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Characteristics of arsenic elution from sewage sludge†

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Characteristics of arsenic elution from sewage sludge were studied at different sludge pH values to develop a removal process for arsenic in sewage sludge. Forms of arsenic compounds (arsenious acid (As(III)), arsenic acid (As(V)), monomethylarsonic acid and dimethylarsinic acid) eluted from the sludge were analyzed using high-performance liquid chromatography–inductively, coupled plasma mass spectrometry. It was confirmed that four compounds of arsenic in the liquid phase separated from the sludge could be clearly classified and directly determined without being interfered with by coexistent matter dissolved from the sludge. An increase in sludge pH effectively increased the amount of arsenic eluted from the sludge. Although the sludge oxidation–reduction potential was increased by decreasing the sludge pH with sulfuric acid, the elution of arsenic was slight at pH 1. The predominant form of arsenic eluted from the sludge was arsenic acid at sludge pH 5, 7, 9 and 11, whereas it was arsenious acid at pH 1. Both monomethylarsonic and dimethylarsinic acids were insignificantly eluted at all of the pH values investigated. The form of arsenic dissolved from the sludge was found to almost correspond with that obtained from the Eh–pH diagram of arsenic in an aqueous system. It was concluded that elution of arsenic from sludge was promoted by increasing sludge pH and the dissolved arsenic existed mainly as arsenic acid at high pH. Copyright © 2001 John Wiley & Sons, Ltd.

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INTRODUCTION

Trace metals released from human and industrial activities enter into sewage and then they are concentrated into sewage sludge through primary and secondary sewage treatment processes.[1,2] In particular sewage treatment plants receiving wastewater from hot-spring facilities and paint factories produce sewage sludge containing a comparatively high concentration of arsenic in some cases. About 70% of sewage sludge (including incineration ash) is disposed to landfills and about 30% is reused as fertilizers or construction materials in Japan.[3] The presence of a toxic substance such as arsenic, in sewage sludge makes the disposal of the sludge extremely difficult because of the potential risk of environmental pollution. Therefore, it is necessary to reduce the content of toxic metals in sewage sludge.

Several leaching methods for heavy metals from sewage sludge have been investigated to remove toxic substances in the sludge.[4–7] These reports show that chemical or biological acidification of the sludge or oxidation of metal sulfide in the sludge effectively elute heavy metals contained in the sludge. Carbonell-Barrachina and coworkers reported conditions to reduce the solubility of arsenic in sewage sludge and sewage sludge-amended soil with the aim of restricting arsenic elution.[8,9] However, as yet there is no approach to the removal of arsenic from sludge.

Arsenic exists as various compounds in the environment. The form of arsenic changes with pH and oxidation–reduction potential (ORP) at an equilibrium state in an aqueous system.[10] Some methods have been proposed to analyze arsenic

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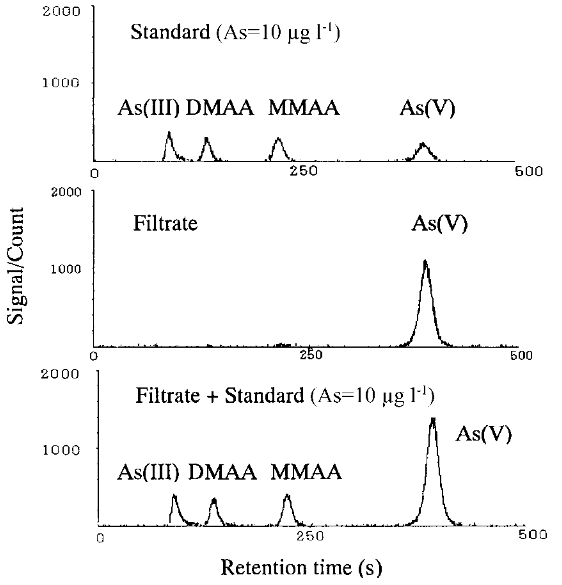

Figure 1 Signal/count chromatograph of arsenic compounds in three samples by HPLC–ICP-MS.

