1. Introduction

In Asia, arsenic contamination of groundwater is seen in the basins of the great rivers, originating in the Himalayan Mountains and the Tibetan Plateau, such as the Ganges River, the Indus River, the Mekong River, the Haw River, and the Yellow River, where people depend on the drinking water for ground water. A thermally altered metamorphic zone in the Higher Himalaya, containing various types of minerals, is considered as the source of arsenic. The arsenic contained in the minerals has caused ground water pollution. Arsenic containing ground water causes carcinogen and cancers of skin, liver, lungs and other internal organs.

Removal technologies of arsenic from water typically rely on adsorption or filtration. Methods such as coagulation with ferric sulphate, lime softening, activated alumina, ion exchangers, reverse osmosis, electrodialysis, and nanofiltration have been tested with various degrees of success. Research is also being done on combination treatments with coagulation and filtration. Presently, the major challenge is to design suitable filtration matrix with or without surface modifications for removal of air/water contaminants. Most of the adsorbent available at present in the market are specific according to their applications, so there is no generalized filtration aids available which can cover a broad range of applications and can be at the same time cost effective. Limitations also exist in these adsorbent with respect to their ap-
propriate chemistry and physical properties which otherwise could have made them applicable for general use. Adsorbents for the removal of arsenic are almost invariably based on bulk or supported particles of transition metal oxides and hydroxides. The preferred transition metals used in adsorbents are Fe, Zr, Ce, Mn and Ti. Iron oxide compounds are commonly used in high throughput applications because of the low cost of fabrication of the adsorbente. The crystal structure and size of the particles of iron oxides have been reported to affect to the adsorption properties of arsenic from aqueous media. It is important to control content, structure and size of particles of iron oxides to develop effective adsorbent for arsenic.

The cryogel can be a suitable choice for efficient and cost effective water filtration aid for heavy metal, microbial and other toxin removals. Cryogels are hydrogels which are synthesized at sub-zero temperatures and have supermacroporous structure with interconnected pores, thus offering a unique combination of high interconnected porosity with high mechanical strength. The composite material of solid micro/nano-particles and cryogels is expected to develop a new adsorbent and filter. Cryogel polymer composite adsorbents embedded metal oxides particles have been reported and expected to be effective adsorbent used for treatment of arsenic contaminated water. Furthermore, the synthesis of solid particles in gel matrixes can control their crystal structure and size. In this work, polyacrylamide (PAA) cryogels containing iron hydroxide oxide particles was prepared by an in situ particle formation method that prepare the particles directly in the wall of cryogel. The effects of the preparation condition on the structures of the PAA cryogels and iron oxide particles, and adsorption property of As(V) from aqueous solution with the cryogels were investigated.

2. Experimental method

2.1. Reagents

Monomeric Acrylamide (AAm), N,N-Methylenbis(acylamide) (MBAAm), ammonium peroxodisulfate (APS), N,N,N′,N′-Tetramethyl ethylene diamine (TEMED), iron (III) chloride hexahydrate, sodium hydroxide, and sodium carbonate was purchased from Wako Pure Chemicals Co. Standard solution of As(V) was obtained from National Institute of Advanced Industrial Science and Technology (AIST). Sulfuric acid and hydrogen peroxide of high purity grade for metal analyses was purchased from Wako Pure Chemicals Co. and used for pyrolysis of the cryogels.

2.2. Preparation of PAA cryogel

The preparation flow and condition of PAA cryogel is shown Fig. 1. The monomers of 4.0 wt% of acrylamide (AAm) and cross-linker 1.0 wt% of N,N-Methylenbis(acylamide) (MBAAm) were dissolved in degassed water with vigorous stirring and cooled to about 0°C for 1.0 hour. Then 0.5 wt% of ammonium peroxodisulfate (APS) was dissolved in 1.0 ml of degassed water, and the solution was added the monomers solution and cooled for 30 minutes. After that, 0.12 wt% of N,N,N′,N′-Tetramethyl ethylene diamine (TEMED) were quickly added to the solution while stirring. About 5 ml of the mixture solution was poured into 6 ml syringe. These syringes were sealed and immersed in ethanol in a program controlled refrigerated bath and frozen at −15°C for 24 hours. Finally, they were thawed out in warm bath and washed with distilled water.

