



## Novel Fe/glass composite adsorbent for As(V) removal

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Received 23 April 2008; revised 24 June 2008; accepted 04 September 2008

### Abstract

An effective adsorbent for arsenic removal was synthesized by hydrothermal treatment of waste glass powder (GP), followed by loading Fe(III) oxyhydroxide onto the surface of waste glass powder. The  $\equiv\text{Si}-\text{O}-\text{H}$  group was formed on the surface of GP and the specific surface area of GP powder was slightly increased after hydrothermal treatment. FeOOH was loaded onto the surface of hydrothermally treated waste glass powder (HGP) by the hydrolysis of  $\text{FeCl}_3$ . The formation conditions of FeOOH were also investigated. The ability of this new adsorbent for arsenic (As(V)) removal was evaluated. The results indicated that the highest removal efficiency was about 97% for 1 mg/L As(V) solution at pH 6 and keeping time 2 h.

**Key words:** arsenic removal; adsorbent; iron oxide; hydrothermal treatment

**DOI:** 10.1016/S1001-0742(08)62288-3

### Introduction

Arsenic contamination in aqueous system, which resulted in human poisoning and death, is a global problem. Recent reports from Taiwan (Tseng *et al.*, 1968; Chen *et al.*, 1994), Chile (Borgono *et al.*, 1977), China (Zhang and Chen, 1997), Bangladesh (Nickson *et al.*, 2000), Vietnam (Berg *et al.*, 2001), India (Jiang, 2001; Dixit and Hering, 2003) and the western United States (Roberts *et al.*, 2004) indicated that many of the natural water resource have been contaminated by arsenic. Therefore, the arsenic concentration of 0.01 mg/L has been recommended by World Health Organization (WHO, 1996) as a guideline for drinking water. This level was also adopted by some industrialized countries (EPA, 2001). In China, the maximum arsenic level of 0.05 mg/L has been permitted in groundwater supplies for drinking purposes (GB/T14848-93). To meet such a low permit level, it is required developing a effective novel technology for arsenic contaminated drinking water at a reasonable cost.

Arsenic exists in natural water system as well as in the industrial wastewater as the major form of inorganic species. In natural water, the arsenate (As(V)) is dominant in surface water, while arsenite (As(III)) in the groundwater. Since  $\text{As}_2\text{O}_3$  is widely used, such as pesticides, the glass industry, and the copper refining industry (Saha *et al.*, 1999; Ferguson and Gavis, 1972). As(III) is expected to be the main form of arsenic pollutant and is known to be

more toxic, mobile, and difficult to be removed than As(V) (Stronach *et al.*, 1997; Zhang and Itoh, 2005). Therefore, for common methods As(III) is always be oxidized before removing (Zaw and Emmett, 2002).

Many technologies such as coagulation (Gregor, 2001), ion exchange, and adsorption (Ghurye *et al.*, 1999) have been employed for arsenic removal. The adsorption technique is becoming more popular because of its simplicity, potential of regeneration, and low cost. It is reported that iron oxides including oxyhydroxides and hydroxides, such as amorphous hydrous ferric oxide (FeOOH), goethite ( $\alpha\text{-FeOOH}$ ) and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), are promising effective adsorbents for As(III) and As(V) removal (Ferguson and Gavis, 1972; Piece and Moore, 1982; Cornell and Schwertmann, 1996; Reed *et al.*, 2000; Altundogan *et al.*, 2000). Among these iron compounds, FeOOH has the highest adsorption capability due to its large surface area. However, FeOOH available as a fine powder is difficult to be separated from aqueous solution after the adsorption process. In addition, amorphous FeOOH is easy to transform into crystalline iron oxides during the preparation process, resulting in a decrease of its surface area and removal capacity for arsenic. To solve these problems, many researchers attempted to load the iron oxide on the sand surface (USEPA, 1999; Thirunavukkarasu *et al.*, 2003) and load amorphous FeOOH on the surface of municipal solid waste melted slag (Zhang and Itoh, 2005).

In the present study, we developed a technology to prepare adsorbent for As removal from contaminated water,

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which involves two steps: hydrothermal treatment of glass powders and the loading of FeOOH on HGP via chemical processes.

