Arsenic Recovery from Water Containing Arsenite Ions by Hydrothermal Mineralization

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Here, we demonstrated the recovery of arsenic from water containing various concentrations of arsenite ions by hydrothermal mineralization treatment using the mineralizer $Ca(OH)_2$. As a result, it was found that the yield recovery of hydrothermal mineralization treatment is independent of initial concentration and arsenic valence. Therefore, the present technique is effective for treating water contaminated by arsenic species.

Arsenic is known as toxic element for human being,[1] especially, in case of arsenite ion ($As^{III}O_3{}^{3-}$). Several methods to remove arsenic from aqueous media were reported[2] by using adsorption,[3–5] electro-coagulation,[6,7] membrane,[8,9] and biological method.[10–12] However, these processes have problems of (1) Removal yield is low, especially, arsenite ion. (2) The applicable range of arsenic concentration is limited. (3) Adsorbent or collected residues must be treated as hazardous waste. In order to solve these problems, it is expected that the establishment of precipitation method to form insoluble arsenic compound is effective. In the previous study, we proposed that hydrothermal mineralization, which is an earth-mimetic process of formation of natural mineral by activity of magma.[13,14] Thus, we investigated the arsenic recovery from water by this technique.

Model wastewaters containing 1–2000 mg/dm^3 of arsenite ions ($As^{III}O_3{}^{3-}$) were prepared by dissolving As_2O_3 in 0.5 M NaOH solution and neutralizing by HCl in distilled and deionized water. And then, the model wastewaters (30 dm^3) were sealed in a pressure vessel lined with fluorocarbon resin together with mineralizer $Ca(OH)_2$ and in some cases, with H_2O_2 as oxidizer.

Treatment time dependence of As concentration in the model wastewater treated at 150 °C with or without 5% of H_2O_2 is shown in Figure 1. Precipitate containing arsenic was found only by adding $Ca(OH)_2$ to the model wastewater (without hydrothermal conditions), and then the concentration of As was reduced down to 4 mg/dm^3. In the hydrothermal mineralization of this model wastewater with $Ca(OH)_2$, As concentration showed concave curves against treatment time. The increase of As concentration at longer treatment-time region was caused by the nature of As compound produced by the treatment as will be described later. The optimal treatment condition was found at the As concentration reduced to ca. 0.4 mg/dm^3, which is one tenth of As concentration before hydrothermal treatment. However, this concentration is still higher than the national effluent standards of Japan (NESJ: 0.1 mg/dm^3). On the other hand, the addition of H_2O_2 effectively reduced the As concentration down to 0.02 mg/dm^3 under optimal hydrothermal condition, which is lower than the NESJ. This result indicates that the hydrothermal mineralization is effective method to recover arsenite from aqueous media as precipitate, even when the model wastewater contains large amount of arsenite. Therefore, the arsenic recovery mechanism in this treatment is supposed different from that of the conventional lime precipitation method.[15,16]

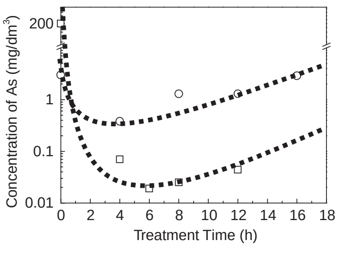

Figure 1. Dependence of the concentration of As in the treated-water on treatment time: As, 2000 mg/dm^3; $Ca(OH)_2$, 0.36 g. ○, 150 °C without H_2O_2; □, 150 °C, with 5% H_2O_2.

From XRD, SEM-EDS, and TG-DTA analyses of the precipitates obtained by the addition of $Ca(OH)_2$ only, the chemical formula of the precipitate was identified as $Ca_5(AsO_3)_3(OH)\cdot 4H_2O$. The analyses of the precipitates after the hydrothermal treatment showed that the crystal water in $Ca_5(AsO_3)_3(OH)\cdot 4H_2O$ was eliminated by hydrothermal mineralization treatment. Additionally, the solubilities of $Ca_5(AsO_3)_3(OH)\cdot 4H_2O$ and $Ca_5(AsO_3)_3(OH)$ to water were found 137.9 and 291.0 mg As/dm^3, respectively, by a simple solubility test. Therefore, the concave tendency in Figure 1 was caused by the elimination of crystal water from $Ca_5(AsO_3)_3(OH)\cdot 4H_2O$ with an increase in the treatment time according to the reaction in Scheme 1f. The concentration of As in the treated-water was lower than the solubility of these compounds. This tendency can

