

PREPARATION OF ARSENIC ADSORBENT FROM NEUTRALIZATION PRECIPITATES OF FERROUS OXIDES PRODUCED AT ABANDONED MINE

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ABSTRACT: Arsenic adsorbents composed of polyvinyl alcohol (PVA) cryogel immobilizing the neutralization precipitates of ferrous hydroxides discharged from Hayahi abandoned mine at Misato-cho in Miyazaki prefecture were prepared under various conditions. The adsorbent has highly porous structure and color of dark brown, and adsorbed both As(III) and As(V) from aqueous solution. The adsorbed amount of As increased with an increase in the As concentration in the aqueous solution. And the adsorption amount also increased with increasing the amount of the precipitates used for the preparation of the adsorbent. The adsorption mechanism between As(III) and As(V) is suggested to be different by the analysis of adsorption equation. The adsorbent was used for a column type operation. Arsenic ion in the aqueous solution could be adsorbed on the adsorbent under continuous flow condition. In the initial stage of the column operation, all of Arsenic ion in the aqueous solution was adsorbed on the adsorbent and no As was contained in the effluent from the column. The As concentration in the effluent gradually increased with an increase of the feed amount of the aqueous solution and finally reached the feed concentration of As at the inlet of the column.

KEY WORDS: Arsenic adsorbent, Cryogel, Polyvinyl alcohol, ferrous oxides,

INTRODUCTION

At Hayahi abandoned mine at Misato town in Miyazaki prefecture, strongly acidic mine wastewater containing large amount of ferrous ion is discharged. In order to protect environmental pollution of this mine wastewater, the neutralization processing of the wastewater is carried out by the addition of calcium hydroxide. From this process, neutralization precipitates which contain iron hydroxide are discharged about 1 ton/day, and are disposed to the landfill site. In the future a shortage of the landfill site is estimated, hence the effective utilization of the precipitates has been required to develop. Iron hydroxide has an affinity for arsenic ion (Gupta *et al.* (2009)) Therefore, the development of arsenic adsorbent using the neutralization precipitates is expected. In this study, the neutralization precipitates are immobilized and fixed into polyvinyl alcohol (PVA) cryogel to prepare arsenic adsorbent. Cryogels are prepared by freezing of the solution containing polymer or monomer and following cross-linking of polymer or polymerization of monomer in the freezing state (Kumar *et al.* (2003), Lozinsky *et al.* (2003)). Cryogel has interconnecting large pores in its inside which likes a sponge. The effects of the preparation condition on the structure of the PVA cryogel containing the precipitates and adsorption property of arsenic on the cryogel were clarified.

EXPERIMENTAL

Preparation of PVA cryogel immobilizing precipitates

The preparation flow of PVA cryogel immobilized the precipitates is shown in Fig. 1. A PVA aqueous solution and an aqueous solution dispersed the precipitations were mixed to prepare the solution at 5 wt% of PVA and 5.0-12.5 wt% of the precipitates. The solution was added the HCl aqueous solution to adjust the pH at 1.0-1.2, cooled for 30 min. in ice bath, and then added 0.25 ml of 25 wt% glutaraldehyde aqueous solution as a cross-linker. After mixing of the reaction mixture for 1 min., 12ml of

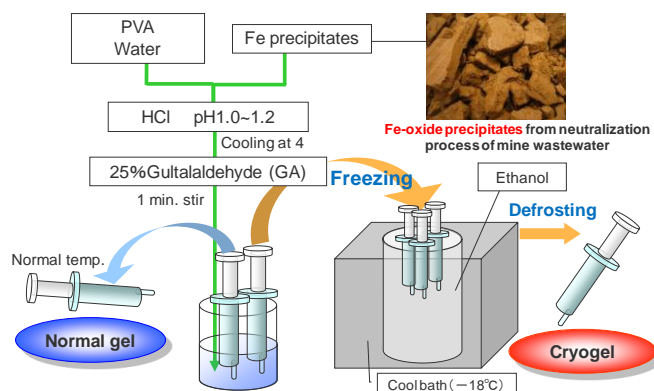


Fig. 1 Preparation flow of the PVA cryogels immobilizing the precipitates from the neutralization process of mine waste water of Hayahi abandoned mine.

the reaction mixture was filled into a 15 ml syringe. The syringe was put into cooling bath at 255 K to freeze the reaction mixture for overnight. The obtained PVA cryogel immobilizing the precipitates was soaked in distilled water, and the distilled water was exchanged until it becomes neutrality. After washing the cryogel was soaked in HCl aqueous solution at pH4 and stored in the refrigerator. The preparation conditions of the PVA cryogels immobilizing the precipitates are summarized in Table 1.

