

Adsorption Properties of Arsenic by Polyacrylamide Cryogel containing Iron Hydroxide Oxide Particles Prepared by Particles Addition Method

*Misa Kurozumi, Koichiro Shiomori

Faculty of Engineering, University of Miyazaki, Japan

Abstract

Cryogel is super-macroporous material prepared by freezing of polymer or monomer solution at low temperature. The hybrid material of cryogels and iron hydroxide oxide(FeOOH) nano-particles, which have affinity to arsenic, are expected as a safe removal adsorbent of arsenic ions from aqueous solutions. In this study, polyacrylamide(PAA) cryogels containing FeOOH particles were prepared by freezing the monomer solution of acrylamide cross-linker *N,N*-methylene bis(acrylamide) dispersing the particles, which were prepared by mixed iron(III) chloride solution (FeCl₃) and alkaline aqueous solution, and polymerizing initiated by *N,N,N',N'*-tetramethyl ethylene diamine and ammonium peroxodisulfate at sub-zero temperatures. The particles formed were observed on a whole of the cryogel wall. The polyacrylamide cryogel containing FeOOH particles successfully adsorbed a large amount of As(V) at both low and high concentrations. The adsorption property showed a Brunauer-Emmett-Teller(BET)-like isotherm. The adsorption of As(V) with the cryogel was not affected by the pH value of the aqueous solution. On the other hand, that of As(III) with the cryogel was affected by the only pH 12 of the aqueous solution. The FeOOH particles entrapped in the cryogel wall had a poorly crystalline. The poorly crystalline FeOOH particles had higher adsorption capacity than the crystalline ones.

Keywords: Arsenic adsorption, Cryogel, Polyacrylamide, Iron hydroxide oxide particles

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, 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 arsenic¹. 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 organs².

Removal technologies of arsenic from water typically rely on adsorption or filtration. Adsorbents for the removal of arsenic are almost invariably based on bulk or supported particles of transition metal oxides and hydroxides. Iron oxide compounds are commonly used in high throughput applications because of the low cost of fabrication of the adsorbent^{3,4,8-14}. 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^{12,13}. It is important to

Contact: Koichiro Shiomori, position title, Faculty of Engineering, University of Miyazaki, Japan
E-mail Address: shiomori@cc.miyazaki-u.ac.jp, phone number: 0985-58-7309

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^{5,6}. The composite material of solid micro/nano-particles and cryogels is expected to develop a new adsorbent and filter^{5,7,8}. Cryogel polymer composite adsorbents embedded metal oxides particles have been reported and expected to be effective adsorbent used for treatment of arsenic contaminated water¹⁵⁻¹⁷. In this work, PAA cryogels containing FeOOH particles were prepared by particles addition method. The effects of the preparation condition on the structures of the PAA cryogels and iron oxide particles, and adsorption property of arsenic from aqueous solution with the cryogels were investigated.

2. EXPERIMENTAL METHOD

2.1 Preparation of PAA cryogel containing FeOOH particles

FeOOH particles were prepared by mixing 10 ml of iron(III) chloride solution (FeCl_3) and 20 ml of sodium carbonate (Na_2CO_3) aqueous solution, and separated those particles and unreacted Na_2CO_3 aqueous solution by a centrifugal separator. Those particles were washed with degassed water twice by a centrifugal separator. Those particles, the monomers of 4.0 wt% of acrylamide (AAm) and cross-linker 1.0 wt% of *N,N*-Methylenebis(acrylamide) (MBAAm) were dissolved in degassed water with vigorous stirring and cooled to about 0 °C for 1.0 hour. Then the solution was charged with nitrogen gas because of deaerating radically for the solution. After that, 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. Then 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.

2.2 Adsorption of As with the cryogels containing FeOOH particles

The arsenic adsorption experiment was conducted with the batch method. The PAA cryogel containing iron FeOOH particles was put into the sample tube, the aqueous solution containing As 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 on the adsorbents were calculated based on the lyophilized weight of them (mg/g-dry).

3. RESULTS AND DISCUSSION

3.1 Preparation of PAA cryogels containing FeOOH particles

The cryogels obtained from freezing bath were reddish brown that is due to FeOOH particles in the cryogel wall. Photographs of the external appearance and the cross-section of the cryogels containing FeOOH particles are shown in Fig. 1. The color of outer surface of the cryogels was even (Fig. 1(a)). That of the cross-section was also even (Fig. 1(b)). It was found from this that the particles formed were on a whole of the cryogel wall.