## 1 Materials and methods

### 1.1 Materials

The  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and NaOH powder (analytical grade, Wako Pure Chemical Industries, Ltd., Japan) were used to prepare  $\text{FeCl}_3$  and NaOH solution, respectively. Arsenic-containing solution with an As(V) concentration of 1 mg/L was prepared from the standard As(V) solution (Wako Pure Chemical Industries, Ltd., Japan).

A commercially available glass powder (GP) produced by used glass bottles, was purchased from Toyo System Plant Co., Ltd., Japan. In this work, the glass powder with the particle size of 250–350  $\mu\text{m}$  was used to prepare adsorbent.

### 1.2 Hydrothermal treatment of glass powder

A mixture of the raw GP (15 g) and the distilled water (30 mL) was transferred into a Teflon container with 40% volume filling, and then sealed by a stainless steel autoclave. The autoclave was put into an oven for heating and hydrothermal reaction was conducted at 180°C for 2 h. Hydrothermally treated waste glass powder (HGP) and the raw GP were observed by scanning electron microscopy (SEM S530, Hitachi, Japan). Nitrogen adsorption behavior of the adsorbent was measured using a NOVA 1200 (Quanta Chromo, USA), and the specific surface area of the adsorbent was calculated based on the BET model.

### 1.3 Formation of $\beta\text{-FeOOH}$

The formations of  $\beta\text{-FeOOH}$  were carried out in a water bath (70°C, 2 h) by the hydrolysis of  $\text{FeCl}_3$  solution with the addition of HGP. The effects of solution pH, solution concentration, treating temperature, and time on arsenic removal were examined to determine the optimum conditions for preparing effective arsenic adsorbents. For each 1 g powder sample, 1, 2, 5, 10 mL  $\text{FeCl}_3$  solution with the concentrations of 0.01, 0.1, 0.5 and 1 mol/L was added, respectively, and treated at 70°C for 2 h in the water bath. After cooling, filtering and drying at the room temperature in vacuum, the Fe(III) oxyhydroxide-loaded glass powder (IGP) was obtained, which was used as an adsorbent for arsenic removal in this study.

The amount of the loaded iron on the IGP was also determined by inductively coupled plasma (ICP) spectrometry (SPS7000A, Seiko, Japan). Sample powder 0.5 g was dissolved in 30 mL 6 mol/L HCl with an ultrasonic stirring for 10 min.

The hydrolyzed productions were identified by powder X-ray diffraction (XRD, RTP-300RC, Rigaku Co., Japan) with  $\text{Cu } K_\alpha$  radiation (40 kV and 100 mA). The surface of the IGP was observed by SEM.

### 1.4 Arsenic removal test

The synthesized adsorbent IGP 1 g was putted into the 10 mL 1 mg/L As(V) standard solution and reacted

at different pH. Then treated at different temperatures for different time in a water bath incubator. The arsenic concentration was determined by atomic absorption spectrometry (AAAnalyst200, Perkin-Elmer, Japan). The arsenic removal efficiency ( $R$ ) was calculated using the following Eq. (1):

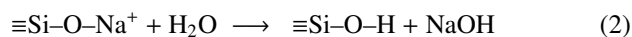
$$R = \frac{C_{\text{Asb}} - C_{\text{Asa}}}{C_{\text{Asb}}} \times 100\% \quad (1)$$

where,  $C_{\text{Asa}}$ ,  $C_{\text{Asb}}$  are the arsenic concentration after and before the adsorption through the synthesized adsorbent.

## 2 Results and discussion

### 2.1 Hydrothermal treatment of glass powder

In this work, GP was hydrothermally treated at 180°C for 2 h according to a previous work (Yanagisawa *et al.*, 2006) and used as adsorbent after loading Fe compounds through the hydrolysis of  $\text{FeCl}_3$  solution. Figure 1 shows XRD patterns of the original glass powder and HGP. A broad peak, ranging from 10° to 40°, indicates GP amorphous property. After hydrothermal treatment, the powder still mainly consisted of amorphous materials. It is supposed that  $\text{Na}^+$  were dissolved under hydrothermal condition by the following Reaction (2).



The  $\equiv\text{Si-O-H}$  group was formed on the surface of the glass powder.

Figure 2 shows SEM micrographs GP and HGP surfaces. After the hydrothermal treatment, the morphology of the GP surface was changed greatly. It was getting rough. Many fine flocky bulges were formed on the GP surface, which might be crystalline calcium silicate and sodium silicate. The change of glass powder surface resulted in the variation of specific surface area of GP. It was checked by BET. The results showed that the specific surface areas for GP, HGP, and IGP were 1.04, 1.24, and 40.59  $\text{m}^2/\text{g}$ , respectively.

