



## Arsenic removal from aqueous solutions by adsorption onto hydrous iron oxide-impregnated alginate beads



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### ABSTRACT

Hydrous iron oxide impregnated alginate beads were developed for effective arsenic removal from water. As(III) adsorption was maximized at neutral pH while As(V) adsorption was higher in acidic conditions. Adsorption efficiency for both As(III) and As(V) mostly increased with increasing iron loading, but As(V) adsorption slightly decreased at high iron loading. Phosphate showed a pronounced interfering effect, especially at high concentration. Kinetics data fitted to pseudo-second-order and intra-particle diffusion model suggested chemisorption and intra-particle diffusion might mainly govern As(III) and As(V) adsorption, respectively. Beads were regenerated using NaOH solution and successfully reused for multiple cycles.

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### Introduction

Arsenic, which is ubiquitous in nature, is a serious worldwide concern due to its high toxicity and carcinogenicity [1]. Long-term exposure to arsenic can cause skin lesions, peripheral neuropathy, gastrointestinal symptoms, diabetes, renal damage, cardiovascular disease, and various types of cancer [2]. Humans are exposed to arsenic mainly through ingestion of arsenic-contaminated water and foods from natural and anthropogenic sources [3]. Naturally occurring arsenic contamination of groundwater has been discovered in at least 70 countries, and an estimated 140 million people are at risk of consuming contaminated water [4].

Arsenic usually occurs in inorganic form as arsenite and arsenate in natural water, which are the oxyanions of trivalent As(III) and pentavalent As(V), respectively. Arsenite is 20 to 60 times more toxic than arsenate and more mobile in the environment [5]. However, typical arsenic treatment techniques such as anion exchange and coagulation with ferric salts are less effective to remove As(III) because As(III) mostly occurs as uncharged arsenious acid,  $\text{H}_3\text{As(III)O}_3$ , in the natural environment [6]. When water contains appreciable amount of As(III), the contaminated water is usually pretreated with oxidants to convert As(III) to As(V) before applying the treatment techniques. Among

various arsenic treatment technologies, adsorption is one of the most effective methods for removing As(III) and/or As(V) [6,7]. Many previous studies have revealed that iron oxides and hydrous iron oxides (iron oxide-hydroxide) have high affinity toward both As(III) and As(V) species [8,9]. Mayo et al. [10] found that the adsorption capacities of magnetite particles for both As(III) and As(V) was increased nearly 200 times when the particle size decreased from 300 to 12 nm. The decrease in particle size increased specific surface area of the magnetite, prevented agglomeration of magnetite particles in water and improved solute transport into the interior surface of the magnetite.

Iron oxides in the amorphous phase are known to exhibit higher adsorption capacity than other phases due to their large surface areas [11]. The small particle size and high reactivity of iron oxides, however, make it difficult to separate iron particles from reactors after adsorption in full-scale applications [12,13]. Such limitations have been overcome by coating, doping, or packing iron oxides and hydrous iron oxides on support materials. The use of iron oxide-containing sand, zeolite, and activated carbon have been well documented [9,14,15,16,17]. Polymer-supported metal oxide based composite adsorbents have recently gained considerable attention for heavy metal removal due to their biocompatibility, water permeability, and ability to load large amounts of solid particles. Cho et al. [18] encapsulated akaganeite in alginate beads for arsenic, Lv et al. [19] immobilized  $\text{Fe(0)-Fe}_3\text{O}_4$  in polyvinyl alcohol-alginate for chromium(VI), Cho et al. [20] immobilized clay-magnetite in chitosan for arsenic(V) and copper(II), and Pan

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et al. [21] impregnated hydrous iron oxide in a cation exchange resin for heavy metal adsorption. Ociński et al. [22] immobilized iron oxide in polystyrene-divinylbenzene for arsenic removal, but observed a low As(V) adsorption rate for the supported beads. Major limitations of these studies include low adsorption capacity due to, for instance, low iron loading, and little information on the regenerability and reusability of adsorbents considering the potential for practical applications.

The objective of this study was to develop hydrous iron oxide-impregnated alginate beads (HIO-alginate beads) for effective removal of inorganic arsenic from water. Amorphous hydrous iron oxides prepared by chemical precipitation method were homogeneously dispersed into alginate gels. Composite beads were then synthesized from the gel matrix and finally dried on air. Beads were characterized with scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM-EDX), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and N<sub>2</sub> adsorption-desorption analysis. The arsenic adsorption efficiency of beads was investigated as a function of contact time, pH, iron loading, and concentrations of competing ions in batch experiments. Studies were performed to investigate the effects of interfering ions on arsenic adsorption. Kinetic and equilibrium studies were applied to analyze the mechanisms of arsenic adsorption by the prepared beads. The capability for regeneration and reusability of HIO-alginate beads were also examined.