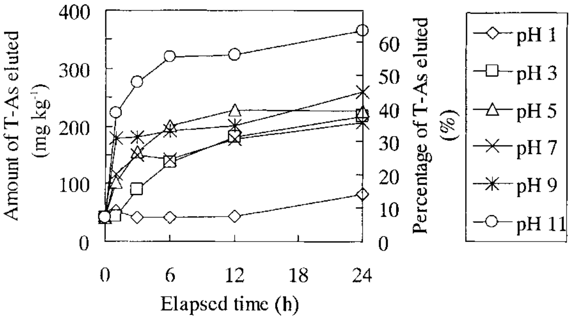

Figure 2 Variation of amount of T-As eluted from sewage sludge at different pH values with time.

forms in various samples.[11–15] Among them, an inductively coupled plasma-mass spectrometer (ICP-MS) equipped with a high-performance liquid chromatography (HPLC) can easily classify arsenic in solution into four forms (arsenious acid (As(III)), arsenic acid (As(V)), monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA)) and measure their concentrations with high sensitivity.[14,15] Therefore, analysis of arsenic forms in the liquid phase of the sludge by HPLC–ICP-MS would be useful for understanding the mechanism of arsenic elution from the sludge with change in pH or ORP.

The purpose of this study was to clarify characteristics of arsenic elution from sewage sludge to establish an efficient removal process for arsenic in the sludge. Elution experiments of arsenic from sludge were conducted using batch reactors. Furthermore, forms of arsenic eluted from the sludge at different pH values were analyzed by HPLC–ICP-MS and the mechanism of arsenic elution was discussed by comparing experimental results with the Eh–pH diagram, showing the form of arsenic at equilibrium in an aqueous system.

MATERIALS AND METHODS

Sewage sludge used in this study was taken from the thickener in a sewage treatment plant in Miyagi Prefecture, Japan. This plant receives effluent containing arsenic from hot-spring hotels and inns and treats sewage by an oxidation ditch process. Solid concentration, pH and ORP of the sludge were 19 g l^{-1}, 7.1 and −0.17 mV respectively. The ORP was measured with a pH meter (TOA, HM-5S) using a redox combination electrode (TOA, PTS-5011C). The total arsenic (T-As) content of the sludge was measured with an atomic absorption spectrophotometer (Shimadzu, AA-680) equipped with a hydride vapor generator (Shimadzu, HVG-1) after decomposing the sludge with nitric, perchloric and sulfuric acids.[16] T-As was 576 mg per kilogram of dry sludge.

Elution experiments for arsenic from sewage sludge were carried out using shaking 1 l flasks. The flasks containing the sludge at 19 g l^{-1} were agitated with a shaker at 120 rpm and 25 °C under an open system for 24 h. The sludge pH values were kept at 1, 3, 5, 7, 9 and 11 with sulfuric acid and sodium hydroxide throughout the experiment. Sludge (of 50 ml) taken from the flask was centrifuged at 10 000 rpm for 10 min and then the supernatant was filtered using a glass fiber filter with pore size 0.6 µm (Advantec, GS 25) to analyze the concentration of arsenic eluted from the sludge. The filtrate was defined as the liquid phase of the sludge. The concentration of T-As in the filtrate was measured by the same method as the arsenic content of the sludge. Classification and determination of four arsenic compounds (As(III), As(V), MMAA and DMAA) in the above filtrate was conducted using an ICP-MS (Yokogawa Analytical Systems, HP-4500) equipped with HPLC (Shimadzu, LC-10ATvp) utilizing an anion-ion-exchange column (Hitachi Chemical Co., Gelpack GL-IC-A15). A 2 mM phosphoric acid buffer solution containing 0.2 mM EDTA-2Na (pH 6) was used as the mobile phase of the column.[14] The

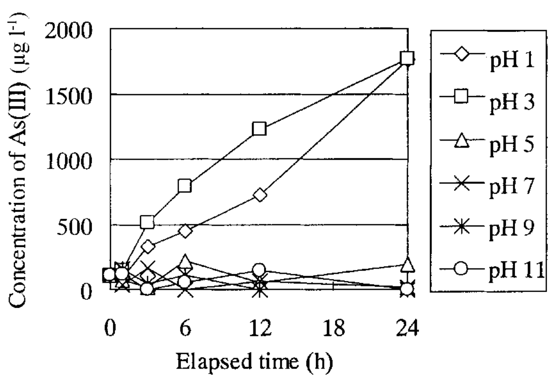

Figure 3 Variation of As(III) in the filtrate of sewage sludge at different pH values with time.