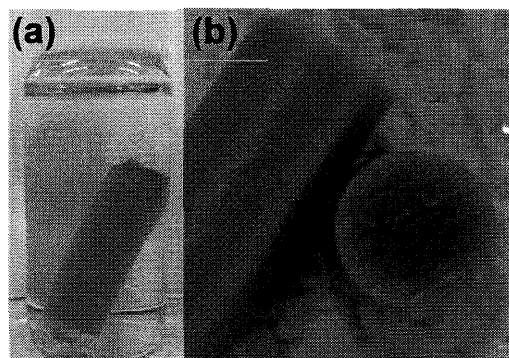


Fig.1 Photographs of the cryogels containing FeOOH particles.
(a) External appearance
(b) Cross sectioning view

3.2 Effect of pH on the adsorption As(V)

The adsorption of As(V) with the cryogels was carried out in the pH range of 2-12 and at 10 mg/L of the initial As(V) concentration. The effect of pH on the As(V) adsorption is shown in Fig.2. The adsorption ratio of As(V) was constant independent of pH. However, the arsenic solution which coordinated pH from 5 to 10 greatly changed after adsorption. This is why, there is possibility of the chemisorption in the adsorption mechanism.

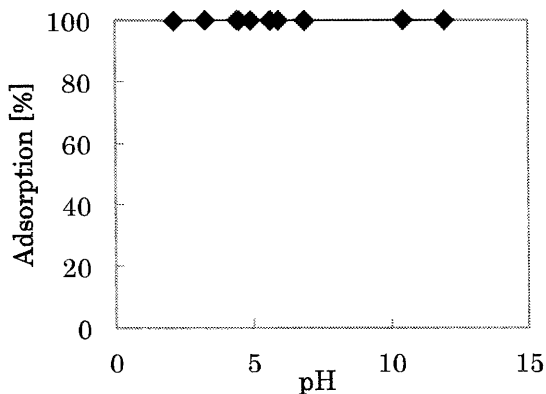


Fig.2 Effect of equilibrium pH on the adsorption of As(V) with the cryogel containing FeOOH particles.

3.3 Effect of pH on the adsorption As(III)

The adsorption of As(III) with the cryogels was carried out in the pH range of 2-12 and at 10 mg/L of the initial As(III) concentration. The effect of pH on the As(III) adsorption is shown in Fig.3. The adsorption ratio of As(III) was constant independent of pH from 2 to 11. Then, the arsenic solution which coordinated pH from 4 to 11 greatly changed after adsorption. So, there is also possibility of the chemisorption in the adsorption mechanism. However, the only pH 12 of the aqueous solution affected the adsorption ratio of As(III). As(III) is present as dissociated form of HAsO_3^{2-} in pH 12.13 as shown below. It is thought that this influenced an adsorption rate.

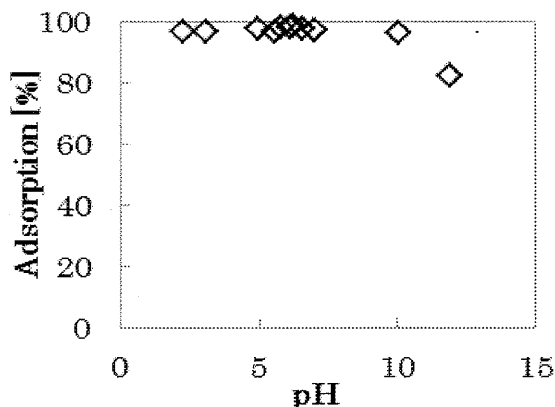
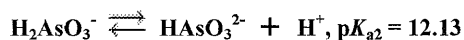


Fig.3 Effect of equilibrium pH on the adsorption of As(III) with the cryogel containing FeOOH particles.

3.4 Adsorption isotherm of As(V)

The adsorption isotherms of As(V) with different cryogels of the preparation method (particles addition method and *in situ* particle formation method) and FeOOH particles prepared by air seasoning at pH 7

were measured as shown in Fig. 4. The cryogel was successfully adsorbed As(V) at both low and high concentrations of As(V). The adsorption property showed a BET-like isotherm. The FeOOH particles entrapped in the cryogel wall by particles addition method had a poorly crystalline. The poorly crystalline FeOOH particles had higher adsorption capacity than the crystalline ones entrapped in the cryogel wall by *in-situ* method or prepared by air seasoning.