(a) $H_2O_2 + Ca(OH)_2 \rightarrow CaO_2 + 2H_2O$
(b) $2CaO_2 + 2H_2O \rightarrow 2Ca(OH)_2 + O_2$
(c) $H_2O_2 \rightarrow H_2O + 1/2O_2$
(d) $CaO + H_2O \rightarrow Ca(OH)_2$
(e) $3AsO_3{}^{3-} + 5Ca(OH)_2 + 4H_2O \rightarrow Ca_5(AsO_3)_3(OH)\cdot 4H_2O + 9OH^-$
(f) $Ca_5(AsO_3)_3(OH)\cdot 4H_2O \rightarrow Ca_5(AsO_3)_3(OH) + 4H_2O$
(g) $Ca_5(AsO_3)_3(OH) \rightarrow 3AsO_3{}^{3-} + 5Ca^{2+} + OH^-$
(h) $AsO_3{}^{3-} + CaO_2 \rightarrow AsO_4{}^{3-} + CaO$
(i) $AsO_3{}^{3-} + H_2O_2 \rightarrow AsO_4{}^{3-} + H_2O$
(j) $3AsO_4{}^{3-} + 5Ca(OH)_2 \rightarrow Ca_5(AsO_4)_3(OH) + 9OH^-$

Scheme 1. Possible reactions in the hydrothermal treatment.

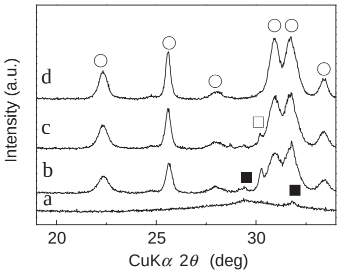

Figure 2. XRD patterns of the precipitates obtained by hydrothermal mineralization at 100 °C with $Ca(OH)_2$ and 5% of H_2O_2. As, 2000 mg/dm^3. (a) before the treatment, (b) 4 h, (c) 6 h, (d) 18 h. ○, $Ca_5(AsO_4)_3(OH)$; ■, CaO_2; □, $Ca_5(AsO_3)_3(OH)$.

be explained by a low solubility of these compounds under hydrothermal condition and/or by the slow solubility rate with relatively large crystal size. Figure 2 shows the XRD patterns of precipitates obtained before and after the hydrothermal treatment using both $Ca(OH)_2$ and 5% of H_2O_2. The peaks of $Ca_5(AsO_3)_3(OH){\cdot}H_2O$ and $Ca_5(AsO_4)_3(OH)$ (arsenate apatite) were observed in all the XRD patterns of the precipitates obtained by 4–8 h treatments. Finally, the diffraction peaks changed to $Ca_5(AsO_4)_3(OH)$ only. These results indicate that the oxidation of arsenite to arsenate occur in the presence of H_2O_2. This valence change by oxidation is also evident from the XPS spectra of As 3d orbital of them. Thus, the coexistence of H_2O_2 with $Ca(OH)_2$ immediately gives rise to the oxidation of As^{III} and will simultaneously produce arsenate apatite which is known as one of the natural minerals. Additionally, solubility of arsenate apatite is very low (19.5 mg/dm^3).[16] Therefore, it is found that the hydrothermal mineralization with $Ca(OH)_2$ and H_2O_2 is effective to reduce the concentration of As in the water containing As^{III} ions, which are usually difficult to remove. The treatment-time dependence of As concentration showed a concave tendency, even when H_2O_2 is added (cf. Figure 1). This result indicates the As^{III} species are still remain in water. However, the As concentration after the hydrothermal treatment for 12 h is lower than the NESJ.