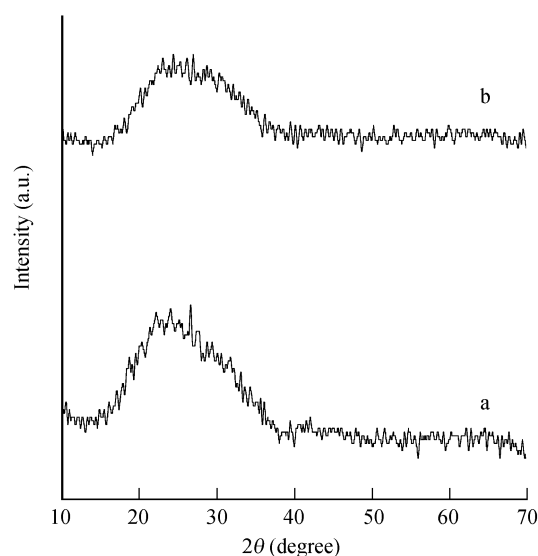
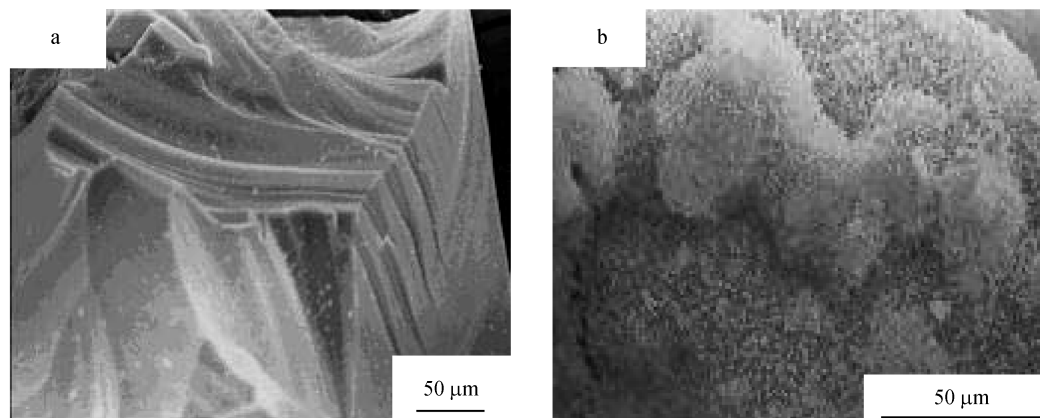


Fig. 1 X-ray diffraction (XRD) patterns of the used glass powder (a) and hydrothermally treated glass powder (b) at 180°C for 12 h.



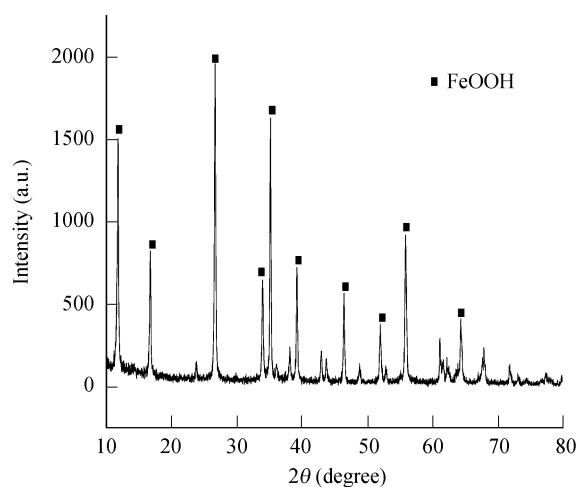
**Fig. 2** SEM micrographs of glass powder (GP) (a) and hydrothermally treated glass powder (HGP) (b) surface at 180°C for 12 h.

