Occurrence of Arsenic in Groundwater in the Suburbs of Beijing and its Removal Using an Iron-Cerium Bimetal Oxide Adsorbent

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The occurrence of arsenic (As) in groundwater in fourteen villages in Houshayu Town, Shunyi District, Beijing, China, was investigated, and a column experiment for the removal of As was conducted on-site with a pellet type iron-cerium (Fe-Ce) bimetal oxide adsorbent prepared in lab. The As concentration in the groundwater of twelve villages exceeds the maximum contamination level (10 µg/L) of the World Health Organization, and two of them exceed that of China (50 µg/L). A column experiment at a space velocity of 3 h⁻¹ shows that the Fe-Ce adsorbent could remove As(V) (total As, 71 ± 19.7 µg/L) from groundwater with high efficiency. Around 11,500 bed volumes were gained when As(V) in the effluent exceeds 10 µg/L, giving an accumulated adsorption capacity of 6.0 mg As(V)/g adsorbent. Both batch tests and the column test suggest that humic substances might compete with As(V) for the adsorption sites, which disappeared after the column was continuously operated for more than two weeks. The effluent quality including heavy metals, radioactivity, etc., was confirmed to meet the drinking water standards of WHO and China.

Key words: arsenic, arsenic removal, groundwater, adsorption, column experiment

Introduction

Arsenic (As) contamination in groundwater has long been a worldwide problem (Jain and Ali 2000; Smedley and Kinniburgh 2002). In mainland China, 40 counties and 1047 villages in 8 provinces including Taiwan, Xinjiang, Inner Mongolia, Shanxi, Ningxia, Jinlin, Qinghai and Anhui, with a population of 2.3 million are reported to be exposed to high As drinking water (Wang 1984; Wang et al. 1997; Guo et al. 2001; Jin et al. 2003; Smedley et al. 2003; Sun 2004; Xia and Liu 2004). The As levels in drinking water in most cases are between 50 and 2000 µg/L (Xia and Liu 2004), and new high As areas continue to be discovered. Though no cases of As poisoning had been found thus far, the highest As level in groundwater was 143 µg/L, with 60,306 people (Jin et al. 2003) being exposed to high As (>50 µg/L) groundwater in 5 villages in the suburbs of Beijing. Since groundwater has long been the main source of water in many suburban areas in China, As contamination is of increasing concern.

The World Health Organization (WHO) recommended a maximum As concentration of 10 µg/L in drinking water in 1993 (WHO 1993). U.S. EPA adopted a new standard on January 22, 2001, and following the standard, public water systems had to comply with the 10 ppb standard beginning on January 23, 2006 (U.S. EPA 2001). The Ministry of Construction, China, also promulgated a new standard for urban water supply with strict criteria for As (10 µg/L) (CJ/T 206-2005) which took effect on June 1, 2005. With the increasing trend of more stringent standards for As concentrations in drinking water, more efforts have been devoted to As removal from groundwater. Among many As removal technologies, the adsorption technique has been considered the most promising for small-scale treatment plants or household systems in suburban areas. A wide range of adsorbents, including natural minerals (Lenoble et al. 2002), synthesized iron and aluminium oxides (Lin and Wu 2001), hydroxides (Thirunavukkarasu et al. 2001; Sperlich et al. 2005), iron-doped or loaded materials (Katsoyiannis and Zouboulis 2002; Zouboulis and Katsoyiannis 2002; Zeng 2003; Kuriakose et al. 2004; Gu et al. 2005), zero-valent iron (Nikolaidis et al. 2003; Su and Puls 2003; Kanel et al. 2005), titanium oxides (Pena et al. 2005), zirconium oxide (Suzuki et al. 2000), rare earth oxides (Tokunaga et al. 1997), carbon and fly ash (Diamadopoulos et al. 1993), etc., have been utilized for As removal. However, most of these materials do not have much value in commercial application either because of their poor performance or high costs. In our

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previous studies, we have successfully developed an iron-cerium (Fe-Ce) bimetal oxide adsorbent, which has an adsorption capacity higher than many of the adsorbents reported (Zhang et al. 2005). The results of studies on the surface properties of the Fe-Ce bimetal oxide demonstrate that As(V) adsorption might be realized through the replacement of the M-OH group of Fe (Fe-OH) with arsenate (Zhang et al. 2005). Preliminary studies on As(V) adsorption performance using groundwater samples from Inner Mongolia show that the adsorbent is a promising one although the performance might be affected by coexisting substances in the groundwater (Zhang et al. 2003b).

