Application of iron-coated sand on the treatment of toxic metals

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Abstract Iron-coated sand (ICS) prepared by using FeCl₃ and Joomoonjin sand widely used in Korea was used in this study. In batch adsorption kinetics, As(V) adsorption onto ICS was completed within 20 minutes, while adsorption of Pb(II), Cd(II), and Cu(II) onto ICS was slower than that of As(V) and strongly depended on initial pH. At pH 3.5, ICS showed a selective adsorption of Pb(II) compared to Cd(II) and Cu(II). However, above pH 4.5, near complete removal of Pb(II), Cd(II), and Cu(II) was observed through adsorption or precipitation depending on pH. As(V) adsorption onto ICS occurred through an anionic-type and followed a Langmuir-type adsorption behaviour. In column experiments, pH was identified as an important parameter in the breakthrough of As(V). As(V) breakthrough at pH 4.5 was much slower than at pH 9 due to a strong chemical bonding between As(V) and ICS as similar with batch adsorption behaviour. With variation of ICS amounts, the optimum amount of ICS at pH 4.5 was identified as 5.0 grams in this research. At this condition, ICS could be used to treat 200 mg of As(V) with 1 kg of ICS until 50 ppb of As(V) appeared in the effluent.

In this research, as a new treatment system, ICS can be potentially used to treat As(V) and cationic heavy metals.

Keywords Adsorption; arsenic; iron-coated sand; toxic metals

Introduction
Arsenic causes serious environmental problems in water systems and is known as a primary concern to humans exposed to water systems. From the natural geochemical process and anthropogenic activities such as mining wastes, petroleum refining, and agricultural chemicals, surface and groundwater are widely contaminated with arsenic (Bhumbla and Keefer, 1994). Recently, the U.S. Environmental Protection Agency (EPA) proposed lowering the current maximum contaminant level (MCL) of arsenic from 50 ppb to 10 ppb (U.S. Environmental Protection Agency, 2001). To treat arsenic in the water system, activated alumina, coagulation, membrane or electrolysis have been used (Chen et al., 1999). However, as these processes are expensive or need to control pH or other parameters to achieve optimum adsorption capacity of arsenic, a highly effective and economic technique is highly required. In this study, as a promising technique for the treatment of arsenic, iron-coated sand (ICS) synthesized with Joomoonjin sand widely used in Korea and FeCl₃ was used to investigate the adsorption kinetic of As(V) as well as the effect of pH and concentration of As(V) on adsorption behaviour of As(V) on ICS in batch experiments. In addition, applicability of ICS on the treatment of cationic heavy metals such as copper, lead, and cadmium was also investigated. Finally, column experiments were performed with variation of pH and amount of ICS to investigate an optimum condition in a dynamic adsorption process.
Materials and methods

Preparation of ICS

Joomoonjin sand known as one of Korean standard sands having particle size ranging from 0.5 to 1.2 mm was used as supporting material of iron. ICS was prepared by the following method. FeCl₃ solution (500 mL of 0.5 M) adjusted to pH 10 was mixed with Joomoonjin sand (1 kg) in a rotary evaporator. By rotating the rotary evaporator at 30 rpm and 70°C, water in the sand suspension mixed with iron was continuously removed by applying vacuum until approximately 10% of water was remained in the suspension. After then the sand was dried with different baking temperature (105 ~ 550°C) and time (1 ~ 24 hrs) as shown in Table 1. To remove uncoated iron, dried sand was rinsed with distilled water several times and then dried again 105°C. Amount of iron coated on the sand was measured by using an acid digestion method (U.S.EPA 3050B). After filtration, the resulting acid-iron solution was then diluted and the iron content was measured using an atomic absorption spectrophotometer (AAS). The Joomoonjin sand itself had iron as 2,440 mg/kg. ICS-J1 baked at 105°C showed the highest amount of coated iron on sand, while similar coating was observed at 550°C without depending on baking time.

Batch experiments

In order to study adsorption kinetics of As(V), Pb(II), Cd(II), and Cu(II) onto ICS-J1, seven or eight polyethylene bottles were used in each metal. In each bottle, 0.1 g of ICS was mixed with As(V) solution (20 mL of 1.0 mg/L) or 0.5 g of ICS was mixed with Pb(II), Cu(II), and Cd(II) solution (30 mL of 1.0 mg/L) with a constant ionic strength (0.01 M NaNO₃). After the solution pH was adjusted to 4.5, the bottles were placed in a shaker maintained a constant temperature (25°C) and allowed to equilibrate for the specified time. After the desired time, the samples were filtered with 0.45 μm syringe filters and measured dissolved metal concentration with AAS.

Adsorption isotherms of As(V) onto ICS were obtained at constant initial pH (3.5 or 4.5) and at constant ionic strength (0.01 M NaNO₃) with variation of As(V) concentration ranging from 0.01 to 2 mg/L. In each bottle, ICS (0.5 g) was mixed with 30 mL of As(V) solution. The bottles were then also placed in the shaker maintained 25°C and allowed to reach equilibrium (5 hours as determined from the kinetic experiment). The samples were filtered with 0.45 μm syringe filters and measured As(V) concentration in the filtered solution with AAS having a hydride generator.

