Study of As(III) and As(V) oxoanion adsorption onto single and mixed ferrite and hausmannite nanomaterials

Sandra Garcia, Saima Sardar, Stephanie Maldonado, Velia Garcia, C. Tamez, J.G. Parsons *

Department of Chemistry, The University of Texas-Pan American, 1201 W University Dr. Edinburg, TX 78539, United States

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ABSTRACT

The removal of arsenic(III) and arsenic(V) from an aqueous solution through adsorption on to Fe_3O_4, $MnFe_2O_4$, 50% Mn substituted Fe_3O_4, 75% Mn substituted Fe_3O_4, and Mn_3O_4 nanomaterials was investigated. Characterization of the nanomaterials using XRD showed only pure phases for Mn_3O_4, $MnFe_2O_4$, and Fe_3O_4. The 50% and 75% substituted nanomaterials were found to be mixtures of Mn_3O_4 and Fe_3O_4. From batch studies the optimum binding pH of arsenic(III) and arsenic(V) to the nanomaterials was determined to be pH 3. The binding capacity for As(III) and As(VI) to the various nanomaterials was determined using isotherm studies. The binding capacity of Fe_3O_4 was determined to be 17.1 mg/g for arsenic(III) and 7.0 mg/g for arsenic(V). The substitution of 25% Mn into the Fe_3O_4 lattice showed a slight increase in the binding capacity for As(III) and As(VI) to 23.8 mg/g and 7.9 mg/g, respectively. The 50% substituted showed the maximum binding capacity of 41.5 mg/g and 13.9 mg/g for arsenic(III) and arsenic(V). The 75% Mn substituted Fe_3O_4 capacities were 16.7 mg/g for arsenic(III) and 8.2 mg/g for arsenic(V). The binding capacity of the Mn_3O_4 was determined to be 13.5 mg/g for arsenic(III) and 7.5 mg/g for arsenic(V). In addition, interference studies on the effects of SO_4^{2-}, PO_4^{3-}, Cl^-, and NO_3^- were investigated. All the interferences had very minimal effects on the As(III) and As(V) binding never fell below 20% even in the presence of 1000 ppm interfering ions.

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1. Introduction

Arsenic is an element that is ubiquitous throughout the world: found in the earth's crust, in both surface and groundwater, and within in the human body [1,2]. The toxic effects of arsenic in humans come from the ingestion of arsenic contaminated food and water. However, in general the inorganic compounds of are arsenic more toxic than the organic arsenicals and are common contaminates in drinking water [1]. The As(III) (arsenite) compounds are much more toxic than the As(V) (arsenate) compounds [2]. Arsenic has been linked to variety of health effects when ingested in small consistent dosages through combined food or drinking water [1,2]. The effects of As include abnormal skin conditions, gastrointestinal problems, neurological effects, and diabetes [1–5]. Furthermore, links between arsenic exposure and several types of cancer have been established, which includes: lung, skin, kidney, liver, and prostate [4]. Due to the numerous health risks the Environmental Protection Agency has set the MCL of arsenic in drinking water from 0.050 to 0.010 ppm in an effort to reduce number the health effects caused by the long-term ingestion of arsenic in the US population [2,6].

There are several methods to remove arsenic from drinking water, which include precipitation, ion exchange, membrane process, coagulation, and adsorption [7–12]. In general technologies to remove arsenic from drinking water are generally non-specific and expensive to water treatment plants. However, nano-adsorbents may provide a more cost effective technology for the removal of As(III) and As(V) from contaminated water [10,11,13–17]. Nanomaterials are a promising emerging technology with many different applications due to their enhanced reactivity and high surface area to volume ratio. Adsorbents have been studied for the remediation/removal of many different ions from aqueous solution. More recently, nanomaterials have been investigated for the removal of inorganic contaminates from aqueous solution, including the inorganic forms of arsenic. Adsorbents such as activated alumina, clay based materials, red mud (the waste from aluminum processing), Al-WTR (water treatment residuals) Fe-WTR, iron oxide materials, manganese oxide nanomaterials, granular ferric oxide, as well as metal sulfide nanomaterials [14–19].