After freeze-drying of the PVA cryogel, it was observed with digital microscope and scanning electron microscope.

Sample No.	PVA conc. [wt%]	Fe-oxides conc.[wt%]	GA conc. [wt%]
No.1	5.0	5.0	0.0625
No.2	5.0	7.5	0.0625
No.3	5.0	10.0	0.0625
No.4	5.0	12.5	0.0625
No.5	5.0	15.0	0.0625
No.6	4.25	15.0	0.0625
No.7	4.0	20.0	0.0625

Table 1 Preparation conditions of the PVA cryogels

Adsorption of Arsenic by cryogel

The PVA cryogel immobilizing the precipitates was put into an aqueous solution containing As(III) or As(IV) . After 12hr, the cryogel and the aqueous solution was respectively separated. The Arsenic concentration in the aqueous before and after adsorption experiments was measured with atomic adsorption spectrometer with hydride generation apparatus of very low temperature collection type.

Continuous adsorption of As using the column of the PVA cryogel

The column packed the PVA cryogel immobilizing the precipitates at 15wt% was used for the continuous

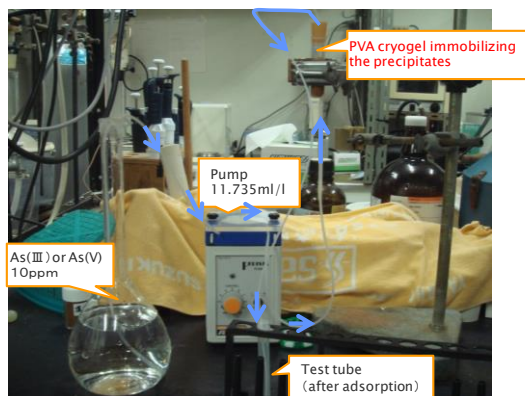


Fig. 2 The apparatus used for the continuous adsorption.

adsorption experiment. The aqueous solution containing 10 ppm of As(III) or As(V) was flowed into the column using peristaltic pump at 2.0 ml/h. The apparatus used for the continuous adsorption is shown in Fig. 2.

RESULTS AND DISCUSSION

Preparation of the PVA cryogel immobilizing the precipitates

The PVA cryogel immobilizing the precipitates at 5.0 wt% (Sample No. 1) is shown in Fig. 3. The PVA cryogel colored in dark brown which is due to the original color of the precipitates. The gel has elasticity and the water entrapped in the PVA gel was easily discharged by pushing the cryogel. A number of large pores were observed on and inside of the cryogel. And, the spherical particles which seemed to be the precipitates were observed at several places on the surface of the pore and the number of spherical particles increased with an increase in the initial amount of the precipitates in the preparation. With the increase in the content of the precipitates, the color of the cryogel became thick, and it tended to become fragile, and however little changes of the properties of the cryogel were observed. There is no falling out of the precipitates from the PVA cryogel during the adsorption experiment, hence the precipitates seem to have completely been immobilized to the wall of the cryogel.

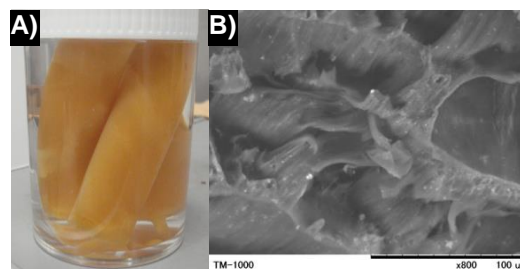


Fig. 3 The PVA cryogels immobilizing the precipitates at 5 wt% . A) The whole of the gel. B) SEM observation of the cross section of the gel.

