Article**Adsorption Behavior of Arsenic Using Spherical Porous Silica Particles Covered with Magnetite**

***Kaoru Ohe, Tatsuya Oshima and Yoshinari Baba**

*Department of Applied Chemistry, Faculty of Engineering,, University of Miyazaki, 1-1 Nishi Gakuenkibanadai,
Miyazaki 889-2192, Japan*

Yasuyuki Tagai

KINSEI MATEC CO.,LTD, 2-3-7 Hirano-cho, Chuo-ku, Osaka-shi, Osaka 541-0046, Japan

Masayuki Shimizu and Toshikazu Miyake

*Department of Chemical Engineering, Faculty of Engineering, Kansai University, 3-3-35 Yamate-cho, Suita-shi,
OSAKA 564-8680, Japan*

Toshihide Horikawa

*Department of Chemical Science & Technology, Faculty of Engineering, The University of Tokushima
2-1 Minamijosanjima-cho, Tokushima 770-8506, Japan*

(Manuscript submitted April 5, 2007; accepted June 28, 2007)

Abstract

The adsorption behavior of arsenic from water on spherical porous silica particles(SiMAG) covered with magnetite was investigated under batch equilibrium conditions at 303K. The specific surface area and the pH at zero point of charge of SiMAG were 540 m²/g and 4.6, respectively. Both of As(V) and As(III) were adsorbed on SiMAG. The adsorption of As(V) increased with decreasing pH, while that of As(III) was slightly dependent on pH. The adsorption capacity of SiMAG towards As(V) was 0.85 mmol/g.

Key words: silica, magnetite, arsenic removal, adsorption, spherical porous particles

1 Introduction

Arsenic is a carcinogen and a toxic element for humans. Arsenic is present in nature in both inorganic and organic forms. The toxicity of the inorganic form is higher than the organic form. The arsenic contamination in groundwater has become problem in Asian countries such as India, Bangladesh and China[1-3]. The contamination was caused by arsenic of inorganic form eluted from minerals. The drinking water including arsenic causes skin cancer and damages of liver and lungs for human. The patients of chronic arsenic poisoning have been increasing. In the WHO guidelines, the standard value of arsenic is less than 10 mg/m³[4]. Therefore, removal for arsenic from drinking water and groundwater is very important and urgent.

In order to remove arsenic, many researchers have been developing adsorbents such as iron oxides[5-11] which adsorb arsenic effectively. However since metal oxides are generally obtained as fine powders, their handling is difficult to utilize as the adsorbents[11,12]. In the previous report[10], magnetite particles effectively adsorbed arsenic. The particles containing magnetic materials such as magnetite can be collected easily using magnet. Wakui and co-workers investigated the adsorption of As(V) using resin beads containing magnetite

crystals and they reported the maximum capacity was 0.05 mmol/g[11]. Then, in the present study, the spherical porous silica particles as good adsorbent material covered with magnetite(SiMAG) were prepared to investigate the adsorption behavior of arsenic. SiMAG has also spherical porous particles. The porous structure of SiMAG was expected to increase the adsorption capacities of arsenic.

2 Experimental

2.1 Materials

Silica particles covered with magnetite(SiMAG) were obtained by a preparation method reported by Horikawa et al.[12]. Monodispersed spherical silica particles were prepared using tetraethoxy orthosilicate(TEOS), ethanol and 1-aminododecane as a surfactant and an alkali catalyst at 298K. The obtained spherical silica particles(wet) were dispersed in an aqueous iron(II) sulfate solution. The suspension was stirred at 298K for 24h. After the resulted product was dried at 383 K, it was calcined for 5 h at 773 K under CO₂.

2.2 Characterization of SiMAG

The resulted product was identified by Powder X-ray diffraction(XRD) measurement made on a Rigaku RINT2000/PC with Cu K α radiation. The pH at the zero point of charge(=pH_{zpc}) was determined by an acid-base titration method in 0.1mol/dm³ aqueous sodium chloride solution. Specific surface area(=SSA) was calculated by Brunauer-Emmett-Teller(BET) method using the nitrogen adsorption measurement at 77 K using BELSORP mini(BEL JAPAN, Inc). Surface condition and molar ratio of Fe/Si of SiMAG were observed by Scanning electron microscopy(SEM; Hitachi High-Technology, S-4100) and energy dispersive X-ray spectrometer(EDX; HORIBA Ltd., EMAX-5770), respectively.

2.3 Adsorption experiment

Adsorption experiments were carried out by a batchwise method. SiMAG of 5 mg was added to 0.08 mmol/dm³ arsenic solution (20 cm³) and its sample was shaken(120 rpm) at 303 K for 24h. The pH was adjusted using hydrochloric acid and aqueous sodium hydroxide solution. After filtration, the concentrations of As(III) and As(V) in filtrate were measured by atomic absorption spectrophotometer on a Shimadzu AA6800. Distribution ratio(cm³/g) was defined as $D = 1000q/C_{eq}$, where q and C_{eq} were the amount of arsenic adsorbed into 1 gram of the adsorbent(mmol/g) and remaining in 1 dm³ of the solution(mmol/dm³), respectively.

3 Results and Discussion

3.1 Characterization of SiMAG

Fig.1 SEM image of SiMAG

Fig.2 XRD pattern of SiMAG.

SiMAG was found to be 700 to 800 nm particles with smooth surface(Fig.1) with SEM. The BET specific surface area and pH_{zpc} were determined as $540 \text{ m}^2/\text{g}$ and 4.6, respectively. XRD pattern of SiMAG is shown in Fig.2. The broad diffraction peak of $2\theta = 25$ degree and the other peaks were assigned to silica and magnetite(JCPDS card No. 19-0629), respectively. A molar ratio of Fe/Si in SiMAG was obtained by EDX to be 0.07.