Studies investigating the adsorption of As(III) and As(V) using activated alumina have shown the effect of pH, surface oxidation, and competing ions [6]. It has been shown that between pH 7 and 8 activated alumina has a net positive charge, which showed a preference for the adsorption of anions from solution including arsenic. Acidic pHs are generally considered optimum for arsenic removal with activated alumina. Genc-Fuhrman et al. found arsenic adsorption using activated

red mud was effective for As(V) adsorption. The optimum pH for As(V) adsorption was 4.5 with a removal of approximately 100%. In addition, the desorption of As(V) was found to be optimum pH 11.6 with a maximum desorption of 40%. In contrast, the optimum pH for As(III) binding was found to be 8.5, and the removal efficiency was dependent on the initial As(III) concentration [20]. In a similar study Altundogan et al. also investigated the application of activated red mud on arsenic removal [21]. Altundogan et al. showed the optimum binding pH range for As(III) was from 5.8 to .5 and the optimum pH range for As(V) binding was from 1.8 to 3.5; with a maximum removal of As(V) was 96.52% and 87.54% for As(III) [21].

Adsorption techniques using nanoparticles have shown promise as being an effective technique to remove ions from water. Luther et al. showed that the adsorption of As(III) to Fe_2O_3 and Fe_3O_4 nanomaterials was 1.250 mg/g and 8.196 mg/g after 1 h of contact time, respectively [22]. However, at a contact time of 24 h the 20 mg/g for Fe_2O_3 and 5.680 mg/g for Fe_3O_4 were observed for As(III) binding to the nanomaterials [22]. The binding capacities for As(V) were lower in magnitude at both the 1 h and 24 hour contact times. The Fe_2O_3 nanomaterials had similar capacities of 4.6 mg/g and 4.9 mg/g for the 1 h and 24 hour contact times for As(V) binding, respectively. Whereas, the Fe_3O_4 nanomaterial had capacities of 6.7 and 4.8 for the 1 h and 24 hour contact times, respectively for As(V) binding [22]. Parsons et al. have investigated the binding of As(III) and As(V) binding to Mn_3O_4, a $MnFe_2O_4$ and Fe_3O_4 nanomaterials [11]. In this study the maximum binding capacity for the Fe_3O_4 was 0.0322 mg/g and 1.575 mg/g for the As(III) and As(V), respectively [11]. The binding capacity of the $MnFe_2O_4$ nanomaterial had a binding capacity of 0.718 and 2.212 mg/g for As(III) and As(V) respectively. The Mn_3O_4 nanomaterial had a binding capacity of 0.0089 and 0.211 for the As(III) and As(V), respectively [11]. In addition, at the concentrations used the pH dependency of the arsenic binding was pH dependent increasing from pH 2 to pH 6. Al-WTRs have been shown to have varied between capacities for As(III) and As(V) of 1.8–15 mg/g for As(V) and between 7.500– 15 mg/g for As(III) after 48 h of equilibrium with a pH range from 6 to 6.5 [17]. Laterite iron concretions have been shown to have As sorption capacities of 909 µg/g and 714 µg/g for As(III) and (V), respectively at pH 7 [23].

In the present study the adsorption of arsenic(III) and arsenic(V) on to single and mixed phase ferrite and hausmannite nanomaterials was investigated. The nanomaterials investigated were synthesized through a precipitation process and subsequently characterized using XRD for phase and average grain size of the material. Batch studies were performed to determine the effect of pH and the effect of interfering ions on the adsorption of both As(III) and As(V) onto the different metal oxide nanomaterials. In addition, the binding capacities for the different materials were determined using isotherm studies, which were found to follow the Langmuir isotherm.