Adsorption properties of As(III) and As(V) on the PVA gel

The adsorption of As(III) and As(V) by the PVA cryogel was carried out at various pH values and their concentrations. The effect of pH on the adsorption of As(III) and As(V) by the PVA cryogel immobilizing the precipitates at 5wt% is shown in Fig. 4. The effect of pH on the adsorption of As was not so large. The adsorption amount of As(III) tends to increase with an increase in pH, whereas that of As(V) tends to decrease with an increase in the pH value. The adsorption amount of As(V) was larger than that of As(III)

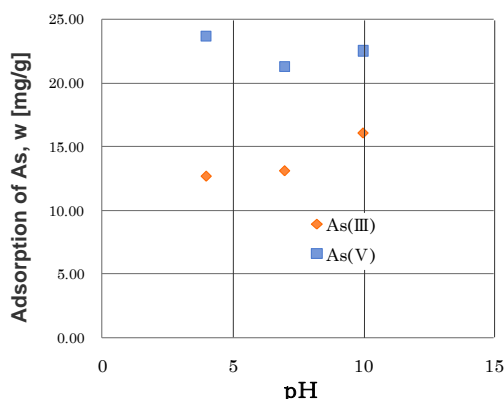


Fig. 4 Effect of pH on the adsorption of As(III) and As(V) on the PVA cryogels immobilizing the precipitates at 5 wt%.

The effect of the concentration of As in the aqueous phase on the adsorption amount of As was investigated. The Adsorption isotherms for As(III) and As(V) are shown in Figs. 5 and 6, respectively. In both cases, the adsorption amounts of As increased with an increase in the As concentration in the aqueous solution and in the amount of the precipitates used for their preparation. The adsorption amounts of As(V) at low concentration range were very high compared with those of As(III). However, in the higher concentration range, the adsorption amount of As(III) was slightly higher than those of As(V).

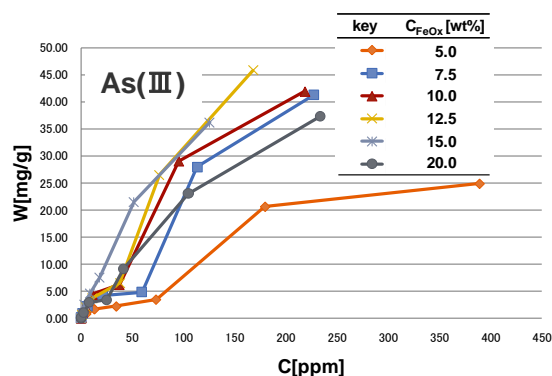


Fig. 5 Adsorption isotherm of As(III) on the PVA cryogel immobilizing the precipitates which amount was changed.

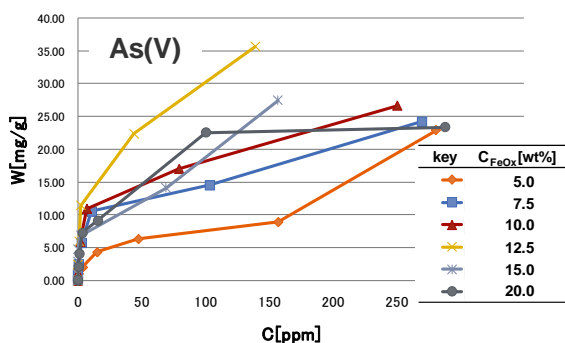


Fig. 6 Adsorption isotherm of As(V) on the PVA cryogel immobilizing the precipitates which amount was changed.

In order to investigate the adsorption mechanism, the experimental results were analyzed using various adsorption models. Freundlich isotherm plots were carried out for the experimental results in Figs. 5 and 6 as shown in Figs. 7 and 8, respectively. In the case of As(III), the experimental results were plotted on the straight lines having same slope depending on the amount of the precipitates. However, in the case of As(IV), the experimental results were not plotted on straight line and two different adsorption steps were suggested. This result show the adsorption mechanism between As(III) and As(V) would be different. Further investigation is needed to clarify the adsorption mechanism of As(III) and As(V) on the PVA cryogel immobilizing the precipitates.