This paper includes two sections: (1) investigation of As occurrence in groundwater in a town in the suburbs of Beijing, and (2) As removal tests using the above Fe-Ce adsorbent. Column experimental equipment was constructed by filling the adsorption column with the Fe-Ce adsorbent pellets prepared in lab, and the performance of the equipment for As removal was investigated through continuous operation. The effects of coexisting substances on As removal were investigated in both batch and column experiments. Also, the heavy metal contents and radioactivity of the effluent were inspected to verify the safety of the Fe-Ce adsorbent for drinking water treatment.

Materials and Methods

Materials

All the chemicals used were of analytical grade. As(V) and As(III) stock solutions were prepared by Na3HAsO4·7H2O (Beijing Chemical Reagent Corporation, China) and As2O3 (Merck, Germany), respectively. As-bearing water was prepared by diluting As(V) or As(III) stock solution to given concentrations with deionized water. Fe-Ce bimetal oxide adsorbents were prepared by a coprecipitation method (Zhang et al. 2003a) and then fabricated into pellets with a mean diameter of 1.0 mm using a shaking-dropping method, which is a kind of technology to prepare small-sized pellets using powder. The pellets were prepared at Japan Nuclear Fuel Industries, Ltd.

Batch Tests and Column Experiment for Arsenic Removal

All of the batch and column experiments for As removal were conducted using groundwater from Jixiangzhuang Village, which contains total As concentrations of 71 ± 19.7 µg/L, as shown in Table 1. Excessive sodium hypochlorite was added to the samples to oxidize As(III) to As(V) during the experiments (Lenoble et al. 2003). Anionic ions such as F-, Cl- and PO43- in Jixiangzhuang Village groundwater were analyzed using ion chromatogram (4500i, Dionex Corporation, U.S.A.). Total organic carbon (TOC) was measured using a total organic carbon analyzer (Phoenix, 8000, Tekmar-Dohrmann Corporation, U.S.A.). Fe and Mn were determined by atomic absorption spectrophotometers (Z-6100, Hitachi Corporation, Japan).

Sampling and Analysis

The town of Houshayu, which has 16 administrative villages and about 36,000 villagers, located in Shunyi District, Beijing, near the Beijing Capital International Airport, was selected as the investigation location. The town covers an area of 42.6 km2, and all of the residents use groundwater from wells as drinking water. There are one or two deep wells with a depth of 100 to 120 m in each village. Groundwater from these deep wells is pumped into a pressurized vessel and then distributed to each household via pipelines. From February 2004 to January 2005, three investigations were conducted in Houshayu Town. In each village, three sampling points were selected randomly, and water samples were collected from the tap of each household. Parallel samples were taken at each sampling point. At a sampling site, one sample was immediately acidified following filtration with a 0.45-µm cellulose acetate filter after samples were taken, and then bottled in a polyethylene bottle for total As analysis; the other sample was bottled without acidification for As(III) analysis. After sampling, the samples were transported (about 2 h) to the lab and stored at 4°C as soon as possible. The concentrations of total As and As(III) were obtained on a hydrogen generation atomic fluorescence spectrum (HG-AFS 6100, Beijing Relay Corporation, China), with a method reported by Faouzia et al. (2000) and Shi et al. (2003), respectively. Following this method, the concentration of total As and As(III) was measured first, then the As(V) concentration was obtained by the difference of total As and As(III) (Shi et al. 2003). Anionic ions such as F-, Cl- and PO43- were determined by atomic absorption spectrophotometers (Z-6100, Hitachi Corporation, Japan).
installed in Jixiangzhuang Village, Houshayu Town. The treatment process is shown in Fig. 1. As a pretreatment measure, sodium hypochlorite (3 mg/L) was added for oxidizing As(III), Fe(II) and Mn(II), and the sedimentation and filtration units were used to remove Fe and Mn hydroxides formed after oxidation. After settling for 50 min, water was pumped to the filtration column filled with quartz sand (mean diameter 1.0 mm) in an up-flow mode. Backwash was conducted every 12 h with the settled water. The pretreated water flowed gravitationally to the adsorption column (effective volume, 1 L; inner diameter, 6 cm; packing height, 8.85 cm) packed with the 1.0-mm Fe-Ce adsorbent pellets. The space velocity (SV) was 3 h⁻¹, and backwash was conducted every 6 h with the treated effluent. Heavy metals in the effluent including Cu, Pb, Zn, Co, Be, Cd, Ni, Cr, Fe, Mn, Mg, Mo, B, Al, Be, Ba, Se and Ce were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS, Plasma Quad 3, VG Corporation, U.K.). Heavy metals were analyzed once every week within the first two weeks and then once every three weeks over a long-term period. Radioactivity and other water quality items were determined at the Central Laboratory of the Beijing Water Works Cooperation Group.