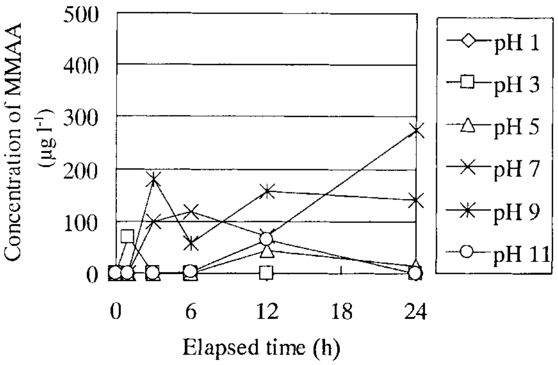

Figure 5 Variation of MMAA in the filtrate of sewage sludge at different pH values with time.

flow rate of the mobile liquid was 1.0 ml min^{-1} and the injection volume was 50 µl. The column temperature was kept at 40 °C. Three samples were prepared by diluting 1 ml of the standard solution, 1 ml of the filtrate and 1 ml of both the standard solution and the filtrate to 100 ml (so as to contain 2 ml of 250 mM phosphoric acid buffer solution) with pure water obtained from a New Milli-Q system (Nihon Millipore). The standard solution contained four kinds of pure arsenic compound (As(III), As(V), MMAA and DMAA). The concentrations of arsenic compounds in the standard solution, the filtrate and their mixture were measured and compared to investigate the influence of coexistent matter in the filtrate on the analysis of arsenic.

RESULTS AND DISCUSSION

Figure 1 shows signal/count chromatograms of arsenic compounds in three samples containing the standard solution of 10 µg-As/L of As(III), As(V), MMAA and DMAA, the filtrate obtained by the elution experiment with sludge at pH 5 and their mixture by HPLC–ICP-MS. The total organic carbon (TOC), solids concentration and electric conductivity of the sample containing the filtrate were 1.21 mg l^{-1}, 54.6 mg l^{-1} and 0.11 mS cm^{-1} respectively. This indicates that the filtrate contains various matters eluted from the sludge besides arsenic compounds. It can be seen that arsenic in the standard solution, the filtrate and the mixture could be clearly classified into four forms. Other arsenic compounds were not observed in the filtrate. The recovery percentages of four standards calculated from the difference in signal/count between the filtrate and the mixture were as follows: 97.5% of As(III), 106.6% of As(V), 100.4% of MMAA and 105.1% of DMAA. From these results, it was confirmed that the four compounds of arsenic in the filtrate could be clearly classified and directly determined without interference by coexistent matter dissolved from the sludge used in this study.

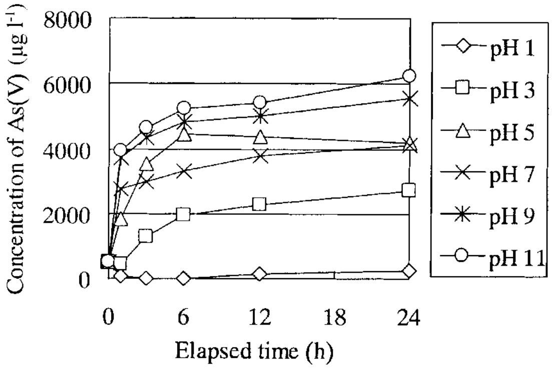

Figure 4 Variation of As(V) in the filtrate of sewage sludge at different pH values with time.

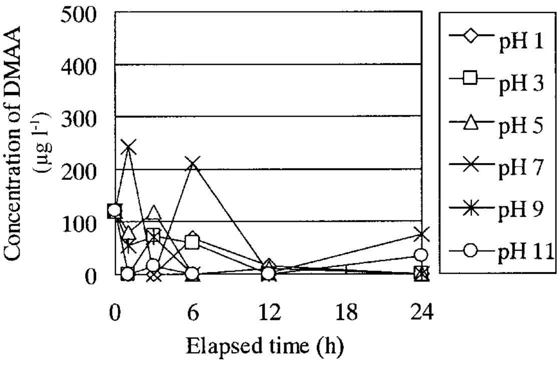

Figure 6 Variation of DMAA in the filtrate of sewage sludge at different pH values with time.

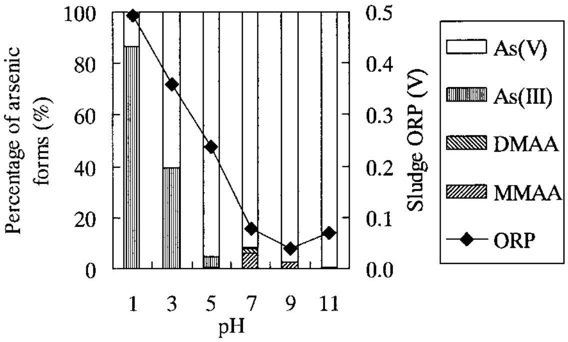

Figure 7 Percentage of each arsenic compound and sludge ORP at different pH values after 24 h of elution experiment.