Adsorption of As(V) onto ICS was also performed with variation of pH. In each bottle, ICS (0.1 g) was mixed with As(V) solution (20 mL of 1.0 mg/L) and the pH of the solution was varied using 0.01 M NaOH and HNO₃. As same with above batch experiments, samples were filtered after the equilibration and measured As(V) concentration in the filtered solution.

Table 1 Preparation of iron-coated sand with variation of baking temperature and time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Time (hrs)</th>
<th>Content of Iron (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICS-J1</td>
<td>110</td>
<td>24</td>
<td>8,550</td>
</tr>
<tr>
<td>ICS-J2</td>
<td>550</td>
<td>1</td>
<td>6,610</td>
</tr>
<tr>
<td>ICS-J3</td>
<td>550</td>
<td>2</td>
<td>6,220</td>
</tr>
<tr>
<td>ICS-J4</td>
<td>550</td>
<td>3</td>
<td>6,430</td>
</tr>
<tr>
<td>ICS-J5</td>
<td>550</td>
<td>4</td>
<td>6,990</td>
</tr>
<tr>
<td>Blank</td>
<td></td>
<td></td>
<td>2,440</td>
</tr>
</tbody>
</table>
Table 2 Dissolution of iron from ICS as a function of time at pH 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dissolution of iron (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 hr</td>
</tr>
<tr>
<td>ICS-J1</td>
<td>0</td>
</tr>
<tr>
<td>ICS-J2</td>
<td>0</td>
</tr>
<tr>
<td>ICS-J3</td>
<td>0</td>
</tr>
<tr>
<td>ICS-J5</td>
<td>0</td>
</tr>
<tr>
<td>Blank</td>
<td>0</td>
</tr>
</tbody>
</table>

Column experiments

Column experiments were conducted in a 1.0 cm diameter glass column at room temperature (~25°C) and constant ionic strength (0.01 M NaNO₃). In a column, ICS was packed with 2.4, 3.0, 5.0, and 7.5 grams depending on experiment. The arsenic solution (1 mg/L) was pumped upward through the bottom of the column using Acuflow Series II high pressure liquid chromatography at a flow rate of 0.18 mL/min. Effluent samples were then received using Spectra/Chrom CF-1 Fraction Collectors. The arsenic concentration of the effluent samples was then determined using the AAS.

Results and discussion

Chemical stability of iron-coated sand

In order to apply ICS in the treatment of acid mine drainage containing arsenic, iron coated on sand should have a chemical stability even at lower pH. Therefore, dissolution of iron from each ICS was tested at several pH values as a function of time. Table 2 shows dissolution of iron as a percentage of the total iron content from each ICS at pH 2. ICS-J1 baked at 105°C showed the highest dissolution of iron compared to all ICS samples baked at 550°C over all reaction time. This result suggests that ICS baked at higher temperature has greater resistance to dissolution. However, there was no specific trend between dissolution of iron and baking time at 550°C. The original Joomoonjin sand also showed 2% dissolution of iron from the control amount of iron (2,440 mg/kg) after 24 hrs, showing a similar resistance to dissolution compared to other ICS samples. Above pH 3, dissolution of iron was negligible in all ICS samples over 24 hrs (data not shown). Therefore, ICS could be effectively used in the treatment of arsenic above pH 3 without any significant dissolution of iron.

Batch adsorption

Figure 1 shows adsorption kinetics of As(V) onto ICS-J1 at pH 4.5. Figure 2a and 2b show adsorption kinetics of Pb(II), Cd(II), and Cu(II) onto ICS-J1 at pH 3.5 and 4.5, respectively.

Figure 1 Adsorption kinetics of As(V) onto ICS-J1 at pH 4.5 (1 mg/L As(V), 200 mL-solution/g-ICS, 0.01 M NaNO₃)
As(V) adsorption was completed within 20 minutes, while Pb(II), Cd(II), and Cu(II) adsorption onto ICS was relatively slower than As(V) and strongly depended on initial pH. As a control, when uncoated Joomoonjin sand was tested for the adsorption kinetics of As(V), approximately 20% of initial As(V) was removed within 20 minutes. This result suggests that iron in the control sand also had in some adsorption capacity of As(V). The adsorption kinetics of cationic heavy metals such as Cd(II), Pb(II), and Cu(II) strongly depended on the pH. At pH 3.5, although 50% of initial Pb(II) was adsorbed onto ICS after 12 hours, however, any significant adsorption was not observed with Cu(II) and Cd(II), suggesting higher affinity of Pb(II) to the surface of ICS than that of Cd(II) and Cu(II). In contrast, little discernable difference was observed at pH 4.5 due to rapid adsorption of all three heavy metals. Similar trend of metal affinity has been reported in the adsorption of heavy metals onto hydrous ferric oxide (Stumm and Morgan, 1996) and onto TiO₂ (Vohra and Davis, 1997). As similar at pH 4.5, near complete removal of Cd(II), Pb(II), and Cu(II) was observed above pH 4.5. However, this heavy metal removal was not only contributed by an adsorption process. Above neutral pH, precipitation was identified as an important way to the removal of these cationic heavy metals as shown in Figure 3. Without presence of ICS, each heavy metal (1 mg/L) was quite stable up to pH 6, while soluble fraction of each heavy metal gradually decreased above pH 6 and showed negligible presence of soluble Cu(II) and Pb(II) above pH 9. In contrast, As(V) was not precipitated over all pH ranges.

