

Removal of Arsenic Ion with Manganese Oxide Compounds

Toshihiro Kasai and Hideki Koyanaka*

Department of Applied Physics and Chemistry, Fukui University of Technology, Fukui 910-8505, Japan

Fax: 81-776-22-8111, e-mail: kasai-t@mx1.fctv.ne.jp

*Department of Civil Engineering, School of Engineering, Nippon Bunri University, Oita 870-0397, Japan

Fax: 81-97-569-0242, e-mail: koyanahk@ce.nbu.ac.jp

In the present study, the adsorption of As on manganese oxide compounds in aqueous solution was investigated. The manganese oxide compounds were prepared by heating a mixture of MnCO_3 and $\text{Bi}_2(\text{CO}_3)_2\text{O}_2$ (molar ratio Mn:Bi=1:0 to 0.45) at 200°C for 4.5 hours and then treated with 0.5 mol/dm³ nitric acid. The findings of the present study are as follows. (1) It was found that the As adsorption ability of the manganese oxide compounds was promoted by the addition of Bi. (2) The manganese oxide compounds, which has the capability of As adsorption in aqueous solution, showed a X-ray diffraction pattern of an amorphous material. (3) The manganese oxide compounds showed the maximum ability of As adsorption at the mixture ratio of Mn:Bi=1:0.08. (4) The manganese oxide compounds adsorbent is able to reuse by desorption with sulfuric acid or hydrochloric acid. (5) The manganese oxide compounds are applicable to As removal from actual As wasted water which contains other components. We applied to remove As from aqueous solution by the column method and the pack method. The column method is appropriate for treating a large amount of waste water. And the pack method is an effective and simple method for As removal from the As polluted drinking water.

Key words: Arsenic Ion, Manganese oxide, Bismuth, Adsorbent

1. INTRODUCTION

There are many problems concerning arsenic pollution in river and lake waters in the world⁽¹⁻⁹⁾. It is especially reported in the case of Bangladesh in the foreign affairs of arsenic pollution⁽³⁾. There are many cases of disease seen by arsenic poisoning in the local people who drink arsenic polluted well water because the soil of this area is arsenic rich. It has been reported that the arsenic concentration of drinking water in the "Nawabganj district" area of the country reaches 0.01 to 1 mg/dm³ (The environmental standard of arsenic by WHO is 0.01 mg/dm³). But any substantial measures have not carried out yet⁽³⁾. On the other hand, the arsenic pollution problems in domestic area have arisen mainly from the waste water of closed mines⁽⁴⁻⁹⁾. It has been reported that the arsenic concentration of rivers around Sasagaya mine in Shimane prefecture was 0.08-1.3 mg/dm³, which exceeded the environmental standard of arsenic due to inflow of waste water from the closed mine⁽⁴⁻⁵⁾. And the arsenic concentration of river waters near Sobetu town in Hokkaido had exceeded the environmental standard until 1975 because Benkei river had been contaminated by a lot of strong acid water with arsenic. However the arsenic concentration has been decreased by one tenths of the initial concentration since 1981 in consequence of applying measures such as filling the gallery and installing of neutralization installation. However, there are two serious problems. The installation exhausts a large amount of precipitate and it costed about 400 million yen because the installation spends 40 to 50 thousand tons of lime cake, slaked lime, and calcium carbonate.

There are many cases of water pollution problems with arsenic such as the waste water from geothermal

power plants⁽⁸⁾ and industrial waste water⁽⁹⁾. The coprecipitation method generally used for removing arsenic has problems in the waste after treatment and the treating cost. Therefore the adsorption method is suitable for removing arsenic compared with the precipitation method. In this study, we found that the ability of arsenic adsorption of manganese oxide compounds is increased by adding small amount of bismuth and calcination.

2. EXPERIMENTAL

2.1 Synthesis of manganese oxide compounds

Analytical grade MnCO_3 and $\text{Bi}_2(\text{CO}_3)_2\text{O}_2$ were used for the preparation of the manganese oxide compounds adsorbent precursor. These reagents were mixed in various proportions with agate mortar and pestle. The obtained mixture was put in a crucible and calcined with an electric furnace for 4.5 hours at 200°C. The calcined mixture was dispersed in 0.5 mol/dm³ nitric acid and stirred for 1 hour at room temperature, washed with distilled water, and dried at 100°C for 1 hour (Acid treatment). These manganese oxide compounds were analyzed by X-ray diffraction (XRD) and observed with scanning electron microscopy (SEM).