## 2.2 Optimization of $\beta$ -FeOOH formation

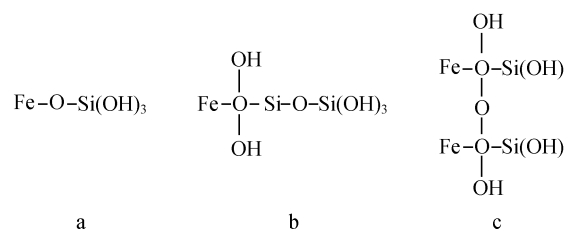
The pH effect of  $\text{FeCl}_3$  solution on the  $\beta$ -FeOOH formation on the surface of HGP was investigated firstly. One gram HGP was added to the  $\text{FeCl}_3$  solution with different concentrations. The original pH of the glass powder containing solution was adjusted with NaOH solution to be in a range of 1.5–9.3. After treatment at 70°C for 2 h in the water bath, the pH value decreased due to the hydrolysis of the  $\text{Fe}^{3+}$ . The yellow precipitant could be formed on the surface of GP in the  $\text{FeCl}_3$  solution with original pH range 1.5–2.4. In contrast, there are nothing on the surface of GP in the  $\text{FeCl}_3$  solution with original pH range 2.5–7. The fulvous precipitant could be formed on the surface of GP in the  $\text{FeCl}_3$  solution with original pH range 8–9.3. The result shows that it is no effective when the fulvous precipitant was used for As adsorption.

Under optimum condition, 10 mL  $\text{FeCl}_3$  solution 0.1 mol/L (pH 2) was treated at 70°C for 2 h without addition of HGP, which resulted in the formation of the yellow precipitant. The phase of the yellow precipitant was identified by XRD (Fig. 3) to be pure  $\beta$ -FeOOH (JCPDS 34-1266). Thus, the loaded Fe compounds must be  $\beta$ -FeOOH. It has been reported when  $\text{Si}(\text{OH})_4$  contacts with FeOOH, polymerization of silicic acid on FeOOH likely occurs to form silicatoiron (III) surface complexes between Si and Fe typically in the form of  $\text{Fe}-\text{O}-\text{Si}(\text{OH})_3$  (Swedlund and Webster, 1999). The schematic bonding between  $\text{Si}(\text{OH})_4$  and FeOOH is shown in Fig. 4.

It is known that Fe(III) salt solution is strongly acidic. If Fe(III) salt solution, for example,  $\text{FeCl}_3$ , is mixed with the mixture of  $\text{Na}_2\text{SiO}_3$  and NaOH, the above Reaction (2) should occur simultaneously. The main components of IGP are  $\text{Si}(\text{OH})_4$ ,  $\text{Na}_2\text{SiO}_3$ ,  $\text{Ca}_2\text{SiO}_3$  and FeOOH, and Fe-Si complexes are formed easily. The complexation between Fe and Si enhances the binding of FeOOH and hence increases the physical strength of the adsorbents produced. Since the crystallization of iron oxides, for instance, the transformation of ferrihydrite to goethite, is strongly inhibited by the presence of silicate species, the FeOOH formed through co-precipitation with silicate should be in an amorphous (or poorly crystalline) form. However, the quantity of GP to be added in the adsorbent should be determined in the balance of two factors: strength of



**Fig. 3** XRD pattern of the yellow precipitate formed after the hydrolysis of the 0.1 mol/L  $\text{FeCl}_3$  at 70°C for 2 h in the bath water incubator.



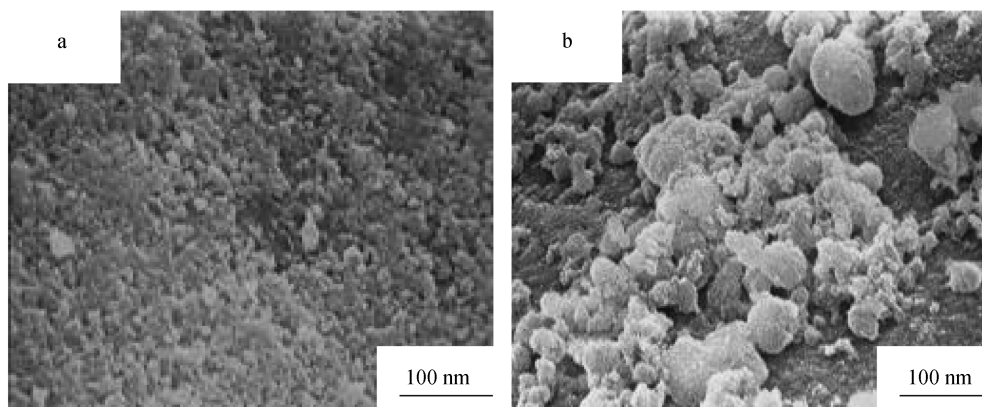
**Fig. 4** Schematic bonding between  $\text{Si}(\text{OH})_4$  and FeOOH. (a) bonding with  $\text{Si}(\text{OH})_4$  monomer; (b) polymerization; (c) siloxane linkage between  $\text{Si}(\text{OH})_4$  monomers.

the adsorbent (resistance to disintegration) and adsorption capacity for any designated species, such as arsenic. In this work,  $\equiv\text{Si}-\text{O}-\text{H}$  group was formed on the surface of HGP, which enhanced the combination between FeOOH and the surface of GP.