3.2 Effect of the pH

Figure 3 shows the distribution ratio of As(V) and As(III) as a function of pH. Arsenic(V) and As(III) were adsorbed on SiMAG and their adsorption behaviors were different. The adsorption of As(V) increased with decreasing pH in the region of pH 4-8. The adsorption of As(III) increased slightly in the region of pH 4-6 and decreased slightly in the region of pH 6-8. These similar adsorption tendencies were observed in the case of magnetite[10]. Silica could adsorb slightly As(V), however As(III) wasn't quite adsorbed [6]. These results should be considered that As(III) and As(V) were adsorbed by magnetite coated on silica. Figure 4 shows the ratio of chemical species of arsenate and arsenite against pH. As you can seen from Fig.4, the predominant species of As(V) and As(III) are H_2AsO_4^- , HAsO_4^{2-} and H_3AsO_3 , respectively in the region of pH 4-8. Therefore, As(V) as anion species can be effectively adsorbed by SiMAG, which is due to the electrostatic interaction with positively charged SiMAG. However the adsorption of As(V) decreased in this pH region because the electrostatic repulsion was occurred between the negative As(V) and SiMAG with the negatively charged surface at $pH > 4.6$. On the other hand, As(III) was adsorbed as neutral chemical species, H_3AsO_3 on SiMAG. Therefore, it was considered that As(III) was adsorbed by interaction among H_3AsO_3 and hydroxyl groups of SiMAG surface .

Fig.3 Effect of pH on the distribution ratio of As(V) and As(III) on SiMAG. (experimental conditions: 5 mg adsorbent in 20cm^3 solution containing 0.08 mmol/dm^3 As(V) or As(III) at 303K.

Fig.4 The ratio of chemical species of arsenate(As(V)) and arsenite(As(III)) against pH.

3.3 Adsorption isotherms for As(V) and As(III)

Adsorption isotherms were measured for both As(V) and As(III) on SiMAG at 303K. The results are shown in Fig.5. The adsorption behavior can be described by the Langmuir adsorption equation as

$$1/q = 1/(Kq_{\max}C_{eq}) + 1/q_{\max}$$

where K and $q_{\max}$ are the adsorption equilibrium constant (dm^3/mmol) and adsorption capacity (mmol/g). Langmuir model was found to fit well for the adsorption of As(V) and As(III) on SiMAG. The adsorption capacities of As(V) and As(III) were 0.85 mmol/g (approximately 3.5 times for magnetite) and 0.22 mmol/g , respectively. It should be noted that adsorption capacity of As(V) is much larger than that of As(III). Silica

selectively adsorbed As(V) in comparison to As(III). SiMAG was charged positively in lower pH than its pH_{zpc} . Therefore, As(V) existing as anionic species was selectively adsorbed compared with As(III) existing as neutral molecules in lower pH. In spite of a very low molar ratio of Fe/Si (0.07), SiMAG had the large adsorption capacity for As(V). It is expected that the adsorption capacity for As(V) increases greatly by increasing the molar ratio of Fe/Si in SiMAG because the adsorption of As(V) on magnetite is very larger than on silica.

Fig.5 Adsorption isotherms for As(V) and As(III) on SiMAG. at 303K (experimental conditions: 20 mg adsorbent in 20 cm^3 solution As(V) or As(III) at approximately pH 4.5)

References

- 1) Kadono, T. Inaoka, N. Maruyama, K. Yshijima, M. Nagano, S. Nakamura, C. Watanabe, K. Tmaki, R. Ohtsuka, (2002), *International Journal of Dermatology*, **41**, 841-846(2002).
- 2) A. V. Geen, H. Ahsan, A. H. Horneman, R. K. Dhar, Y. Zheng, I. Hussain, K. M. Ahmed, A. Gelman, M. Stute, H. J. Simpson, S. Wallace, C. Small, F. Parvez, V. Slavkovich, N. J. Lolacono, M. Becker, Z. Cheng, H. Momotaj, M. Shahnewaz, A. A. Seddique, and J. H. Graziano (2002), *Bulletin of the World Health Organization*, **80**, 732-737(2002).
- 3) F.C. Harbey, N. K., Ashfaq, W. Yu., A. B. M. Badruzzaman, M.A Ali, M. O. Oate, H.A. Michael, R.B. Neumann, *Chemical Geology*, **228**, 112-136(2006).
- 4) The World Health Organization Home Page, <http://www.who.int> (2007)
- 5) B.A. Manning, S. E. Fendorf, S. Goldberg, *Environ. Sci. Technol.*, **32**, 2383-2388(1998).
- 6) L. Zeng, *Wat Res.*, **37**, 4351-4358(2005).
- 7) Y. Wakui, T. Ebina, H. Matsunaga and T.M.Suzuki, *Anal. Sci.*, **18**, 793-798(2002).
- 8) H. Fukuoka, N. Shigemoto, H. Inomo and W. Shiraki, *J. Chem. Eng. Jpn.*, **39**, 948-955(2006).
- 9) R.L. Vaughan Jr. and B. E. Reed, *Wat. Res.*, **39**, 1005-1014(2005).
- 10) K.Ohe, Y. Tagai, S. Nakamura, T. Oshima and Y. Baba, *J. Chem. Eng. Jpn.*, **38**, 671-676(2005).
- 11) Y. Wakui, A. E Persulesy, T. Ikeda, T. Ebina, Y. Onodera and T.M.Suzuki, *Anal. Sci.*, **21**, 433-435(2005).
- 12) T. Horikawa, D. Ichimiya, M. Katoh, T. Tomida, J. Hayashi, and Y. Miyake, *Proc. Chemica 2005 in Brisbane, Australia*(2005)