Changes of humic substance compositions (Specht et al. 2000; Nagao et al. 2003) in raw and treated groundwater samples were monitored every three days for four weeks and then backwash was conducted every 6 h with the treated effluent. Heavy metals in the effluent including Cu, Pb, Zn, Co, Be, Cd, Ni, Cr, Fe, Mn, Mg, Mo, B, Al, Be, Ba, Se and Ce were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS, Plasma Quad 3, VG Corporation, U.K.). Heavy metals were analyzed once every week within the first two weeks and then once every three weeks over a long-term period. Radioactivity and other water quality items were determined at the Central Laboratory of the Beijing Water Works Cooperation Group.

Results and Discussion

Arsenic Occurrence in Houshayu Town

The average results of three investigations are shown in Fig. 2. It was found that samples from twelve villages contained As higher than 10 µg/L, the maximum contamination level (MCL) of the WHO, and two of them could not meet China’s MCL (50 µg/L). Only two of the 14 samples had As below 10 µg/L (Tiejiang Village and Huoshengying Village). Five samples contain As(III) with a ratio higher than 50%, which was lower than that reported by Kim et al. (2002). The relatively low percentage of As(III) might be caused by the oxidation of As(III) during storage and distribution.

<table>
<thead>
<tr>
<th>Sample sites/parameters</th>
<th>Jixiangzhuang Village</th>
<th>A well of an enterprise in Huoshengying Village</th>
<th>Sample size</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (spot)</td>
<td>7.6 ± 0.2</td>
<td>7.4 ± 0.2</td>
<td>6</td>
</tr>
<tr>
<td>Dissolved oxygen, mg/L</td>
<td>1.4 ± 0.4</td>
<td>0.6 ± 0.4</td>
<td>6</td>
</tr>
<tr>
<td>Total arsenic, µg/L</td>
<td>71 ± 19.7</td>
<td>154 ± 14</td>
<td>6</td>
</tr>
<tr>
<td>Arsenite, µg/L</td>
<td>20 ± 13.9</td>
<td>85 ± 23</td>
<td>6</td>
</tr>
<tr>
<td>Total iron, mg/L</td>
<td>0.7 ± 0.4</td>
<td>1.65 ± 0.5</td>
<td>6</td>
</tr>
<tr>
<td>Manganese, mg/L</td>
<td>1.34 ± 0.81</td>
<td>2.01 ± 1.2</td>
<td>6</td>
</tr>
<tr>
<td>Sulfate, mg/L</td>
<td>0.43 ± 0.2</td>
<td>0.06 ± 0.4</td>
<td>6</td>
</tr>
<tr>
<td>Nitrate, mg/L</td>
<td>0.06 ± 0.3</td>
<td>0.02 ± 0.2</td>
<td>6</td>
</tr>
<tr>
<td>Phosphate, mg/L</td>
<td>0.015 ± 0.1</td>
<td>0.01 ± 0.05</td>
<td>6</td>
</tr>
<tr>
<td>Fluoride, mg/L</td>
<td>0.12 ± 0.07</td>
<td>0.06 ± 0.02</td>
<td>6</td>
</tr>
<tr>
<td>Total organic carbon, mg/L</td>
<td>1.71 ± 0.6</td>
<td>1.58 ± 0.6</td>
<td>6</td>
</tr>
</tbody>
</table>