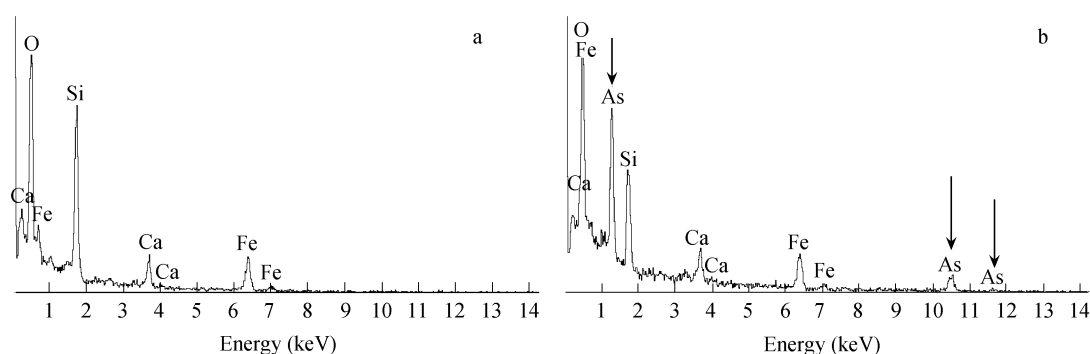
Figure 5 shows the SEM micrographs of HGP and IGP surface. It was found that the white particles with the size of about 50 nm were formed on the surface of HGP after the iron oxyhydroxid-loading (Fig. 5b). The white particle should be  $\beta$ -FeOOH precipitant according to the result of Fig. 3.

## 2.3 Arsenic adsorption

The initial arsenic concentrations of 100, 10, and 1 mg/L were used for arsenic removal efficiency test. The arsenic



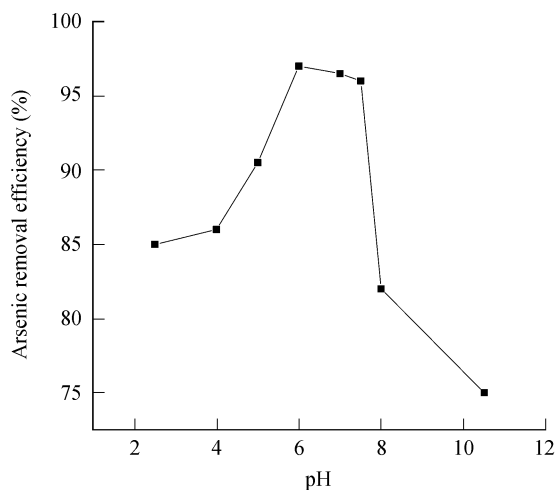
**Fig. 5** SEM micrographs of the surface of HGP at 180°C for 12 h (a) and Fe(III) oxyhydroxide-loaded glass powder (IGP) (b).



**Fig. 6** X-ray photoelectron spectrometer (XPS) analysis of IGP before (a) and after arsenic removal (b).

removal capacity increased linearly with the increase of arsenic concentration, but the removal efficiency decreased. Moreover, the arsenic concentration of groundwater is less than 1 mg/L. Therefore, arsenic concentration 1 mg/L was set for adsorption test with IGP as adsorbent (data not shown).

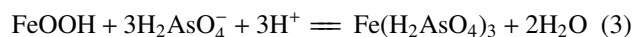
Figure 6 shows X-ray photoelectron spectrometer (XPS) analysis of IGP before and after arsenic removal. The XPS spectrum of the IGP after arsenic removal clearly indicates the presence of peaks originating from elemental As. Figure 7 shows the variation of arsenic removal efficiency



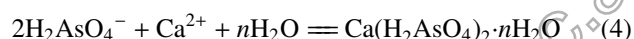
**Fig. 7** Arsenic removal efficiency on the adsorbent in 1 mg/L As(V) standard solution with different pH values. Adsorbent amount 1 g; keeping time 2 h; temperature 40°C.

