

Arsenic Removal Using Iron Oxide and Sodium Ferrate Loaded Alginate Beads

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ARSENIC REMOVAL USING IRON OXIDE AND SODIUM FERRATE LOADED ALGINATE BEADS

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Abstract

In this study, the application of the iron oxide and sodium ferrate loaded alginate beads have been investigated for As (III), As (V) removal. Calcium alginate beads were treated with hydrous ferric oxide and sodium ferrate. The effect of sorbent concentration on the gel bead, solution pH, and the contact time has been studied, pH 7 was chosen for iron oxide for both of As (III) and As (V) removal. In case of ferrate, pH 3 was chosen. Arsenic removal was sufficient after 24 hours of contact time for both sorbent. Dose of the adsorbents was 4 g. The most efficient sorbent was found to be the beads doped with iron oxide. The removal of 90-96 % was obtained for As (III) and As (V) removal. In case of ferrate the removal of 56.60-62.88 % was obtained for As (III) and As (V). The amount of iron loaded on calcium alginate was determined by XRF. Alginate bead characterization was performed by scanning electron microscopy.

Keywords: Arsenic Removal, Sorption, Calcium alginate, Iron oxide, Sodium ferrate

1. INTRODUCTION

Mongolia is a country where chemical industry, automobile industry, nuclear energy industry have not been developed. Therefore, it could be assumed that the environment is not polluted by heavy metals and chemical toxic substances. However, during the utilization and exploration of gold primary and placer deposits in entire Mongolian territory, environmental pollution is becoming a big issue. Due to gold mining the soil, water and air have been polluted with heavy metals especially with arsenic [Government Report, 2007]. Therefore it is necessary to determine the content of arsenic in waste water and soil, to develop the arsenic removal method.

Various studies have investigated arsenic removal using different technologies, including oxidation, coagulation, sorption and membrane filtration. Sorption techniques are relatively simple to conduct and cost effective [Mohan et al., 2007]. In the adsorption system, adsorbent is the most important factor of the system because the period of operation depends on the capacity of the adsorbent. Among the various adsorbents, iron oxide-containing materials usually used to remove arsenic because the adsorption

capacity of iron oxides is better than other materials [Mohan et al., 2007; Jang, et al., 2008]. Also ferrate is strong oxidizer and widely used in heavy metal treatment [Sharma et al., 2005].

In the present study, alginate gel beads have been applied as a support matrix for the immobilization of hydrous ferric oxides and sodium ferrate. Alginate is the most abundant marine biopolymer and, after cellulose, the most abundant biopolymer in the world. The major source of alginate is found in the cell walls and the intracellular spaces of brown seaweed. Alginic acid is a linear polymer based on two monomeric units, β -D-mannuronic acid and α -L-guluronic acid. Calcium is the cation mostly used in the preparation of alginate beads [Fundueanu at al.,1999; Mohan at al., 2007; Mushollaeni W. (2011)].

The objective of this research was to examine the efficiency of alginate beads as possible supports for hydrous ferric oxides and sodium ferrate for As (III) and As (V) treatment.

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2. MATERIALS AND METHODS

2.1 Reagents and Stock Solutions.

All reagents used were of AR unless otherwise stated. Laboratory grade distilled water was used throughout. Alginate beads were prepared from sodium alginate (Japan AR). Arsenate and arsenite stock solutions were prepared from sodium arsenate heptahydrate (Na2HAsO4·7H2O, Japan Extra pure reagents) and arsenictrioxide (As₂O₃, German AnalaR) dissolving in distilled water, respectively. The final concentration of the working solution for both arsenate and arsenite was 50 mg/l. Arsenic standard solution of 1000 mg/L (Tianjin UnionLab. Chem. Reagent Ltd., China) was used for Atomic Absorption calibration. Calcium solutions used in gel synthesis were prepared from CaCl₂ Chem. Reagent Ltd., China) (Tianjin UnionLab. dissolving in distilled water. Hydrous ferric oxide (HFO) suspensions used for gel activation were prepared from FeCI₃·6H₂O (Russia AR) by dissolving in distilled water with adjustment of the pH to 5.0 using 1 M NaOH solution. The sodium ferrate was prepared by mixing Na₂O₂ (Tianjin UnionLab. Chem. Reagent Ltd., China) with ferrous oxide (Russia AR) with molar ratio of 3:1 and burnt at 300°C for 3 hours at 400°C for 2 hours, recpectively.

2.2 Bead Preparation.

Sodium alginate (1g) was dissolved in 100 mL of distilled water to give a 1% w/v alginate solution; this solution was mixed with a mechanic stirrer until a transparent, viscous solution was obtained, 0.2 M CaCl₂ solution was prepared. Calcium alginate beads were prepared by dropping sodium alginate aqueous solution into a continuously stirred calcium chloride solution. The beads were soaked in CaCI2 solution for 24 hours to ensure its hardness. They were rinsed three times with distilled water and dried at room temperature. For the preparation of Ca-Fe-immobilized beads, biopolymer powder (1 g of sodium alginate) was dispersed in 100 mL of various concentrations of HFO suspensions at pH 5.0; then, the aforementioned procedure was followed. Gel bead containing ferrate was prepared. The desired amount of ferrate (within the range 0-2g) was added to 100 ml distilled water under rapid constant magnetic stirring. To the homogeneous suspensions, Ig alginate powder was slowly added and the mixture was stirred until total biopolymer dissolution was achieved.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Arsenic Adsorption Experiments.