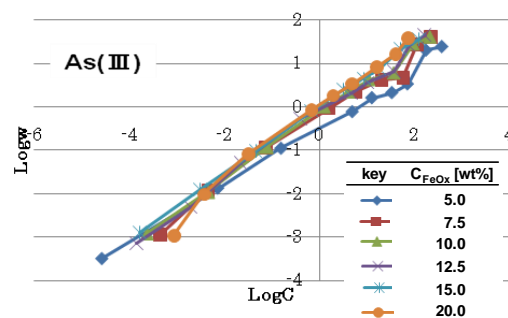


Fig. 7 Relationship between $\log W$ and $\log C$ of the adsorption of As(III) on the PVA cryogel immobilizing the precipitates at various amounts

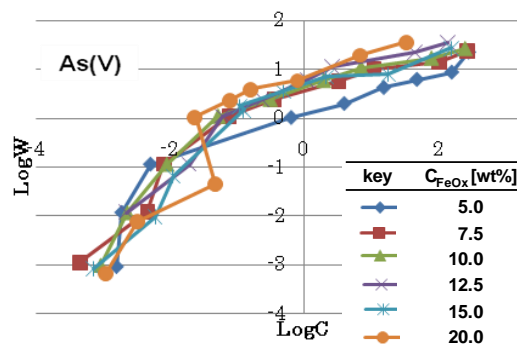


Fig. 8 Relationship between $\log W$ and $\log C$ of the adsorption of As(V) on the PVA cryogel immobilizing the precipitates at various amounts

Continuous adsorption of As using the column of the PVA cryogel

The arsenic concentrations at the outlet of the column were plotted against the flow time as shown in Figs 9 and 10 for As(III) and As(V), respectively. In the initial stage of the column operation, all of Arsenic ion in the aqueous solution was adsorbed on the PVA cryogel and no Arsenic ion was contained in the effluent from the column. The Arsenic concentration in the effluent gradually increased with an increase of the time and finally reached to the feed concentration of Arsenic at the inlet of the column.

The maximum adsorption amounts of As(III) and As(V) onto the PVA cryogel was obtained by the graphical integration of the results in Figs. 9 and 10. The maximum adsorption amount to the PVA cryogel immobilizing the precipitate at 15 wt% was 20.3 mg/g-dry gel for As(III) and 12.4 mg/g-dry gel for As(V), respectively.

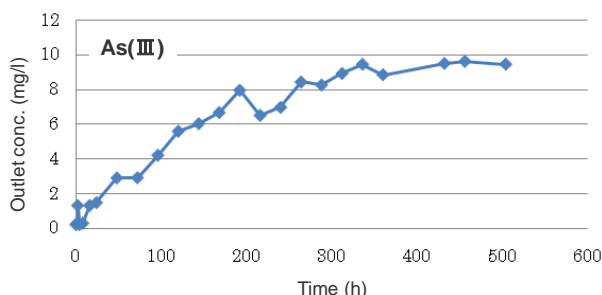


Fig. 9 Concentration change of As(III) at outlet of column of PVA cryogel immobilizing the precipitates at 15 wt% with time.

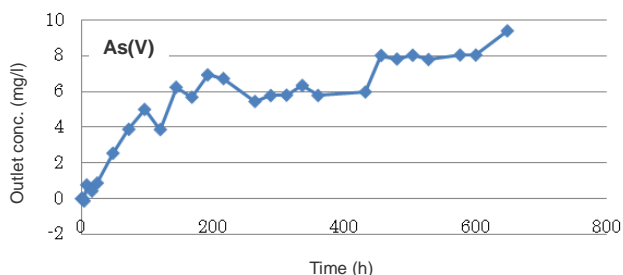


Fig. 10 Concentration change of As(V) at outlet of column of PVA cryogel immobilizing the precipitates at 15 wt% with time.

CONCLUSION

The PVA cryogels immobilizing the neutralization precipitates of ferrous hydroxides from abandoned mine were successfully prepared under various conditions. The PVA cryogel adsorbed both As(III) and As(V) from aqueous solution. The adsorbed amount of As increased with an increase in the As concentration in the aqueous solution and an increase in the amount of the precipitates used for the preparation of the adsorbent. The adsorption mechanism between As(III) and As(V) is suggested to be different by the analysis of the adsorption isotherm. The continuous adsorption of Arsenic using the column packed with the PVA cryogel was successfully possible to be carried out.

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