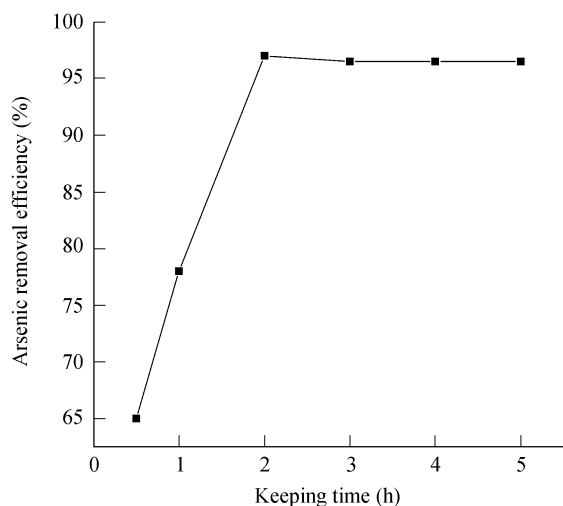
on the adsorbent in 1 mg/L As(V) standard solution with different pH values. The optimum pH for As(V) removal was 6.0. The highest arsenic removal efficiency was about 97%. It indicates that the concentration of As(V) after adsorption is about 0.03 mg/L, which is near to the level (0.01 mg/L) recommended by WHO (1996) as a guideline for drinking water. In addition, a maximum arsenic level of 0.05 mg/L has been permitted in groundwater supplying for drinking water according to GB/T14848-93 in China. It is a great advantage that IGP could be operated at a neutral pH without sacrificing the adsorption capacity.

Arsenic removal by the IGP is supposed to be mainly through: (1) affinity adsorption; (2) reaction with iron oxides; (3) reaction with calcium and other metallic elements initially contained in GP. Affinity adsorption relates to the surface area of IGP while chemical reactions relate to the existing forms of arsenic species. The dominance species of arsenic in aqueous solution correlate closely with the solution pH. For As(V), the corresponding stable species and pH values are:  $\text{H}_3\text{AsO}_4$  (pH 0–2),  $\text{H}_2\text{AsO}_4^-$  (pH 2–7),  $\text{HAsO}_4^{2-}$  (pH 7–12) and  $\text{AsO}_4^{3-}$  (pH 12–14) (Bard *et al.*, 1985). In this work, As(V) may be removed through the following Reaction (3) since  $\text{H}_2\text{AsO}_4^-$  is predominant:



On the other hand, calcium and other metallic elements are supposed to be also effective for As(V) removal in terms of the following Reaction (4) (Bothe and Brown, 1999):





**Fig. 8** Arsenic removal efficiency on the adsorbent in 1 mg/L As(V) standard solution under different keeping time. Adsorbent amount 1g; pH 6.0; temperature 40°C.

Figure 8 shows that the variation of arsenic removal efficiency on the adsorbent in the 1 mg/L As(V) standard solution at pH 6, 40°C for different time. The removal of arsenic increased sharply and reach 97% in the first 2 h, and then slowed down. The results indicate that IGP is effective adsorbent for As(V) removal.

After arsenic removal test, the iron amount dissolved in the solution was 0.06 mg/L. It indicates that Fe is very difficult to be desquamated from the IGP, and this does not affect the quality of water according to Quality Standard of Drinking Water (GB5749-2006).

### 3 Conclusions

A method for preparing the adsorbent for As(V) removal has been developed by loading iron oxide onto the HGP. The adsorbent was prepared by adding 1 g HGP into 10 mL 0.1mol/L FeCl<sub>3</sub> solution, and treated at 70°C for 2 h in the water bath. The adsorbent was effective for As(V) removal. The optimum removal conditions are pH 6 and adsorption-time 2 h. The highest arsenic removal efficiency is about 97%. It indicates that the concentration of As(V) after adsorption is about 0.03 mg/L. It is believed that IGP developed in this study is environmentally acceptable and industrially applicable for wastewater treatment.

#### Acknowledgments

This work was supported by the National Science and Technology Pillar Program in the Eleventh Five-Year Plan Period (No. 2006BAF02A28) and the Science Research Fund of ShaanXi University of Science and Technology (No. ZX07-14).

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