Adsorption behavior of arsenic with cobalt and manganese ferrites

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Abstract

Cobalt(Co) and manganese(Mn) ferrites were prepared to remove arsenic from the groundwater contaminated with arsenic. Co and Mn ferrites exhibited a high adsorption performance for arsenic in acidic and neutral media. Adsorption percentages of As(III) and As(V) using Co ferrite were higher than those using Mn ferrite in the region of pH 8 – 12. These results are due to a higher zero point of charge of Co ferrite more than that of Mn ferrite.

Keywords: Arsenic, Groundwater, Ferrite, Adsorption

1. INTRODUCTION

Arsenic is one of toxic elements. In nature, arsenic does not exist as a simple substance but as sulfide or minerals. These inorganic arsenic compounds are highly toxic than organoarsenic compounds. Among them arsenite has 60 times as toxicity of arsenate. Thus, the guideline value for arsenic in drinking water is defined as less than 0.01 mg dm^{-3} by WHO. However, in some areas such as China, West Bengal and Bangladesh, total arsenic concentration in groundwater has being observed over the standard value. On the other hand, arsenic is a useful element in the high-technology industries. It is used in process of manufacture of the glass in large quantities: green decoloration owing to the impurities such as iron compounds, and breaking down the foam generated in a melting process of the raw materials (Kaise, 2002). In addition, it has been widely used as a pesticide, the coloring agent of fireworks and paint. In particular arsenic is superior as a semiconductor material, therefore, semiconductor elements such as gallium arsenide and indium arsenide are produced. However, the increase in arsenic discharged from factories causes water pollution. Therefore, removal of arsenic from the environmental water is necessary.

We focused on the ferrites which was iron-based compound oxide as adsorbents of arsenic (Ohe, 2014). Ferrites are expressed in chemical formula MFe_2O_4 (M = Mn, Fe, Co, etc.), and a molar ratio of divalent metal ions and trivalent iron ion is 1:2. In addition, it can be collected easily by a magnet due to its magnetism. In this study, Co and Mn ferrites were prepared by co-precipitation method and their adsorption behavior for arsenic was investigated.

2. EXPERIMENTAL

2.1 Preparation and characterization of ferrites

Cobalt and manganese ferrites were prepared by a co-precipitation procedure. Each aqueous solution of MCl_2 (M = Co, Mn) and $FeCl_3$ was mixed at a molar ratio of 1:2. A 1.0 mol dm^{-3} NaOH solution was dropped into the aqueous mixture solution to adjust to pH 12 and the solution was stirred at 100 °C for 60 minutes. The precipitates were freeze-dried after washing by distilled water. The products were identified by a powder X-ray diffraction spectrometer (XRD) (X'Part – Pro MRD, Panalytycal). Zero points of charge (pH_{zpc}) of ferrites were determined by a nano particle analyzer (SZ-100, HORIBA). The BET surface area was determined by measuring an adsorption isotherm of N_2 at 77 K using a volumetric adsorption measurement instrument (BELSORP mini, BEL JAPAN). The mole ratio of M:Fe was determined by analyzing the solution of products dissolved in hydrochloric acid using an ICP-AES spectrometer (ICPS-7000, SHIMADZU).

2.2 Adsorption experiment

Adsorption experiments were carried out in a batchwise method. 15 cm^3 of aqueous arsenic solution (0.1 mmol dm^{-3}) and 10 mg of ferrites were mixed and

shaken in thermostated shaker at 303 K. After 24 h, the mixture was filtrated. The pH was adjusted using hydrochloric acid and aqueous NaOH solution. The concentrations of As(III) and As(V) were determined by ICP-AES spectrometer.

The amount of adsorption and the adsorption percentage of arsenic were calculated by the following equations,

$$q = (C_i - C_e)v/w \text{ [mmol/g]} \quad (1)$$

$$Adsorption\ percentage = (C_i - C_e)/C_i \times 100\ [\%] \quad (2)$$

where q is the amount of arsenic adsorbed [mmol g^{-1}], C_i is the initial concentration of arsenic [mmol dm^{-3}], C_e is the equilibrium concentration of arsenic [mmol dm^{-3}], v is the volume of solution [dm^{-3}], w is the amount of adsorbent [g].