Figure 4a and 4b show adsorption trends of As(V) onto ICS-J1 with variation of solution pH and As(V) concentration, respectively. Arsenic adsorption followed a typical anionic-type and resulted in complete adsorption of As(V) below pH 7 but a gradual decrease of As(V) adsorption was observed with increase of pH. However, even at pH 12, 90% of initial
As(V) was still adsorbed onto ICS due to forming a strong surface complex between As(V) and Fe(III) on the surface of ICS. Adsorption isotherms of As(V) with variation of As(V) concentration at pH 3.5 and 4.5 are shown in Figure 4b. Adsorbed amount of As(V) onto ICS (q, denoted as mg/kg) was little affected by variation of pH and adsorption isotherm followed Langmuir-type. From the reciprocal plot of q and Ce (equilibrated concentration of As(V) in aqueous phase as mg/L), maximum adsorption amount of As(V) onto ICS (Q, denoted as mg/kg) was identified as 190 mg-As(V)/kg-ICS. This Q value was above two-times greater than that of As(III) (92 mg/kg) obtained with same ICS (Yang et al., 2003). This comparison clearly indicates that ICS has greater capacity in the removal of As(V) than As(III).

Column adsorption

Figure 5 shows As(V) breakthrough results with ICS-J1 (2.4 grams) at pH 4.5 and 9.0 with variation of cumulative pore volume (V/Vo) of effluents. The pore volume with 2.4 gram of ICS (Vo) was 0.74 mL by considering a porosity as 0.45. As(V) breakthrough occurred after 320 V/Vo at pH 4.5 while earlier breakthrough was observed from 65 V/Vo at pH 9.0, matching with the adsorption trend with variation of pH in the batch experiment. As current drinking water standard of arsenic is 50 ppb, column experiments were performed to determine how long ICS column could be used to treat arsenic solution with based on the current standard.

Figure 4a  As(V) Adsorption onto ICS-J1 with variation of pH (1 mg/L As(V), 200 mL-solution/g-ICS, 0.01 M NaNO3)  

Figure 4b  Adsorption Isotherm of As(V) onto ICS-J1 as a function of As(V) concentration at pH 3.5 and 4.5 (200 mL-solution/g-ICS)  

Figure 5  As(V) breakthrough curves at pH 4.5 and 9.0 (1 mg/L As(V), 2.4 g ICS, Q = 0.18 mL/min)
Table 3 shows result for the treatment of As(V) (1 mg/L) with ICS-J1 (2.4 grams) until 50 ppb of As(V) appeared in the effluent at two different pH with flow rate of 0.18 mL/min. ICS showed greater capacity in the treatment of As(V) at pH 4.5 than that at pH 9.0 as similar with batch adsorption results. ICS column could be used to treat As(V) up to 1330 minutes at pH 4.5 which was approximately 5-times longer than at pH 9.0. Up to this time, 99.6 and 20.2 mg of As(V) was treated with ICS-J1 (1 kg) at pH 4.5 and 9, respectively. Also, until the same time, 99.6 and 20.2 L of As(V) solution (1 mg/L) were treated at pH 4.5 and 9, respectively.

In order to determine an optimum amount of ICS-J1 in the treatment of As(V), column experiments were performed with variation of the amounts of ICS at pH 4.5 and at 0.18 mL/min. As shown in Figure 6, treatment efficiency denoted as mg-As(V)/kg-ICS initially not much increased between 2.4 and 3.5 grams of ICS and then greatly increased up to 5.0 grams. The retention time of As(V) solution in the column with 2.4 and 3.5 grams of ICS was approximately 4 and 6 minutes, respectively. By considering adsorption kinetics of As(V) in the batch experiment, these retention times were not considered as efficient times to remove As(V). However, As(V) was efficiently removed with above 5.0 grams of ICS due to having the retention greater than 9 minutes. Therefore the optimum amount of ICS was determined as 5.0 grams at pH 4.5 and 0.18 mL/min with 1.0 cm column in this work.

**Conclusions**

From this research, As(V) adsorption onto ICS followed a Langmuir-type and was not much affected with pH variation while adsorption or removal of cationic heavy metals were much affected by pH variation. Therefore pH was identified an important parameter to remove both As(V) and cationic heavy metals. In the column research, the filtration system consisted with iron-coated sand could effectively used to treat As(V) at pH 4.5 with sufficient retention time approximately match with adsorption kinetics in the batch test.
References