found to follow the Langmuir isotherm and the capacities (mg/kg) of 1250 (Fe_2O_3) and 8196 (Fe_3O_4) for As(III) as well as 20,000 (Fe_2O_3) and 5680 (Fe_3O_4) for As(V), at 1 and 24 h of contact time, respectively. The As(V) capacities were determined to be 4600 (Fe_2O_3), 6711 (Fe_3O_4), 4904 (Fe_2O_3), and 4780 (Fe_3O_4) mg/kg for nanomaterials at contact times of 1 and 24 h respectively.

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1. Introduction

Both inorganic and organic forms of arsenic are natural elements in the environment. Since arsenic is a known human carcinogen, environmental and human health concerns are prevalent with regards to well water containing arsenic obtained from arsenic containing geological sources as well as arsenic contaminated lakes and streams. Surface water can become contaminated as a result of the weathering of rocks, geochemical reactions, industrial waste, fertilizers, and mining/smelting operations [1–7]. Exposure to elevated arsenic levels has been attributed to adverse health related issues such as changes in skin pigmentation, diabetes, lung ailments, and cancers of the kidney and bladder [8]. The U.S. Environmental Protection Agency (EPA) has reduced the maximum contaminant level for arsenic from 50 ppb to 10 ppb as a result of the known serious health problems caused by arsenic [9–11].

Significant research has been completed in attempt to remove arsenic from aqueous solutions. Removal of As (V) and As (III) from groundwater has been researched using natural siderite in both batch and column studies. Results for this research indicated that the high efficiency high for As(III) rather than As(V) was attributed to adsorption of the As (III) to the pristine siderite and the fresh

iron oxide coatings [12]. Competing anions such as phosphate and silica have been shown to affect the adsorption of As(V). In another study arsenic adsorption to Fe_2O_3 was shown to be higher than Al_2O_3 [13]. Using iron oxide for the removal of arsenite ions from groundwater showed that the removal was independent of both the arsenic and suspended solid concentrations. In addition, ferrites have been shown to be more stable to dissolution than either metal hydroxides or metal sulfides [14].

More recently nanomaterials have been studied for their ability to remove arsenic among other contaminants from aqueous solution, with much promise. For example, nanoscale zerovalent iron (nZVI) is effective for the removal of arsenic through reduction mechanisms to elemental arsenic which in turn immobilizes the arsenic anions onto the iron for easy removal [15]. Nanoparticles can also be surface modified for environmental applications. Iron nanoparticles have shown improved reactivity by coupling with catalytic metals [16]. Jeong found that adsorption to Fe_2O_3 was better than Al_2O_3 , but neither of them had high adsorption capacities [13]. Manganese dioxides may be effective in removing As(V), but has been shown to be ineffective in removing As(III). Furthermore, manganese could contaminate a water supply in high amounts as manganese has recently been shown to be an endocrine disrupting chemical [17].

Fe_3O_4 can be recovered from a water column through magnetic separation [18]. Makris et al. found that aluminum and iron based water treatment residuals exhibit high affinities for soluble As(V) and As(III). The aluminum water treatment residual was effective in

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removing both As(V) and As(III), but the As(III) removal occurred at a much slower rate. The iron based water treatment residual showed greater affinity for As(III) than for As(V) and reached As(III) adsorption capacity levels similar to those obtained with the Al-water treatment residual-As(V) system (15,000 mg/kg) [19]. Parsons et al. found that the amount of As(III) and (V) increased with the change of concentration of As in solution. Binding capacities of Fe_3O_4 , Mn_3O_4 , and MnFe_2O_4 for As(III) were found to be 32.2, 8.9, and 718 $\mu\text{g/g}$, respectively, and were 1575, 212, and 2125 $\mu\text{g/g}$ for As(V) respectively [9].

The efficiency of the removal of arsenic is dependent on the nanoparticle size. Mayo's et al. results indicate that nanoparticle size has a significant effect on adsorption and desorption of arsenic. When the particle size is reduced from 300 to 12 nm, the adsorption capacities increase nearly 200 times for As(III) and As(V) [18].

In the present study, nanoadsorbents Fe_3O_4 and Fe_2O_3 were synthesized and studied for their ability to remove arsenic from aqueous solutions. The iron oxide nanomaterials were synthesized using a precipitation method, that consisted of a slow titration of iron(III) or iron (II) with sodium hydroxide. The synthesized iron oxide nanomaterials were then tested for the removal of As(III) and (V) from aqueous solution. The iron oxide nanoparticles were characterized using X-ray diffraction, which showed the Fe_3O_4 and the Fe_2O_3 nanoparticles had the crystal structures of magnetite, and hematite, respectively. Batch studies were performed to determine the optimum pH for the binding using 300 ppb of either As(III) or (V) from pH 6 to pH 10. Furthermore, batch studies were performed to determine the capacities of iron oxide nanomaterials for As(III) and (V). Finally, studies were performed at the optimum binding pH to determine the effects of interfering ions CO_3^{2-} , SO_4^{2-} and PO_4^{3-} on the binding of As(III) and As(V) to iron oxide nanomaterials.