Sorption of As (III) and As (V) in ferrate and iron oxide-immobilized alginate beads were investigated. 4 g of

bead for iron oxide and ferrate was added to 50 mL arsenic solutions with concentrations of 50 ppm As (III) or As (V) and placed at different pH and room temperature (20°C). The experiments were conducted by shaking in shaker (Apparatur for shaker, Russia ABU-6C) at 200 rpm. Arsenic concentration was measured after 20 min, 3 h, 12 h, 24 h, and 48 h of agitation time, and then filtered. Temperature and pH was measured by microprocessor pH meter (Hanna instruments). The amount of arsenic that remained after contact time was subtracted from the initial amount of arsenic in the solution, and the amount of arsenic absorbed by the beads was determined.

The determination of arsenic was performed by flame atomic absorption spectrometry (AA400 Perkin Elmer). The calibration curve enables the determination of arsenic in the concentration range from 10 to 60 mg/L.

3.2 Alginate Bead characterization.

Alginate bead characterization was performed by scanning electron microscopy (Microtrac SEMTRAC mini,Nikisso Japan). The mean diameter of bead was 2 mm.

The pictures and SEM image of prepared alginate beads are shown in Figure 1 and Figure 2.





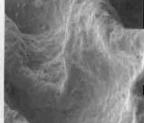


Fig. 1 Photos and SEM image of calcium alginate

The color of calcium alginate beads were white and an even surface. The iron oxide-alginate and ferrate-alginate were colored red brown and brown due to original color of the precipitates.

SEM micrographs showed that surface topology of iron oxide-alginate and ferrate-alginate changed compared to the micrographs of calcium alginate and became more porous.

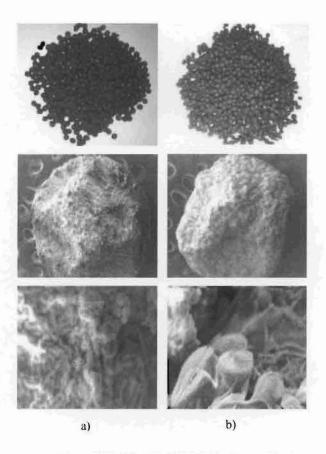


Fig. 2 Photos and SEM image iron oxide-alginate (a), ferrate-alginate (b)

4.2 Effect of sorbent concentration

Calcium iron alginate beads were prepared, depending on the concentration of the FeCI₃ and Na₂FeO₄, because adsorption processes are greatly dependent on the available amount of adsorbent. In order to verify the adsorption behavior of obtained ferrate and iron oxide-immobilized alginate beads, preliminary experiment were carried out. The experimental results are shown in Figure 2.

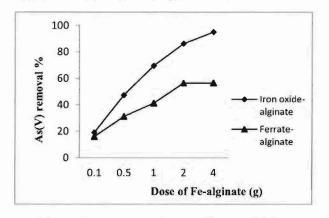


Figure 2. Arsenic removal by iron oxide-alginate (a) and ferrate-alginate (b) (Conditions: pH = 8.3; solution volume 50 ml; quantity of bead 4 g; Initial concentration of As 50 mg/L)

An increase of the FeCl₃ and Na₂FeO₄ concentration in the gel bead provoked an increase of arsenic sorption. The removal of arsenic was greatly influenced by the FeCl₃ and Na₂FeO₄. The removal of 90-96 % was obtained for As (III) and As(V) removal with iron oxide loaded alginate beads. In the case of ferrate, the removal was 56.60-62.88 % for As(III) and As(V).

4.4 Effect of contact time

To investigate the kinetics of iron oxide and ferrate loading on the calcium alginate beads, the procedure was performed for 0.3 h, 3 h, 12 h, 24 h and 48 h. Experimental results are presented in Figure 3. As shown in the Figure 3, when increase the contact time removal of arsenic was improved. After 24 hours, both adsorbents reached equilibrium states. Therefore a contact time of 24 h was needed for both adsorbents.

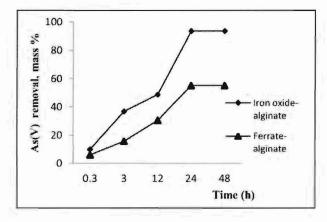


Figure 3. Arsenic removal by iron oxide-alginate (a) and ferrate-alginate. (Conditions:pH-8, 3; solution volume-50 ml; quantity of bead-4 g; Initial concentration of As-50mg/L)

4.5 Effect of pH

The effect of pH on the removal of As(III) and As(V) was studied. Figure 4 shows the adsorption pattern in various pH ranges. Iron oxide-alginate showed a better removal efficiency in wide range of pH 3 -8 for both As(III) and As(V). However the removal was achieved to 90%, but the beads were swollen and broken. We also observed that sorption removal decreased at pH < 3.

For ferrate-alginate, the removal efficiency increases with decreasing pH for both As(III) and As(V). Under strong acidic condition the removal of arsenic was sufficient but recovery of arsenic was not exceeded 60%.

From the results in Figure 3, the removal of As (III) was lower than the removal of As (V) for both adsorbents. It is shown that recovery of arsenic will be efficient after oxidization As(III) to As(V).

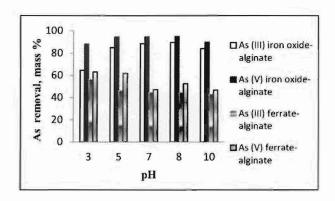


Figure 3. Arsenic removal by iron oxide-alginate (a) and ferrate-alginate (Conditions:solution volume-50 ml;quantity of bead-4g;Initial concentration of As-50mg/L)

5. CONCLUSION

Simple batch tests indicated that iron oxide loaded alginate beads have a higher adsorption capacity than ferrate loaded alginate beads.

The results of the study suggested that iron loaded alginate could be effective for arsenic removal. Further investigations must be carried out in order to clarify the role of the gel matrix on the arsenic sorption. In addition, the effects of co- and counter-ions on arsenic removal from natural water should be tested.

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