2.2 Adsorption and desorption of arsenic ion

Arsenic standard solution (As 1000 mg/dm³: Wako Pure Chemical Industries, Ltd.) was diluted with distilled water for preparation of 20 mg/dm³ artificial arsenous acid solution. 1.0 g of the manganese oxide compounds adsorbent was dispersed in 1 dm³ of 0.5 mol/dm³ nitric acid and stirred with a magnetic stirrer for 1 hour at room temperature. Then the activated adsorbent by this acid treatment were filtered with suction and washed with 1 dm³ of distilled water. The

As adsorption activity is increased by this acid treatment. The activated adsorbent was dispersed in 1 dm³ of the artificial arsenous acid solution and stirred with a magnetic stirrer for 1 hour. 20 cm³ of treated water samples were then collected by using a disposable syringe filter unit (Dismic GS-25: ADVANTEC) at varying times. The arsenic ion remaining in the solution was determined by inductivity coupled plasma atomic emission spectroscopy (ICP) and the amount of As adsorbed for the adsorbent was calculated.

0.1 g of the adsorbent (Mn:Bi=1:0.09), As previously adsorbed by the above method, was dispersed in 0.1 dm³ of 0.5 mol/dm³ acid (hydrochloric acid, sulfuric acid, and nitric acid) and stirred with a magnetic stirrer for 1 hour at room temperature. The arsenic ion desorbed in the acid was measured by ICP and the desorption rate was calculated at varying times.

Readsorption experiments were attempted by As desorption from the adsorbent and reactivation with the acid treatment. 1.0 g of the adsorbent (Mn:Bi=1:0.09) was used for these experiments. The activated adsorbent by acid treatment was dispersed in 1 dm³ of 20 mg/dm³ artificial arsenous acid solution and then stirred for 2 hours until the adsorbent saturated. The saturated adsorbent was filtered with suction. Then the adsorbent was dispersed in 1 dm³ of 0.5 mol/dm³ sulfuric acid and stirred with a magnetic stirrer for 30 minutes. Readsorption experiment was carried out in a similar manner as above with the As desorbed adsorbent.

We tried to remove As from actual waste water which contains arsenous ion. Chemical composition of the actual waste water is shown in Table I. The concentration of arsenic ion is 3.5 mg/dm³. The value of arsenic concentration is seriously in excess of the environmental standard of arsenic (0.01 mg/dm³). The pH and the Eh values of the actual waste water were 6.0 and 0.19 V respectively. The form of arsenic which was contained in the waste water was arsenous ion by means of these values. The silicate suspension particle in the waste water was first removed by filtration with suction. 1.0 g of adsorbent was dispersed in the 1 dm³ of filtered waste water and stirred with a magnetic stirrer for 1 hour. Treated waste water samples were collected by using a disposable syringe filter unit at varying times. The arsenic ion remaining in the solution was measured by ICP.

Table I Chemical composition of a geothermal effluent.

Element	Concentration (mg/dm ³)
Na	1800
K	260
Ca	28
Li	11
Fe	4.5
As	3.5
Mg	0.70

2.3 Application of column method and pack method

Adequate amounts of ash less filter pulp and 2 g of the adsorbent were dispersed in 2 dm³ of 0.5 mol/dm³ nitric

acid and stirred for 1 hour. The As adsorption column was prepared in a glass chromatograph tube of 2 cm diameter by packing the mixture (Fig. 1). The nitric acid in the adsorption column was removed by passing sufficient amount of distilled water. The 0.1 dm³ of artificial arsenous acid solution (1 mg/dm³ or 10 mg/dm³) per 1 hour was passed through the column and the As concentration of treated water was measured by ICP by varying the amount of treated water. Desorption of As from the column was carried out as follows. 0.1 dm³ of 0.5 mol/dm³ sulfuric acid was made to flow through the column per 1 hour. The concentration of As was measured by ICP for each 50 cm³ in eluted acid solution and calculated the rate of desorption.

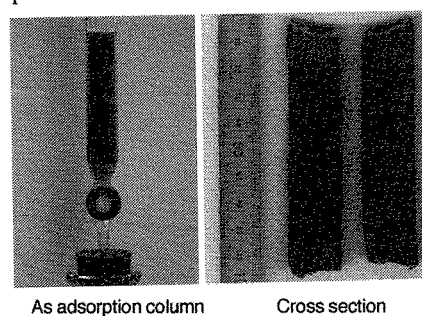


Fig. 1 Photographs of As adsorption column.

The pack method is a simple method for arsenic removal. The experiment was performed as follows. The arsenic concentration of the artificial arsenous solution which was used in this experiment was determined at 1 mg/dm³ from the arsenic concentration of drinking water in polluted area. An adsorption pack which has 2.0 g of acid treated adsorbent was thrown into 1 dm³ of the arsenous solution (Fig. 2). Then the solution was stirred slowly with a magnetic stirrer and some samples were collected for determination of arsenic concentration at varying times.