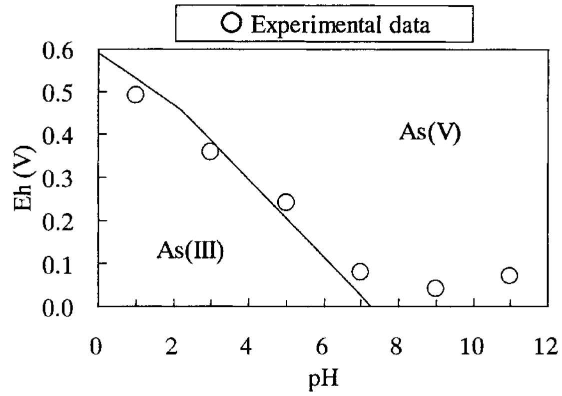

Figure 8 Eh–pH diagram illustrating the predominant form of dissolved inorganic arsenic at equilibrium in an aqueous system.

Figure 2 shows the variation of the amount of T-As eluted from the sewage sludge at different pH values with time. At pH ≥ 3, the amount of T-As eluted increased significantly as time passed, whereas it gradually increased at pH 1. An increase in the sludge pH enhanced the final T-As. It was found that arsenic in the sewage sludge used in this study could be effectively removed from the sludge by increasing sludge pH. Figures 3, 4, 5 and 6 respectively show the variation of the concentration of As(III), As(V), MMAA and DMAA in the filtrate of sewage sludge at different pH values with time. The concentration of As(V) increased rapidly at pH ≥ 3, whereas that of As(III) increased gradually at pH ≤ 3. The concentrations of both MMAA and DMAA were much lower than those of As(III) or As(V) at all pH values. This shows that organic arsenic compounds, such as MMAA and DMAA, remain in the sludge even if the sludge pH is changed to an extremely low or high value or that their contents in the sludge used in this study were slight.

Figure 7 shows the percentage of each arsenic compound and the sludge ORP at different pH values after 24 h of the elution experiment. The total amount of the four arsenic compounds corresponded to that of T-As eluted from the sludge at pH ≤ 9. In addition to the peaks for the four arsenic compounds, there is a hint of another peak at pH 11, although the identity of this substance remains unclear. It is seen that the major form of arsenic eluted from the sludge was As(III) at pH 1 and As(V) at pH ≥ 5, thus being clearly dependent on the sludge pH. The final sludge ORP was higher than the initial one at all pH values and increased as the sludge pH decreased. This could be due to the supply of oxygen to the sludge caused by agitation under the open system and the addition of sulfuric acid leading to an increase in the concentration of sulfate ions.

Figure 8 shows the Eh–pH diagram illustrating the predominant form of dissolved inorganic arsenic at equilibrium in an aqueous system. Eh was calculated using standard free energies of formation $\Delta G_f°$ for the arsenic species shown in Table 1.[10] By comparing this diagram with experimental results, it was found that the form of arsenic dissolved from sewage sludge almost corresponded with that at equilibrium. The relationship between the amount of T-As eluted from the sludge (Fig. 2) and the arsenic form (Figs 3 and 4) indicates that pH and ORP values at which arsenic can exist as As(III) would inhibit the elution of arsenic from the sludge. Carbonell-Barrachina *et al.* reported that most of the arsenic in sewage-sludge-amended soil remained bound to organic matter or sulfide even under highly aerobic conditions in the range of pH from 4 to 8.[8] It has been reported that several heavy metals in sewage sludge are efficiently removed by decreasing the sludge pH to approximately 2.[6] Therefore, a further increase in

Table 1 Standard free energies of formation for arsenic species at 25 °C and 1 atm

Species	H_3AsO_4	$H_2AsO_4^-$	$HAsO_4^{2-}$	AsO_4^{3-}	H_3AsO_3	$H_2AsO_3^-$	$HAsO_3^{2-}$
$\Delta G_f°$ (kJ mol^{-1})	−769.9	−757.3	−717.6	−651.9	−646.0	−593.3	−524.3

the sludge ORP by addition of an oxidation agent, such as ferric sulfate, would be required to remove arsenic effectively together with other metals from the sludge at a significantly low pH.[17]

The amount of T-As eluted from the sludge increased with an increase in the pH (Fig. 2). This could be due to the exchange of arsenic compounds being bound to an anion-ion-exchanger, such as monovalent organic ligands or metals in the sludge, as hydroxide (OH^-) is added to the sludge, as shown in Eqns [1] and [2].[18]

$$(3-n)R^+, H_nAsO_4{}^{(3-n)^-} + (3-n)OH^- \rightleftharpoons (3-n)R^+, OH^- + H_nAsO_4{}^{(3-n)^-} \quad [1]$$

$$(3-n)R^+, H_nAsO_3{}^{(3-n)^-} + (3-n)OH^- \rightleftharpoons (3-n)R^+, OH^- + H_nAsO_3{}^{(3-n)^-} \quad [2]$$

where R^+ is the anion-ion-exchanger and $n = 0$, 1 or 2.