## Experimental

### Chemical reagents

All chemicals were of reagent grade. Sodium meta-arsenite (NaAs(III)O<sub>2</sub>, >98%), sodium arsenate dibasic heptahydrate (Na<sub>2</sub>HAs(V)O<sub>4</sub>·7H<sub>2</sub>O, >98%), and sodium alginate (medium viscosity grade) were purchased from Sigma-Aldrich, USA. Stock solutions of arsenite and arsenate were prepared by dissolving their respective salts in deionized water. Ferric nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, >98%, Junsei, Japan) was used to synthesize iron oxides. Other reagents were purchased from Duksan, Republic of Korea.

### Synthesis of hydrous iron oxide-impregnated alginate beads

Hydrous iron oxide was prepared by chemical precipitation of ferric nitrate according to the method described by Wilkie and Hering [23]. Hydrous iron oxide precipitate was formed at pH 7.5–8.0 by slowly adding 0.5 M NaOH to 300 mL of 0.02 M ferric nitrate. The precipitate was washed 3 times with deionized (DI) water to remove water soluble ions from the precipitate.

The produced hydrous iron oxide was immobilized using alginate with calcium ion via entrapment. Briefly, 3 wt% alginate gel matrix was prepared. A suspension of hydrous iron oxide precipitate containing 0.34 g of Fe was added into the 100 mL of the alginate gel matrix, and then DI water was added until the final volume of the mixture was 150 mL. The mixture was uniformly mixed with a magnetic stirrer for 4 h. The mixture contained sodium alginate and iron in a proportion of 9:1 (3 g alginate/0.34 g Fe) for 10 wt% iron loading. Finally, HIO-alginate beads were produced from this homogeneous mixture through crosslinking of sodium alginate with calcium chloride (3%) solution. Beads were cured in the calcium chloride solution for 6 h to complete gelation, washed several times with DI water to remove water soluble compounds, and finally air-dried for 48 h. Only dry beads were used in the subsequent adsorption experiments. HIO-alginate beads with a higher proportion of iron (up to 30 wt%) were produced using a similar procedure.

### Characterization and analytical techniques

The SEM images and approximate elemental composition of HIO-alginate beads were obtained with SEM-EDX analysis (Ametek, Inc., USA). The morphology of beads was observed with a TEM (JEM-ARM200F, JEOL), which was operated at 200 kV. Characterization of porous structure of HIO-alginate beads was performed by the method of N<sub>2</sub> adsorption-desorption at 77 K using an ASAP 2010 (Micromeritics, USA). XPS spectra of HIO-alginate beads were acquired using an X-ray photoelectron spectroscopy (Thermo VG, UK) with a monochromatized AlK<sub>α</sub> X-ray source at 12 kV (1486.6 eV). Arsenic concentrations in solutions were determined in terms of As(III) or As(V) using inductively coupled plasma (ICP) spectrometer (IRIS/AP, Thermo-Jarrel Ash Corp., USA).

### Adsorption experiments

Batch experiments were carried out separately on As(III) or As(V) solutions at 23 ± 1 °C in a 50-mL glass vial. The initial pH was adjusted by adding 0.1 M HCl or 0.1 M NaOH to arsenic solution. A total of 40 mL arsenic solution was shaken with 0.040 g of HIO-alginate beads (1.0 g/L) on an orbital shaker at 100 rpm. Aliquots of the samples were taken at certain time intervals to investigate As(III) or As(V) adsorption onto the beads.

### Effect of pH

The effect of pH on As(III) and As(V) adsorption onto beads was investigated. Initial pH was varied within the range of 2–12 by adding 0.1 M NaOH or HCl dropwise to 10 mg/L of As(III) or As(V) solutions. No visible change in the color of the solution was observed, indicating that immobilized iron should not leach from beads.

### Effect of iron loading in beads

Beads with different iron loadings from 10 to 30 wt% were also tested to elucidate the role of hydrous iron oxides in uptake of arsenic species. Initial solution pH was adjusted to 6.0 ± 0.2.

### Effect of competing ions

Various common anions found in surface and ground water may compete with arsenic for adsorption sites. As(III) and As(V) adsorption onto HIO-alginate beads was investigated in the presence of sulfate, silicate, phosphate, bicarbonate, chloride, or nitrate ion at different concentrations of 0.2 and 2.0 mM.

### Kinetic study

A kinetics experiment was conducted to investigate the adsorption rate of As(III) or As(V) onto HIO-alginate beads. Aqueous solutions of As(III) and As(V) with initial concentrations of 2.5 mg/L or 10 mg/L were contacted with HIO-alginate beads for 3–240 h. The solution concentration was monitored over time by collecting samples of each bottle at fixed time intervals. For a blank, the same experiment was performed using bare alginate beads impregnating no iron oxides. Data were fitted with pseudo-first- and pseudo-second-order models [24,25]. An intra-particle diffusion model proposed by Weber and Morris [26] was also applied to analyze experimental data.

### Isotherm study

An equilibrium adsorption experiment was conducted by varying the initial concentration of As(III) or As(V) in a range of 7–500 mg/L. A plot of arsenic concentration in solid (bead) phase at equilibrium,  $q_e$ , versus arsenic concentration in solution at equilibrium,  $C_e$ , after 7 d was obtained. This plot was further analyzed using Langmuir and Freundlich adsorption isotherms [27,28].

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