2. Experimental

2.1. Synthesis of the nanoadsorbents

For the synthesis of the nanomaterials 1.0 L metal ion solutions of each 3.0 mM Fe(II) (from FeCl_2 of the metal ion solution containing 3.0 mM Fe(II) from FeCl_2 , and 3.0 mM of Fe(III) (from FeCl_2) and 3.0 mM Fe(III) (from FeCl_3) were prepared. Each metal ion was slowly titrated for approximately 4 h, adding 90 ml of 1.0 M NaOH to obtain a 1:3 ratio of $\text{M}^+:\text{OH}^-$. The excessive length of time for the titration was required to lessen the precipitation of large FeOH_3 particles during the reaction. After the reaction was complete, each solution was heated to a temperature of 100 °C for 1 h. The solutions were then subsequently left to cool, then centrifuged at 3000 rpm for 5 min, and finally rinsed three times with ultra pure water (18 M Ω) to remove any byproducts from the reaction.

2.2. XRD characterization

The X-ray powder diffraction patterns were collected using a Rigaku Miniflex XRD system using a scintillation counting detector. The scans were collected from 20 to 60 in 2θ with a counting rate of 2 s and a step of 0.1° 2θ . The collected XRD patterns were then background corrected and fitted using the Le Bail fitting procedure to determine the phase of the synthesized nanomaterials Fe_2O_3 and Fe_3O_4 . Subsequent to fitting, the average grain size of the nanomaterials was determined using the Scherrer's equation and the full width half maximum (FWHM) of at least three independent diffraction peaks for Fe_2O_3 and Fe_3O_4 . The average grain size was determined as an average of the values determined from the sizes of three independent diffraction peaks.

2.3. pH profile

The binding of As(III) and As(V) to the Fe_3O_4 and Fe_2O_3 nanoadsorbents was performed for the pH range 6 through 10. The pH

adjustment of the 300 ppb solution of either As(III) or As(V) was adjusted to the desired level using either dilute sodium hydroxide or dilute nitric acid. A 4.0 mL aliquot of the pH adjusted 300 ppb solution of either As(III) or As(V) was then added into 5 ml test tubes containing 10 mg of dried nanomaterial. The tubes were then capped, placed in a rocker, and equilibrated for an hour. In addition, control samples which consisted of 4 mL of the same 300 ppb of the adjusted solution were extracted and added to empty 5 ml test tubes. All sample and control tubes were tested in triplicate for statistical purposes. After equilibration the test tubes were then centrifuged at 3000 rpm for 5 min, and the supernatants were collected for analysis using Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), a Perkin Elmer AAnalyst 800 atomic spectrometer, was used to determine the amount of As remaining in the solution. The analysis was performed using calibration curves with correlation coefficients (R^2) of 0.95 or better.

2.4. Capacity studies

The capacities of the nanoadsorbents were verified at a pH of 6, which was determined to be the optimum binding pH, using solutions with concentrations 0.3, 1, 5, 10, 25, 50, and 100 ppm of either As(III) or As(V). The prepared pH adjusted solutions consisting of either As(III) or As(V) were added to a 10 mg sample of the dried nanomaterials. The tubes were capped and placed on a rocker for 1 h to achieve equilibrium. Also, additional test tubes of the arsenic solutions were rocked for a 24 h period to determine if time would have an effect on the capacity of the nanomaterials for the adsorption of either As(III) or As(V). Following equilibration, the test tubes were then centrifuged at 3000 rpm for 5 min and the supernatants were collected for analysis using inductively coupled plasma-optical emission spectroscopy (ICP-OES), a Thermo Jarrel Ash IRIS ICP-OES, was used to determine the amount of As present in the solution. All of the reactions and control samples were tested in triplicate for quality assurance and statistical purposes. The control samples were treated the same as the reaction samples. The analysis was performed using calibration curves with correlation coefficients (R^2) of 0.95 or better.

2.5. Interference studies

The interferences of the nanoadsorbent were determined at a pH of 6 using interference solutions with concentrations of 0.3, 3, 10, 100, 1000, and 2000 ppm for each CO_3^{2-} , PO_4^{3-} , and SO_4^{2-} , and a mixture of all three interfering species with 300 ppb of either As(III) or As (V). As with the other studies a 4 mL aliquot was extracted and placed into 5 mL test tube containing 10 mg of the nanomaterial. The test tubes were placed on a rocker for 1 h to achieve equilibrium. Control sample consisting of the interfering solutions without the nanomaterials was also prepared and treated the same as the reaction samples. The reaction samples and the control samples were then centrifuged at 3000 rpm for 5 min and the supernatants were collected for analysis using Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) to determine the amount of As present in the solution. The analysis was performed using calibration curves with correlation coefficients (R^2) of 0.95 or better.

3. Results and discussions

3.1. X-ray diffraction of synthesized nanoadsorbents

The collected XRD patterns are present in Fig. 1, which shows that the nanomaterials were the correct phase of the desired material. The XRD pattern for the Fe_2O_3 had the following planes present in the material: 220, 311, 400, 422, and the 511 which correspond to the diffraction planes in $\alpha\text{-Fe}_2\text{O}_3$. The Fe_3O_4 nanomaterial had the 012, 104, 110, 116, 211, 018, and the 122 diffraction planes that are observed in the crystal structure of magnetite. In addition, the average

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