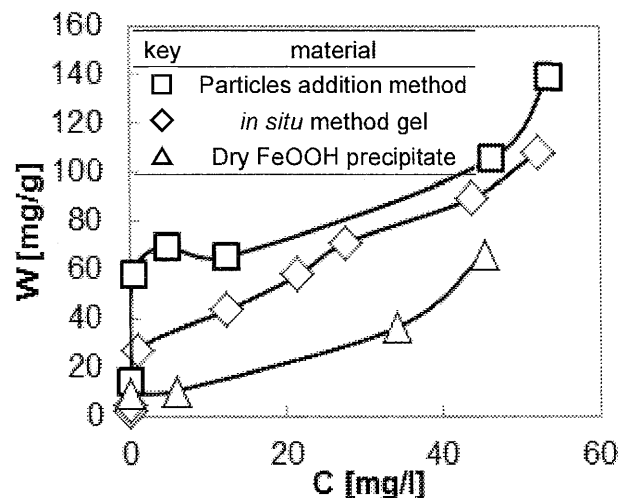


Fig.4 Adsorption isotherm of As(V) with cryogels containing FeOOH particles (particles addition method and *in situ* particle formation method) and dry FeOOH particles at pH 7.

4. CONCLUSION

The PAA cryogels containing FeOOH particles were successfully prepared by particles addition method. The particles formed were observed on a whole of the cryogel wall. The cryogel was successfully adsorbed As(V) at both low and high concentrations of As(V). The adsorption property showed a BET-like isotherm. The adsorption of As(V) with the cryogel was not affected by the pH value of the aqueous solution. On the other hand, that of As(III) with the cryogel was affected by the only pH 12 of the aqueous solution. The cryogel containing poorly crystalline particles had larger amount of adsorbed As(V) than that of the cryogel containing crystalline particles.

5. REFERENCES

1. Y. Yano, K. Ito, A. Kodama, K. Shiomori, S. Tomomatsu, M. Sezaki, H. Yokota: J. Environ. Protect., **3**, pp. 856-862 (2012)
2. T. Kondo, T. Inaoka, N. Maruyama, K. Ushijima, M. Nagano, S. Nakamura, C. Watanabe, K. Tamaki, R. Ohtsuka: Int. J. Dermatol., **41**, pp. 841-846 (2002)

3. United States Environmental Protection Agency, Drinking Water Treatability Database, Arsenic, <http://iaspub.epa.gov/tdb/pages/contaminant/contaminantOverview.do?contaminantId=1175876466>
4. D. Mohan, C. U. Pittman Jr.: *J. Hazard. Mater.*, **142**, pp. 1-53 (2007)
5. G. Ertürk, B. Mattiasson: *J. Chromatography A*, **1357**, pp. 24-35 (2014)
6. Kumar, A. Srivastava: *Nature Protocols*, **5**, pp. 1737-1747 (2010)
7. L. Önnby, V. Pakade, B. Mattiasson, H Kirsebom: *Water Res.*, **46**, pp. 4111-4120 (2012)
8. N. Savina, C. J. English, R. L. D. Whitby, Y. Zheng, A. Leistner, S. V. Mikhalovsky, A. B. Cundy: *J. Hazard. Materials*, **192**, pp. 1002-1008 (2011)
9. M. E. Sigrist, L. Brusa, H. R. Beldomenico, L. Dosso, O. M. Tsendra, M. B. Gonzalez, C. L. Pieck, C. R. Vera: *J. Env. Chem. Eng.*, **2**, pp. 927-934 (2014)
10. K. Ohe, Y. Tagai, S. Nakamura, T. Oshima, Y. Baba: *J. Chem. Eng. Jpn*, **38**, pp. 671-676 (2005)
11. K. Ohe, R. Tomimatsu, T. Oshima, Y. Baba: *J. Ion Exchange*, **18**, pp. 404-407 (2007)
12. K. Ohe, T. Oshima, Y. Baba: *Environ. Geochem. Health*, **32**, pp. 283-286 (2010)
13. C. T. Yavuz, J. T. Mayo, W. W. Yu, A. Prakash, J. C. Falkner, S. Yean, L. Cong, H. J. Shipley, A. Kan, M. Tomson, D. Natelson, V. L. Colvin: *Science*, **314**, pp. 964-967 (2006)
14. S. Minami, T. Miyoshi, N. Murayama, J. Shibata: *Kagaku Kogaku Ronbunshu*, **38**, pp. 318-323 (2012)
15. N. Savina, C. J. English, R. L. D. Whitby, Y. Zheng, A. Leistner, S. V. Mikhalovsky, A. Cundy: *J. Hazard. Mater.*, **192**, pp. 1002-1008 (2011)
16. L. Önnby, V. Pakade, B. Mattiassona, H. Kirseboma: *Water Res.*, **46**, pp. 4111-4120 (2012)
17. P. S. Kumar, L. Önnby, H. Kirsebom: *J. Hazard. Mater.*, **250-251**, pp. 469-476 (2013)