Removal of As(III) and As(V) in Groundwater Using Ferrite Adsorbents

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Abstract

Ferrite adsorbents containing magnesium, cobalt, nickel, zinc were prepared in order to remove As(III) and As(V). They are adsorbents with large specific surface area. The ferrite adsorbents could effectively adsorb As(III) and As(V) at neutral pH. The adsorption percentage of As(III) and As(V) onto cobalt ferrite was larger than the other ferrite adsorbents. The adsorption capacity of cobalt ferrite for As(III) and As(V) was 0.83 and 0.52 mmol/g, respectively. The adsorption capacities of As(III) and As(V) on magnesium ferrites increased with increasing their specific surface area, suggesting that functional groups on the surface participate in the adsorption.

Key words: ferrite, adsorption, As(III), As(V)

1 Introduction

The problems concerning the environmental pollution caused by toxic metals, especially in arsenic-contaminated groundwater and wastewater, have been spreading globally. Arsenic-contaminated wastewater is increasing in the field of the semiconductor industries, and its treatment has become a problem. It has been noted that arsenic-contaminated groundwater causes skin cancer and affects the liver, lungs and the other internal organs[1]. According to the last edition of the WHO (the World Health Organization) Guidelines for Drinking-Water Quality (1993): the guideline value for arsenic in drinking-water should be less than 0.01 mg/m³. Especially, in West Bengal, Bangladesh[2,3] and China, total arsenic concentration in groundwater contaminated have being observed over the standard value. Therefore, the removal of arsenic from drinking water and groundwater is very important.

In general, removal techniques for arsenic are precipitation/coagulation methods using metal salt such as aluminum chloride and ferric chloride, ion exchange, and adsorption[4]. Various types of adsorbents have been used for the removal of arsenic from contaminated groundwater. They are aluminum compounds such as activated alumina[5], rare earth compounds such as yttrium carbonate[6], iron compounds such goethite(α-FeOOH)[7], magnetite (Fe₃O₄)[8] and γ-Fe₂O₃. Many researchers have being studied in regard to iron compounds, which indicate the high affinity for arsenic. In previous report[8], magnetite was found to be good adsorbent towards both As(III) and As(V). In the present study, various ferrites as iron compounds having magnetic property such as magnetite were prepared to investigate their adsorption behavior for arsenic.
2 Experimental

2.1 Preparation and characterization of adsorbents

A set of ferrites were prepared by coprecipitation procedure. Each aqueous solution of $\text{M(NO}_3\text{)}_2$ (M=Co, Ni, Zn, Mg) and Fe(NO$_3$)$_3$ was mixed at a molar ratio of 1:2. Ni or Zn ferrite (Ni-F, Zn-F) was prepared by adding an ammonia solution into the aqueous mixture to adjust to pH7-8. The precipitates were calcined at 500°C for 3 h. Mg ferrite(Mg-F) was prepared using the method reported by Chen et al. [9]. The aqueous mixture solution was added into a 6M NaOH solution to form precipitates. The suspension was aged for 2 h in boiling water bath. After that the suspension was filtered and washed. The resultant powder was calcined under air at various temperatures in an electric furnace. Mg-F500, 800 and 1000 were prepared by calcinations at 500, 800 and 1000 °C, respectively. Co ferrite(Co-F) was prepared by the same procedure as magnetite[9]. A 6 mol/dm$^3$ NaOH solution was added to the aqueous mixture to adjust to pH 11. The precipitates after centrifugation were dried at 50°C after washing by distilled water.

The resulted products were subjected to X-ray analysis by using a Powder X-ray diffractometry (XRD) (RINT2000/PC, Rigaku) using Cu Kα radiation, the pHs at their zero point of charge(=pHzpc) were determined by an acid-base titration method in 0.1 mol/dm$^3$ aqueous sodium chloride solution and BET surface areas(=SSA) were determined from the adsorption isotherms of N$_2$ at 77 K using a constant volume adsorption apparatus (BELORP mini, Bel Japan). A mole ratio of M/Fe was determined by analyzing a solution of resulted products dissolved in hydrochloric acid using atomic adsorption spectrometer (Analyst 100, Perkin-Elmer) or an ICP/AIDS spectrometer (ICPS-7100, Shimadzu).

2.2 Adsorption experiment

Adsorption experiments were carried out in a batchwise method. Aqueous arsenic solution (15 cm$^3$, 0.13 mmol/dm$^3$) and 20 mg of ferrite adsorbents were mixed and shaken in a thermostated shaker at 303 K. After 24 h, the mixture was filtrated. The pH was adjusted using hydrochloric acid and aqueous sodium hydroxide solution. The concentrations of As(III) and As(V) were measured by atomic absorption spectrophotometer (AA6800, Shimadzu).