Fig. 1. Treatment process of column experiment. Effective volume, sampling frequency, removal ratio are provided for each unit.
The highest As concentration (169 µg/L) was found from a well of an enterprise located in Huoshenying Village (Table 1). The low concentrations of nitrate and sulfate in combination with high concentrations of Fe and Mn suggest that the groundwater was in a reducing environment (Smedley and Kinniburgh 2002; Kim et al. 2002; Anawar et al. 2003). The redox potentials were between 0 and 117 mV (average = 62 mV, median = 53 mV). It is interesting that very low total As concentration (below 10 µg/L) was found in the well (110 m in depth) of Huoshenying, which was only 500 m away from the well (120 m in depth) of the enterprise. Jin et al. (2003) also reported that the As concentration in one well was 1000 µg/L while that in another neighbouring well was lower than 50 µg/L in some villages in Inner Mongolia, China.

According to Xia and Liu (2004), the As levels in most of the groundwater in mainland China are between 50 and 2000 µg/L. The highest As level in certain suburbs of Beijing was reported to be 143 µg/L (Jin et al. 2003), which is consistent with our results. The well depth is one of the reasons for different As concentrations in China. It has been reported that in China, a significant number of wells with depths from 10 to 24 m were found to have As concentrations of more than 50 µg/L (Xia and Liu 2004). In this study, the well depths were more than 100 to 120 m, and the As levels were around 0 to 160 µg/L. However, no cases of As poisoning have been found so far.

### Batch Experiment

Spiked pretreated groundwater was compared with spiked pure deionized water at two initial As(V) levels (150 and 1000 µg/L) to evaluate the effects of coexisting components on the removal efficiency of Fe-Ce adsorbent. The results are shown in Fig. 3A and 3B. It was found that the adsorption of As(V) in groundwater was not as good as that in the deionized sample at the initial As(V) level of 150 µg/L. However, the adsorption capacities of As(V) for both the deionized system and actual groundwater system were almost the same at an initial As(V) level of 1000 µg/L. The Langmuir maximum adsorption capacity for the deionized system and actual groundwater system was 52.36 and 53.76 mg As(V)/g adsorbent, respectively, at the initial As(V) level of 1000 µg/L (Fig. 3B). Previous studies (Zhang et al. 2003b) have indicated that common coexisting ions such as Na+, Ca2+, Mg2+, Cl-, NO3- and SO42- do not affect the adsorption efficiency of Fe-Ce adsorbent. PO43-, F- and humic substances have been confirmed to inhibit As adsorption on the Fe-Ce adsorbent (Zhang et al. 2003b). The PO43- and F concentrations in this study were not high enough to affect adsorption performance. Humic substances are present in most natural waters at concentrations of 0.1 to 200 mg C/L (Kinniburgh et al. 1996),
typically found at concentrations between 1 and 50 mg C/L, and its potential influences on arsenic sorption and mobility are great (Redman et al. 2002). It was reported previously that 6 to 21% adsorbed As(V) was released from hematite surface by 10 mg C/L humic substances (Redman et al. 2002). Humic substances in the groundwater samples were characterized by TOC values of 2.0 to 2.3 mg/L. A possible factor affecting the removal of As at the initial As(V) level of 150 µg/L might be humic substances, which was verified by HPSEC analysis in the first two weeks of column experiments, as described in the following section.

Our previous studies demonstrated that metal hydroxyl groups (M-OH) play an important role in As removal by Fe-Ce adsorbent (Zhang et al. 2005). As(V) removal might be realized through the replacement of the M-OH groups on Fe-Ce adsorbent with arsenate. The negative effect of humic substances on As adsorption could be partly explained by competitive adsorption of humic substance on active adsorption sites.