2. Methodology

2.1. Synthesis of the nanoadsorbents

The synthesis of the Fe_3O_4 nanomaterial a 1.0 L of metal ion solution containing 30.0 mM of Fe(II) (from $FeCl_2$), was prepared. For the manganese substituted nanomaterials a specific percentage of the Iron(II) was substituted with manganese(II) (from $MnCl_2$). The solution for the 25% Mn–75% Fe consisted of 7.5 mM Mn^{2+} and 22.5 mM Fe^{2+}. The solution for the synthesis of the 50% Mn–50% Fe, contained 15 mM Mn^{2+} and 15 mM Fe^{2+}. The 75% Mn–25% Fe was synthesized from a solution containing 22.5 mM Mn^{2+} and 7.5 mM Fe^{2+}. Finally the solution for the synthesis of the Mn_3O_4 nanomaterial consisted of a 30.0 mM solution of Mn^{2+}. The prepared solutions were then titrated using 100 mL of a 1.0 M NaOH solution to obtain a 1:3 ratio of M^+:OH^-, over approximately 2 h. The samples were then heated 90 °C for an hour under constant stirring. Subsequent to heating the samples were

then cooled at room temperature and centrifuged at 3000 rpm (Fisher Scientific 8K, Houston, TX) for 5 min. The supernatants were discarded and the solid sample was suspended in 18 MΩ deionized (DI) water and centrifuged again to remove any unreacted starting material and reaction byproducts of the reaction. The samples were washed twice with 18 MΩ DI to ensure clean materials for the subsequent reactions. After washing, the nanomaterials were oven dried at 70 °C until dry.

2.2. XRD characterization

The samples were characterized using X-ray diffraction in combination and fitted for phase using the FullProf Suite programs. The XRD patterns were collected at room temperature using a Rigaku Miniflex X-ray powder diffractometer (Rigaku Corporation, The Woodlands, TX). The samples were homogenized using a mortar and pestle and then placed on an aluminum sample holder. The samples were then diffracted from 20 to 60° in 2θ using a 2 s counting time and a stepping rate of 0.001 /min. The fittings were performed using crystallographic data from the literature and the FullProf 2001 Suite programs using the Le Bail fitting procedure with fixed intensities of the diffraction lines [24–27]. The average grain size of the nanoparticles was determined using the Scherrer's equation and a Gaussian fitting of three independent diffraction peaks.

2.3. pH profile

The effect of pH binding of arsenic(III) and arsenic(V) was evaluated from pH 2 to 6 on the synthesized nanoadsorbents Fe_3O_4, 25% Mn substituted Fe_3O_4, 50% Mn substituted Fe_3O_4, 75% Mn substituted $MnFe_3O_4$, and the Mn_3O_4. Arsenic(III) and arsenic(V) solutions were prepared at a concentration of 300 ppb in 18 MΩ DI water and pH adjusted to pH 2.0, 3.0, 4.0, 5.0 and 6.0. The pH of the solution was adjusted using either dilute sodium hydroxide or dilute nitric acid. A 4.0 mL aliquot of the pH adjusted solutions added to 10 mg of the nanomaterial in a 5 mL polyethylene test tube. The reaction mixture was capped, placed on a rocker, and equilibrated for 1 h. Control samples containing only the arsenic ions were treated the same as the samples. Both samples and control solutions performed in triplicate for statistical purposes. After equilibration, the samples were centrifuged at 3000 rpm for 5 min. The supernatant from each tube was saved for analysis using ICP-OES. All ICP-OES analyses were performed on a Perkin Elmer Optima 8300 DV (Perkin-Elmer, Shelton, CT). All calibration curves had correlation coefficients (R^2) of 0.99 or better.

2.4. Capacity studies

A mass of 10 mg of each of the nanomaterial was weighted out in triplicate, and placed in individual test tubes. The 10 mg of nanomaterial then had 4 mL of a either an As(III) or As(V) solution with concentrations of either 3 ppm, 30 ppm, 150 ppm, 300 ppm or 1000 ppm, which was previously adjusted to pH 3, was added to the tube. The nanomaterials and arsenic solutions were capped, placed on a rocker,

Table 1
Parameters used for the determination of iron and manganese in the supernatants of the reaction using a Perkin Elmer Optima 8300 DV.

Parameter	Setting
RF Power	1500 W
Nebulizer	Gemcone low flow
Nebulizer flow	0.65 L/min
Plasma flow (Ar)	8 L/min
Sample flow rate	1.25 mL/min
Spray chamber	Glass cyclonic
Injector	Alumina 2 mm