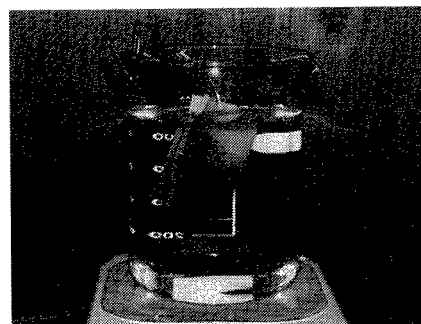


Fig. 2 Appearance of pack method.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction patterns and SEM photographs of manganese oxide compounds

Fig. 3 shows X-ray diffraction results for all adsorbents obtained in this study. The X-ray diffraction pattern of the adsorbent (Mn:Bi=1:0) had peaks of manganese dioxide which were formed because of the decomposition of manganese carbonate by calcination and undecomposed manganese carbonate.

The X-ray diffraction patterns of adsorbents, which were prepared by the addition of bismuth carbonate oxide, had clear peaks of bismuth oxide. The peaks of bismuth oxide increased depending on the mixture ratio of bismuth carbonate oxide. Base line of X-ray diffraction patterns of adsorbents prepared by small amount addition of bismuth carbonate oxide were not flat. The X-ray diffraction pattern of the adsorbent (Mn:Bi=1:0.09) had a broad peak at the 2 θ degree of 22 to 37. The broad peak may originate from amorphous manganese oxide compounds.

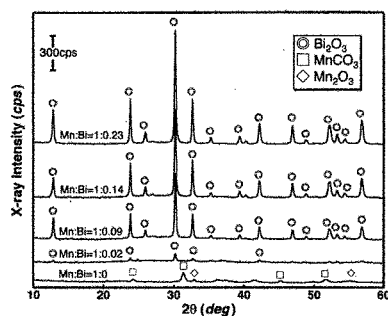


Fig. 3 X-ray diffraction patterns of manganese oxide compounds adsorbents.

Representative SEM photograph of an adsorbent is shown in Fig. 4. The particle size of adsorbent grain was 1 to 3 μm diameter and the surface of the grain was rough.

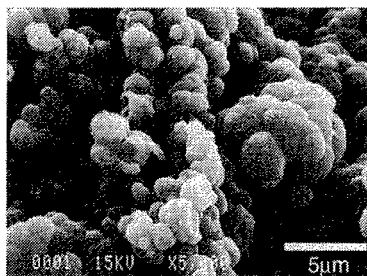


Fig. 4 SEM photograph of manganese oxide compounds grain.

3.2 Adsorption and desorption of arsenic ion

The relationship between adsorption amount of adsorbents and the mixture ratio of Mn:Bi is shown in Fig. 5. This figure indicates that the adsorbent has high efficiency of arsenic adsorption at around the mixture ratio of Mn:Bi=1:0.08. The high efficiency of arsenic adsorption at the mixture ratio is presumed by the reason that the added bismuth behaves like a catalyst which accelerates the arsenic adsorption on the surface of adsorbent grain. The X-ray photoelectron spectroscopy spectrum of an As adsorbed adsorbent is shown in Fig. 6. This spectrum suggests that a redox reaction did not occur on the adsorption process because of the oxidation number of As adsorbed on the adsorbent is three. The results of As desorption experiment are shown in Fig. 7. This diagram indicates that the rate of As desorption reached about 80 percent for 15 minutes in cases where hydrochloric acid or sulfuric acid were used for the desorption experiment. The results of the readsorption

experiment are shown in Fig. 8. It was found that the adsorbent desorbed by sulfuric acid has equivalent adsorption efficiency at first adsorption. The amount of arsenic adsorption decreased slightly because of the small amount of adsorbent was dissolved by the desorption. Fig. 9 shows the result of As desorption from actual waste water from a geothermal power plant. The As concentration of the waste water was decreased to the concentration level that satisfy the environmental standard of arsenic by dispersion of the adsorbent within 5 minutes.

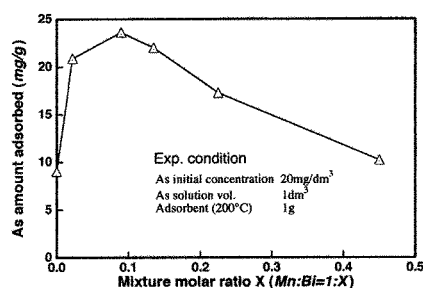


Fig. 5 Effect of mixture ratio on adsorption.

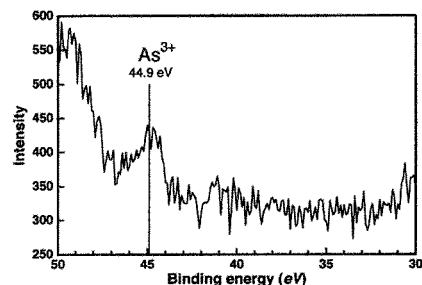


Fig. 6 XPS spectrum of adsorbent (after As adsorption).