Column Experiment

The Fe-Ce adsorbent pellets (mean diameter, 1.0 mm) were successfully prepared using the shaking-dropping method, and the prepared pellets were applied for As removal from groundwater of Jixiangzhuang Village. The column experiment was conducted from June 18, 2004, to December 10, 2005, and the results of the column experiment are shown in Fig. 4. During the experimental period, the total As in raw groundwater was 71 ± 19.7 µg/L. A small ratio of As was removed by the filtration unit. The groundwater was found to contain 0.05 to 1.07 mg/L of Fe, and 0.1 to 2.05 mg/L of Mn. Fe and Mn hydroxides were formed in the oxidation process and then deposited on the filter surface. The Fe and Mn hydroxides are widely reported with a strong affinity to arsenic (Lin and Wu 2001; Thirunavukkarasu et al. 2001; Sperlich et al. 2005). Their contribution to arsenic removal in this study, however, was not so significant because of the low contents of these metals. Most of the As(V) was removed by the Fe-Ce adsorbent pellets in the adsorption unit. Under the SV of 3 h⁻¹, the As(V) in effluent was controlled at lower than 10 µg/L for around 150 d and 11,500 bed volumes. The cumulative adsorption amount of As(V) was 6.0 mg/g media at the breaking point [effluent As(V) = 10 µg/L], which was higher than a test using zero-valent iron (4.4 mg As/g media) under a SV of 1.225 h⁻¹ (Nikolaidis et al. 2003). Several other adsorbents, such as hydrated ferric oxide, iron coated materials, etc., have also been successfully applied to the As removal (Thirunavukkarasu et al. 2001; Sperlich et al. 2005). These iron-based adsorbents are cheaper than the Fe-Ce adsorbent because the price of cerium is about 5 to 10 times that of iron. However, these adsorbents generally have a low adsorption capacity or slow kinetics (Daus et al. 2004). Further, the Fe-Ce adsorbent can be used repeatedly, which will reduce operation costs.

Water samples taken from column experiments were analyzed by HPSEC to evaluate the effect of humic substances on As removal. Separation in HPSEC is based on differential permeation of molecules of various sizes into a porous gel pores matrix. The largest molecules, which cannot penetrate into the gel pores, are eluted first, while the smallest molecules are intercepted and stay longer in the porous gel pores, then exit the column last (Potschka 1993). Analysis of humic substances by HPSEC is shown in Fig. 5A and 5B. It was found that the largest molecule fraction, which was eluted at 9.0 min, had the highest peak area, followed by peaks at 10.5, 10.8, 11.3 and 12.4 min, and the latest peak at 13.8 min.

In the beginning of the column experiment (within two weeks), large molecular size fractions were partly removed through adsorption by Fe-Ce adsorbent pellets. After two weeks of operation, the removal of humic substances through adsorption by the adsorbent could not be identified, indicating that the inhibiting effect of humic substances could be neglected after this length of time. The column maintained effective As(V) removal for more than 4 months, so it is speculated that the inhibition effect of humic substances should not be a serious problem for As(V) removal from groundwater.

During the column experiment, the pH increased from 7.8 ± 0.2 in filtrated water to 8.0 ± 0.1 in effluent, indicating that the Fe-Ce adsorbent could be successfully used in near neutral or alkalescent groundwater. Since the rare earth element Ce was used in the Fe-Ce adsorbent, heavy metals and radioactivity in the effluent were monitored to ensure the safety of drinking water. The results demonstrated that the metal levels were under the MCL of WHO and China for drinking water. Radioactivity analysis of effluent showed that the alpha and beta

![Fig. 4. Arsenic removal from groundwater in column experiment.](image-url)
Gross activities were 0.032 and 0.086 Bq/L, respectively, which were well below the proposed limit values of WHO and China (0.1 and 1.0 Bq/L). The results indicated that the treated water was safe in terms of heavy metals and radioactivity, and determination of heavy metals is not necessary for actual uses.

**Conclusion**

Groundwater samples in 12 of the 14 villages in Houshayu Town, Shunyi District, Beijing, China, contained As levels exceeding the MCL of WHO and the standard of the Ministry of Construction, China, which requires serious consideration. Column experimental results demonstrate that the Fe-Ce adsorbent pellets could be effectively used for the removal of As(V) from groundwater in Jixiangzhuan Village. The existence of humic substances did not affect the As(V) adsorption performance significantly. The heavy metals and radioactivity in the effluent complied with the MCL of WHO and China. The regeneration and reuse of the used Fe-Ce adsorbent, however, requires further study.

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**References**