Figure 3 shows the initial concentration dependence of the As concentration after the hydrothermal mineralization using $Ca(OH)_2$ and H_2O_2 at 100 °C for 12 h. The residual As concentration in the wastewater after hydrothermal mineralization was reduced to less than 0.1 mg/dm^3 except for the case of the wastewater containing 2000 mg/dm^3 of As. Moreover, it was mostly independent on the initial As concentration. From XRD analysis, the crystalline phase of As compound at 1000 mg/dm^3 was $Ca_5(AsO_4)_3(OH)$ (Other conditions could not be measured because of its low concentration). This result means that the As concentration after the treatment may be provided by only the solubility of the precipitate produced during the hydrothermal mineralization, if the amount of H_2O_2 is enough to convert the As^{III} ions into the As^{V} ions. Because, the addition of 5% of H_2O_2 achieved the As concentration reduction to less than 0.1 mg/dm^3, even when As concentration was 2000 mg/dm^3. This result suggests that the lowest limit of added H_2O_2 amount may be fixed by the initial concentration of As in water. The lowest requirement of H_2O_2 concentration can be estimated as approximately 50 times mole against arsenite concentration in the solution. Scheme 1 shows possible reactions among the treatment. It is expected that the optimum amount of H_2O_2 also depended on the added amount of $Ca(OH)_2$, because H_2O_2 was consumed by reacting not only with As^{III} ion but also with $Ca(OH)_2$ (Schemes 1a, 1b, 1c, and 1d). Two reactions occur (Schemes 1a and 1e) and form CaO_2 and $Ca_5(AsO_3)_3(OH){\cdot}4H_2O$ when we add $Ca(OH)_2$ and H_2O_2 in the model wastewater. The reactions shown in Schemes 1a, 1b, 1c, and 1d which are decomposition of H_2O_2 and reduction of CaO_2, proceed according to hydrothermal treatment. Simultaneously, four reactions occur concerning the formation of arsenate apatite from arsenite (cf. Schemes 1g, 1h, 1i, and 1j). The reaction to produce arsenate apatite (Scheme 1j) would be solid–liquid phase reaction. Because, residual concentration of As increased with decreasing added amount of $Ca(OH)_2$ (cf. Supporting Information). Thus, it is expected that the $Ca(OH)_2$ precipitate is necessary to form arsenate apatite. Therefore, excess amount of $Ca(OH)_2$ had to added against the stoichiometric quantities to form arsenate apatite (0.36 g). These reactions are required to produce precipitate of arsenate apatite from aqueous media containing arsenite ion and to induce the hydrothermal mineralization treatment effectively.

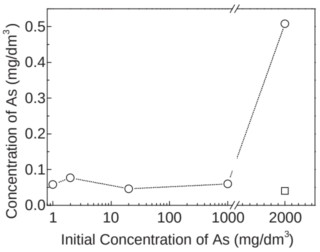

Figure 3. Dependence of the concentration of As in the treated-water on initial concentration of arsenic. $Ca(OH)_2$, 0.36 g. ○, 3% H_2O_2, 100 °C; □, 5% H_2O_2, 150 °C.

In conclusion, this treatment enables effective recovery of arsenic in water. Additionally, the As concentration in treated-water is independent on initial concentration of As, because, it depends only the solubility of $Ca_5(AsO_4)_3(OH)$. Therefore, it can apply any type of wastewater containing arsenic species.

References and Notes

1 M. Bissen, F. H. Frimmel, *Acta Hydrochim. Hydrobiol.* **2003**, *31*, 97.
2 E. O. Kartinen, Jr., C. J. Martin, *Desalination* **1995**, *103*, 79.
3 S. Bang, M. D. Johnson, G. P. Korfiatis, X. Meng, *Water Res.* **2005**, *39*, 763.
4 L. C. Roberts, S. J. Hug, T. Ruettimann, M. M. Billah, A. W. Khan, M. T. Rahman, *Environ. Sci. Technol.* **2004**, *38*, 307.
5 Y. Kim, C. Kim, I. Choi, S. Rengaraj, J. Yi, *Environ. Sci. Technol.* **2004**, *38*, 924.
6 N. Melitas, M. Conklin, J. Farrell, *Environ. Sci. Technol.* **2002**, *36*, 3188.
7 P. R. Kumar, S. Chaudhari, K. C. Khilar, S. P. Mahajan, *Chemosphere* **2004**, *55*, 1245.
8 Ma. de Lourdes Ballinas, E. R. de San Miguel, Ma. T. de Jesús Rodríguez, O. Silva, M. Muñoz, J. de Gyves, *Environ. Sci. Technol.* **2004**, *38*, 886.
9 H. Okada, Y. Kudo, H. Nakazawa, A. Chiba, K. Mtsuhashi, T. Ohara, H. Wada, *IEEE Trans. Appl. Supercond.* **2004**, *14*, 1576.
10 C. T. Kamala, K. H. Chu, N. S. Chary, P. K. Pandey, S. L. Ramesh, A. R. K. Sastry, K. C. Sekhar, *Water Res.* **2005**, *39*, 2815.
11 I. A. Katsoyiannis, A. I. Zouboulis, *Water Res.* **2004**, *38*, 17.
12 M. X. Loukidou, K. A. Matis, A. I. Zouboulis M. Liakopoulou-Kyriakidou, *Water Res.* **2003**, *37*, 4544.
13 T. Itakura, R. Sasai, H. Itoh, *Water Res.* **2005**, *39*, 2543.
14 T. Itakura, R. Sasai, H. Itoh, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1303.
15 J. V. Bothe, Jr., P. W. Brown, *Environ. Sci. Technol.* **1999**, *33*, 3806.
16 J. V. Bothe, Jr., P. W. Brown, *J. Hazard. Mater.* **1999**, *69*, 197.

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