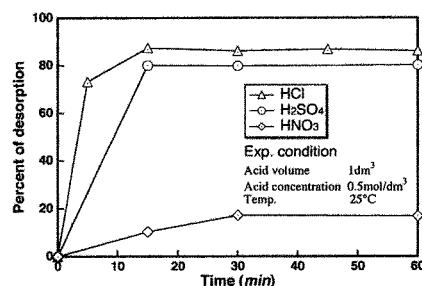


Fig. 7 Relationship between percent desorption and agitation time.

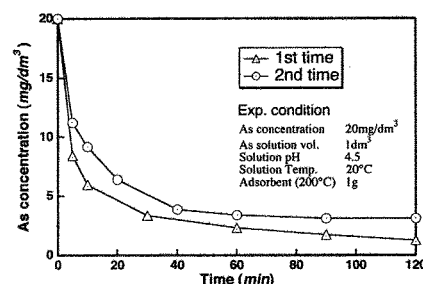


Fig. 8 Relationship between As concentration in test solution and agitation time.

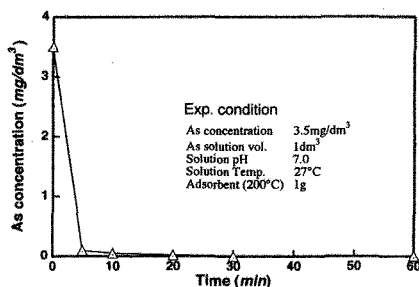


Fig. 9 Application of the adsorbent to a geothermal effluent.

3.3 Application of column method and pack method

Fig. 10 shows the result of As removing experiment with column method. The As concentration of the artificial arsenous acid solution was decreased below the lower limit of As detection by ICP in cases where the initial As concentrations were 1 mg/dm³ and 10 mg/dm³. The result of As desorption from the column is shown in Fig. 11. About 65 percent of As which was adsorbed to the column was desorbed by passing 600 cm³ of 0.5 mol/dm³ sulfuric acid through the column of adsorbent. The As concentration of the sulfuric acid in the eluted volume ranged from 0 to 50 cm³ was 120 mg/dm³, therefore, the As was concentrated at 10 to 100 times compared with the concentration of artificial arsenous acid solution.

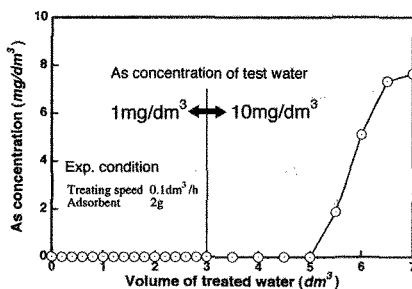


Fig. 10 Relationship between As concentration in treated water and volume of treated water in case of column method.

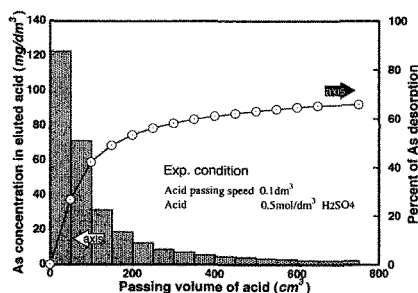


Fig. 11 Relationship among As concentration in eluted acid, percent of As desorption and passing volume of acid.

Fig. 12 shows the results of As removing experiment with pack method. The As concentration of treated water was decreased below the lower limit of As detection for 1 hour although the treating speed was slower than the case of direct putting. Therefore the

pack method is effective and simple method for As removing from the As polluted drinking water.

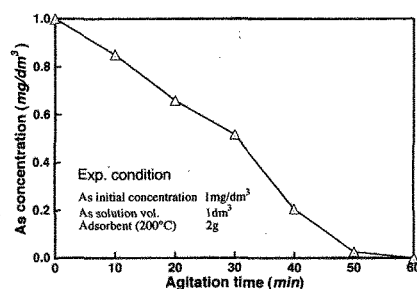


Fig. 12 Relationship between As concentration in test solution and agitation time in case of pack method.

4. CONCLUSIONS

The findings in this study are as follows. (1) It was found that the As adsorption ability of the manganese oxide compounds was promoted by the addition of Bi. (2) The manganese oxide compounds which have the capability of As adsorption in aqueous solution showed a X-ray diffraction pattern of an amorphous material. (3) The manganese oxide compounds showed the maximum ability of As adsorption at the mixture ratio of Mn:Bi=1:0.08. (4) The manganese oxide compounds adsorbent is able to reuse by desorption with sulfuric acid or hydrochloric acid. (5) The manganese oxide compounds are applicable to As removal from actual As wasted water which contains another components. We applied to remove As from aqueous solution by the column method and the pack method. The column method is appropriate for the treating of a large amount of waste water. And the pack method is effective and simple method for As removal from As polluted drinking water.

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