2.3. Preparation of cryogels containing iron hydroxide oxide particles

The PAA cryogels prepared were washed with degassed water until pH = 7. And, they were squeezed by pushing by a plunger in syringe. Then, they were immersed in an iron (III) chloride solution (FeCl3) and shaken for over night. FeCl3 solution was penetrated into the cryogel wall. After that, they were squeezed by pushing by a plunger in the syringe again. Fe3+ ion was remained and kept in the cryogel wall. Then, they were immersed in an alkaline aqueous solution and shaken for 30 min. The alkaline aqueous solution was penetrated into the cryogel wall and iron hydroxide oxide particles formed in the cryogel.
After formation of the particles, the cryogels containing the particles were washed repeatedly until no particles were flowed out from the gel. The cryogels prepared were lyophilized for the observation and the analyses. The preparation conditions of iron hydroxide oxide particles in the cryogel wall are shown in Table 1. On the other hand, in order to compare with the powder of iron oxide, the precipitates of iron hydroxide oxide were prepared by mixing FeCl₃ aqueous solution and Na₂CO₃ aqueous solution. The precipitates were washed with distilled water and dried in air.

2.4. Observation and analysis of the cryogels

The morphologies of the cryogels lyophilized were observed using a scanning electron microscopy (SEM, TM-1000 and SU-3500, Hitachi). Their internal structure was examined by cross-sectioning the cryogels. In order to analyze the distribution of Fe and As elements in the cryogel, energy dispersive X-ray spectrometry (EDX) analysis was also carried out in mapping mode with SU-3500. The qualitative analysis of the particles formed in the cryogel wall were carried out on a X-ray diffractometer (XRD, X’Pert PRO, PANalytical) with a Cu Kα irradiation source (l = 1.5405 Å) at 40 kV and 50 mA at a continuous scan between 10° and 70° 2θ.

2.5. Adsorption of arsenic with the cryogels containing iron hydroxide oxide particles

The arsenic adsorption experiment was conducted with the batch method. The PAA cryogel containing iron hydroxide oxide particles was put into the sample tube, the aqueous solution containing As(V) was added, and it was shaken for 48 hours. Then, solution and cryogel were separated and the concentration of arsenic in the solution was measured by ICP-AES (Shimadzu, ICPS-8100). The adsorption amounts of As(V) on the adsorbents were calculated based on the lyophilized weight of them (mg/g-dry). The original PAA cryogel has no ability to adsorb As(V) which checked in advance.

2.6. Measurement of iron content in the cryogels

The cryogel lyophilized was pyrolyzed in quartz volumetric flask (100 ml) using H₂SO₄ and H₂O₂ using Digesdahl digestion system (Model 23130-20, Hach) at 440°C until clear solution was obtained. The solution digested was cooled and diluted to 100 ml. The iron concentration in the decomposed solution was measured by ICP-AES, and the content of iron in 1.0 g of the lyophilized cryogel was calculated.

3. Results and Discussion

3.1. Preparation of the cryogels containing iron hydroxide oxide particles

3.1.1. Morphologies of the cryogels

The cryogels obtained from freezing bath were translucent milky white before the particle formation in the cryogel wall. After the particles formation, the color of the cryogels was changed to reddish brown that is due to iron hydroxide oxide particles. Photographs of the external appearance and the cross-section of the cryogels containing iron oxide particles are shown in Fig. 2. Although the color of outer surface of the cryogels was even (Fig. 2(a) and (b)), that of the cross-section was uneven and dark at the concentric center of the cross section (Fig. 2(c)). It is considered that the heterogeneous structure of the cryogel was formed at the center part during freezing and polymerization steps and/or iron oxides particles were heterogeneously formed and precipitated due to unevenness of the concentration of iron or hydroxide ions in the inside of the cryogel.