However, the form of arsenic in the sludge solid phase and the change in the form of arsenic after elution remains unresolved and further studies are required.

CONCLUSIONS

In this study, elution experiments for arsenic from sewage sludge were carried out at sludge pHs of 1, 3, 5, 7, 9 and 11 using batch reactors. Application of HPLC–ICP-MS could classify arsenic eluted from the sludge into four forms (As(III), As(V), MMAA and DMAA) and measure their concentrations without being interfered with by coexistent matter. Arsenic in the sludge was effectively eluted from the sludge by increasing the sludge pH. The major form of arsenic eluted from the sludge was As(III) at pH 1 and As(V) at $pH \geq 5$ and was clearly dependent on the sludge pH and ORP. It was suggested that arsenic in sewage sludge could be removed efficiently by changing the pH or ORP of the sludge so as to transform the form of arsenic into As(V).

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REFERENCES

1. Oliver BG, Gosgrove EG. The efficiency of heavy metal removal by a conventional activated sludge. *Water Res.* 1974; **8**: 869.
2. Stephenson T, Lester JN. Heavy metal behaviour during the activated sludge process II. Insoluble metal removal mechanisms, *Sci. Total Environ.* 1987; **63**: 215.
3. Japan Sewage Works Association. *Sewage Works in Japan 1997.*
4. Jenkins RL, Scheybeler BJ, Smith ML, Baird R, Lo MP, Haug RT. Metals removal and recovery from municipal sludge, *J. WPCF* 1981; **53**(1): 25.
5. Olver JW, Kreye WC, King PH. Heavy metal release by chlorine oxidation of sludges, *J. WPCF* 1975; **47**(10): 2490.
6. Tyagi RD, Couillard D, Tran F. Heavy metals removal from anaerobically digested sludge by chemical and microbiological methods, *Environ. Pollut.* 1988; **50**: 295.
7. Ito A, Umita T, Aizawa J, Kitada K. Effect of inoculation of iron oxidizing bacteria on elution of copper from anaerobically digested sewage sludge, *Water Sci. Technol.* 1998; **38**(2): 63.
8. Carbonell-Barrachina A, Jugsujinda A, Delaune RD, Patrick Jr WH. The influence of redox chemistry and pH on chemically active forms of arsenic in sewage sludge-amended soil, *Environ. Int.* 1999; **25**(5): 613.
9. Carbonell-Barrachina AA, Jugsujinda A, Burlo F, Delaune RD, Patrick Jr WH. Arsenic chemistry in municipal sewage sludge as affected by redox potential and pH, *Water Res.* 2000; **34**(1): 216.
10. Ferguson JF, Gavis J. A review of the arsenic cycle in natural waters, *Water Res.* 1972; **6**: 1259.
11. Inoue Y, Kawabata K, Takahashi H, Endo G. Determination of arsenic compounds using inductively coupled plasma mass spectrometry with ion chromatography, *J. Chromatogr. A* 1994; **675**: 149.
12. Inoue Y, Date Y, Yoshida K, Chen H, Endo G. Speciation of arsenic compounds in the urine of rats orally exposed to dimethylarsinic acid ion chromatography with ICP-MS as an element-selective detector, *Appl. Organomet. Chem.* 1996; **10**: 707.
13. Pal BK, Chakraborty D, Dey G. Indirect Spectrofluorimetric determination of arsenic at nanotrace levels in alloys, underground water, industrial waters and sewage sludge, *Mikrochim. Acta* 1997; **127**: 203.
14. Sakai T, Inoue Y. Optimization of separation conditions for the speciation of anionic arsenic species using LC-ICP-MS, *Ind. Water* 1998; (**481**): 14 (in Japanese).
15. Inoue Y, Sakai T, Sawada Y, Nojima Y, Asami M, Aizawa T, Magara Y. Speciation of arsenic species in environmental water using LC-ICP-MS, and a comparative study to current testing methods, *J. Jpn. Water Works Assoc.* 2000; **69**(3): 24 (in Japanese).
16. Japan Sewage Works Association. *Testing Methods for Sewage*, 1997; (in Japanese).
17. Ito A, Umita T, Aizawa J, Takachi T, Morinaga K. Removal of heavy metals from anaerobically digested sewage sludge by a new chemical method using ferric sulfate, *Water Res.* 2000 **34**(3): 751.
18. Freiser H, Fernando Q. *Ionic Equilibria in Analytical Chemistry*, John Wiley & Sons: New York, 1963.