Here, the amount of adsorption and the adsorption percentage of arsenic were calculated according to the following equations, respectively:

$$q = \frac{(C_{\text{int}} - C_{\text{eq}}) v}{w} \text{[mmol/g]} \quad (1)$$

$$A = \frac{(C_{\text{int}} - C_{\text{eq}})}{C_{\text{int}}} \times 100 \% \quad (2)$$

where $C_{\text{int}}$ is the initial concentration of arsenic[mmol/dm$^3$], $C_{\text{eq}}$ is the equilibrium concentration of arsenic [mmol/dm$^3$], $v$ is the volume of solution [dm$^3$], $w$ is the amount of adsorbent[g], $q$ is the amount of arsenic adsorbed[mmol/g] and $A$ is adsorption percentage[%].

3 Results and Discussion

3.1 Characterization of adsorbents

The reflection peaks of the products were assigned to ferrites(CoFe$_2$O$_4$, NiFe$_2$O$_4$, ZnFe$_2$O$_4$ and MgFe$_2$O$_4$ whose JCPDS card numbers are 22-1086, 10-0325, 22-1012 and 17-09464, respectively). The composition ratio (M/Fe), specific surface area and pH$_{zpc}$ were shown in Table 1. A molar of M /Fe in ferrite prepared was approximately 0.5. The specific surface area of Mg ferrites increased with decreasing calcination temperature.
3.2 Adsorption of arsenic

The effect of pH on the adsorption of As(III) and As(V) with ferrite adsorbents such as Co-F, Ni-F, Zn-F, Mg-F500, 800 and 1000 was shown in Figs. 1 and 2, respectively. The adsorption of As(III) and As(V) was dependent on pH. As(III) and As(V) were adsorbed over 80% and 90%, respectively except for Mg-F800 and 1000. The adsorption of As(III) increased with decreasing pH in pH<7 and gradually decreased with increasing pH in pH>7, except for Mg-F. The adsorption of As(III) with Co-F showed larger adsorption percentage in wider pH range than the other adsorbents. The adsorption of As(V) greatly decreased with increasing pH. These results showed that the decrease of the adsorption for arsenic onto Ni-F, Zn-F, Co-F and Mg-F500 began to decrease at pH 6.7, 6.7, 7.3 and 10, respectively. These pHs were the same value as pHzpc of each adsorbent. Therefore it is considered that the pHzpc is very important property in the adsorption. Then As(III) was adsorbed 20% onto Mg-F800 at pH 9 and 0.5% onto Mg-F1000 in the region of pH 5-8. The adsorption percentage of As(III) with Mg-F500 was significantly large compared with Mg-F800 and 1000. It is seen from Table 1, Mg-F500 has very larger specific surface area than Mg-F800 and Mg-F1000. This result showed the specific surface area was also very important property as arsenic adsorbents.

In order to estimate the adsorption capacity of Co-F which indicated the larger adsorption percentage of As(III) and As(V) at the same neutral pH as groundwater, the relationship between the amount of adsorption of As(III) and As(V) and equilibrium concentration of arsenic at 30°C at pH 7 was plotted in Fig.3. These adsorption isotherms were fitted by the Langmuir equation as shown by the following equation,

\[
\frac{1}{q} = \frac{1}{Kq_{max}C_{eq}} + \frac{1}{q_{m}}
\]

where K and q_{max} are the adsorption equilibrium constant (dm³/mmol) and adsorption capacities (mmol/g), respectively. The q_{max}, K and the correlation coefficients of the adsorption of As(III) are 0.85 mmol/g, 7.24 dm³/mmol and 1.00, respectively, and those of the adsorption of As(V) are 0.52 mmol/g, 4.5 dm³/mmol and 0.99, respectively. The Langmuir equation was found to fit well with these adsorption isotherms. The adsorption capacities of Co-F for As(III) and As(V) are high compared to 0.277 and 0.228 mmol/g, respectively, as reported for MAG[8]. The adsorption capacities of As(III) and As(V) on Co-F were approximately 2-3 times more than that of each adsorbent.
Mg-F500, 800 and 1000 prepared by the different calcination temperatures had the different specific surface areas, as shown in Table 1. The adsorbent having the large specific surface is expected to adsorb more arsenic. The adsorption isotherms of As(III) onto Mg-F500, 800 and 1000 were also shown in Fig.4. These results were fitted by the Langmuir isotherm model (the correlation coefficients 0.99-0.98), except for Mg-F1000 which hardly adsorbed As(III). The specific surface area of Mg-F500 was greatly larger than Mg-F1000. The order of their adsorption was the same as that of the specific surface area. The decrease of the adsorption is also related with the decrease of the hydroxide groups to be adsorption sites on the adsorbent surface by dehydration condensation occurred at high temperature.

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