SEM images of the cryogels containing iron oxide hydroxide particles were shown in Fig. 3. The cryogels have super macroporous structure with large inter-connected pores. Fine particles observed as white particles in SEM images are iron hydroxide oxide particles formed in the large pores of the cryogels. These fine particles would be formed from the FeCl₃ solution remained in pores of the cryogel after squeezing. SEM image of the inside pore surface of the cryogel used after

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Table 1 Preparation conditions of the PAA cryogels containing iron hydroxide oxide particles

| Adsorbent | [FeCl₃] [mol/l] | Alkali | [alkali] [mol/l] |
|-----------|----------------|--------|-----------------|
| Gel a     | 1.0            | Na₂CO₃ | 1.0             |
| Gel b     | 1.0            | Na₂CO₃ | 0.50            |
| Gel c     | 1.0            | NaOH   | 0.50            |
| Gel d     | 0.50           | Na₂CO₃ | 1.0             |
| Gel e     | 0.50           | Na₂CO₃ | 0.50            |

Fig. 2 Photographs of the cryogels containing iron hydroxide oxide particles. (a) External appearance of Gel a, (b) External appearance of Gel c, (c) Cross sectioning view of Gel a.
the cryogel prepared by Na₂CO₃ aqueous solution contained larger amount of particles than that prepared by NaOH aqueous solution. The iron contents in the cryogels are summarized in Table 2. The iron content increased with an increase in the FeCl₃ concentration and was hardly influenced by the concentration of Na₂CO₃. The iron content prepared using Na₂CO₃ was higher than that using NaOH. These tendencies are quite same as those of SEM observation.

When the cryogel containing iron hydroxide oxide particles was prepared using NaOH aqueous solution (Gel c), a part of the inside macro-porous structure of the cryogels was collapsed as shown in Fig. 3(c). The cryogel is considered to be hydrided and borken by immersing in strong basic solution of NaOH. All iron ion in the cryogel wall was not changed to iron hydroxide oxide particles when NaOH was used for the preparation, that described in later part of the section 3.2.3. Hence, a part of iron ion would leak out during washing process in the preparation. From these reasons, it is considered that the iron content of the cryogel prepared using NaOH decreased.

3.1.2. XRD Analysis of the cryogel containing iron oxide hydroxide particles

In order to characterize iron oxide particles formed in the cryogel wall, XRD analysis was carried out. XRD measurement result of the cryogel (Gel a) is shown in Fig. 5. Some broad and unclear peaks were observed and sharp peaks did not exist in the result. Some peaks agreed with the peaks of goethite (α-FeOOH) and magnetite high (Fe₂.₉₃O₄). The dried powder of iron oxide precipitates, which were prepared in the aqueous solution at the same concentrations, showed more sharp and clear peaks of goethite (data not shown). The crystallinity of the particles prepared in the cryogel wall is low and the most of them are suggested to be an amorphous state. The formation of iron oxide particles in the cryogel wall may control and hinder their crystal growth.

Table 2  Iron content in the cryogels prepared at various conditions and their adsorption amount of As(V) at pH 7 and the initial As(V) concentration of 100 mg/l

| Adsorbent | Fe content [mmol/g] | W [mg/g-dry] |
|-----------|---------------------|--------------|
| Gel a     | 13.6                | 22.11        |
| Gel b     | 10.4                | 20.30        |
| Gel c     | 11.4                | 15.37        |
| Gel d     | 8.82                | 15.98        |
| Gel e     | 8.78                | 14.29        |
3.2. Adsorption behaviors of As(V) with the PAA cryogels containing iron oxide particles

3.2.1. Effect of contact time on the adsorption

The time courses of the As(V) adsorption with the cryogel (Gel a) and the precipitate powers of iron hydroxide oxide particles prepared at pH 7 and 10 mg/L of the initial As(V) concentration are shown in Fig. 6. The adsorption with the cryogel reached almost the saturated adsorption and kept constant after 1 hr. In contrast, the adsorption with the precipitate powder increased rapidly for 3 hr and after that gradually increased until the saturated adsorption amount for 60 hr. From this result, the cryogel containing iron oxide particles are found to provide fast adsorption rate of As(V). This would be caused by the macroporous structure of the cryogel with easy access of the solution to the inside of the cryogel and high surface area and activity of iron hydroxide oxide particles with amorphous structure.