3. RESULTS AND DISCUSSIONS

3.1 Characterization of ferrites

The products were identified with ferrites ($CoFe_2O_4$, $MnFe_2O_4$) by X-ray analysis. The specific surface areas, the mole ratio of M:Fe, and pH_{ZPC} were shown in Table 1. $CoFe_2O_4$ showed a larger specific surface area and a higher pH_{ZPC} than $MnFe_2O_4$.

Table 1 Properties of ferrites.

	$MnFe_2O_4$	$CoFe_2O_4$
Specific surface area [$m^2\ g^{-1}$]	110	216
Mole ratio of M/Fe [-]	0.467	0.508
pH_{ZPC}	7.40	8.90

3.2 Adsorption experiment

The effect of pH on the adsorption of As(III) and As(V) with ferrites ($CoFe_2O_4$, $MnFe_2O_4$) was shown in Figs. 1 and 2, respectively. The adsorption percentage of As(III) and As(V) was dependent on pH. The adsorption percentage of As(III) with $CoFe_2O_4$ showed over 80 % at pH < 8, and gradually decreased at pH > 8, then showed 60 % at pH 11. The adsorption percentage of As(III) with $MnFe_2O_4$ showed over 90 % at pH < 6.5, and gradually decreased at pH > 6.5, then showed 22 % at pH 11. Therefore, $CoFe_2O_4$ showed larger adsorption percentage at wider pH range than $MnFe_2O_4$. The adsorption percentage of As(V) of each ferrites showed over 90 % at 4 < pH < 6, and decreased at pH > 6, then showed 33 % and 6 % with $CoFe_2O_4$ and $MnFe_2O_4$, respectively, at pH11. These results indicate that the values of pH_{ZPC} of ferrites are very important factor for the adsorption of arsenic.

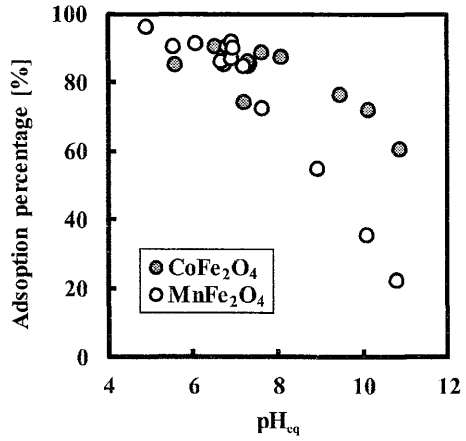

Fig. 1 Effect of pH on the adsorption of As(III) with ferrites.

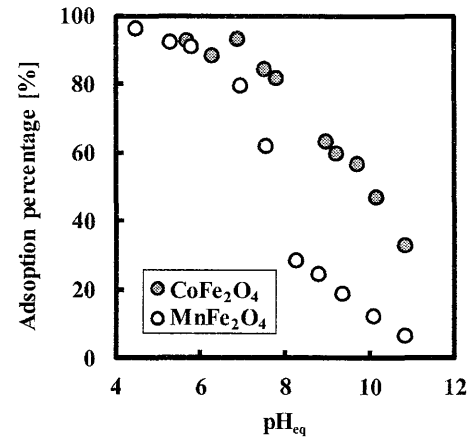

Fig. 2 Effect of pH on the adsorption of As(V) with ferrites.

4. REFERENCES

Kaise, T. (2002), Speciation of Arsenic Compounds in Biological Samples by High Performance Liquid Chromatography — Inductively Coupled Plasma Mass Spectrometry System, J. Plasma Fusion Res. 78(7), 646-652pp.

Ohe, K., Oshima, T., Baba, Y. (2014). Effect of ionic strength, temperature on equilibrium and kinetics of arsenic adsorption using magnetite, Kagaku Kogaku Ronbunshu, 40 (2), 90-97pp.

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