3.2.2. Effect of pH on the adsorption

The adsorption of As(V) with the cryogels (Gel b) was carried out in the pH range of 4–9 and at 10 mg/L of the initial As(V) concentration. The effect of pH on the As(V) adsorption is shown in Fig. 7. The adsorption ratio of As(V) was constant independent of pH. Pentavalent arsenic is present as dissociated form of $\text{H}_2\text{AsO}_4^-$ or $\text{HAsO}_4^{2-}$ in pH range above 2 as shown below. Since iron oxide hydroxide is positively charged under acidic pH range, it was found to adsorb electrostatically between pH 4–9.

$$\text{H}_3\text{AsO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{H}_2\text{AsO}_4^-(\text{aq}), \text{pK}_{a1} = 2.24$$

$$\text{H}_2\text{AsO}_4^-(\text{aq})+ \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HAsO}_4^{2-}(\text{aq}), \text{pK}_{a2} = 6.96$$

3.2.3. Effect of preparation condition on the adsorption

The adsorption of As(V) with the cryogels prepared in various conditions (Gel a–e) was carried out at pH 7 and 100 mg/L of the initial As(V) concentration. The adsorption amount of As(V) with the cryogels in Fig. 8 and Table 2 together with their iron contents. When the cryogels prepared using Na$_2$CO$_3$, the adsorption amount of As(V) with the cryogels increased with an increase in their iron contents. The EDX mapping analyses of Fe and As after adsorption experiment are shown in Figs. 4(b) and 4(c). As element was also observed in the whole of the cryogel wall, however, was concentrated at the same place of Fe element. This result also support that iron hydroxide oxide particles entrapped in the cryogel wall adsorb As(V).

Although the iron content of the cryogel prepared using NaOH (Gel c) was almost same with that prepared using of Na$_2$CO$_3$ (Gel b), the ad-
sorption amount was low. When the cryogel prepared using NaOH was stored in water for long time, the water was changed to yellowish brown (Fig. 2(b)). This means all of iron ion in the cryogel prepared using NaOH was not changed to iron hydroxide oxide particles and a part of them remained in the wall and leaked out into water. When NaOH was used for alkali source for the preparation of iron hydroxide oxide particles in the cryogel wall, it is considered that many particles would be formed rapidly around at the wall surface due to strong alkalinity of NaOH solution and covered the surface, and consequently the diffusion of OH\(^{-}\) ion into the wall would be difficult to occur. Hence, it is found that the Na\(_2\)CO\(_3\) aqueous solution is suitable to prepare the cryogels containing iron hydroxide oxide particles.

3.2.4. Adsorption isotherm of As(V)

The adsorption isotherms of As(V) with cryogels containing the iron oxide particles (Gel a, Gel b and Gel e) at pH 7 were measured as shown in Fig. 9. The adsorption amount with the cryogels increased rapidly at low concentration and increased gradually with an increase in the concentration of As(V) and did not reach constant values. These results suggest the BET type adsorption. Most of the adsorbents using iron oxides and other metal oxides have been reported to show the adsorption behavior of the Langmuir type\(^4\). At low concentration range, the adsorption of As(V) on the surface of iron hydroxide oxide particles would occur by electrostatic interaction, however, at high concentration range, other mechanism would play an important role due to amorphous structure of iron hydroxide oxide entrapped in the cryogel wall as described by Mohan and Pittman Jr\(^4\). The adsorption mechanism at high As(V) concentration and the structural change of the iron compounds during the adsorption will be investigated in future work.

The adsorption amounts of the cryogels for As(V) shown in Fig. 9, which is calculated based on the weight of lyophilized cryogel, are comparable with those of iron oxide adsorbents reported\(^4\) or higher than them. The adsorption amount based on the weight of iron oxide particles in the cryogels will become much higher value. This high adsorption ability of iron hydroxide oxide formed in the cryogel wall is considered to be provided due to their amorphous structure which have active surface.

5. Conclusions

The polyacrylamide cryogels containing iron hydroxide oxide particles were successfully prepared by an in situ particle formation method that is the stepwise penetrations of iron(III) chloride solution and following alkaline aqueous solution to the cryogel. The cryogels containing iron hydroxide oxide particles had an ability to adsorb As(V) from the aqueous phase. The pH value did not affect to the adsorption of As(V) with the cryogels. The Na\(_2\)CO\(_3\) aqueous solution is suitable to prepare the cryogels containing iron hydroxide oxide particles with high iron content and high adsorption amount of As(V). The adsorption of As(V) with the cryogels increased with an increase in the iron content in the cryogel and the As(V) concentration in the aqueous phase. The cryogel containing iron hydroxide oxide particles showed high adsorption ability of As(V).
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