2P4-4

Removal of arsenite from aqueous solutions using ultrasonic irradiation in the presence of a lead electrode

鉛電極存在下における超音波照射を用いた水溶液中の亜ヒ酸の除去

Miyaki Ohta‡, Hirokazu Okawa, Takahiro Kato, Katsuyasu Sugawara
(Grad. School of Engineering Science, Akita Univ.)
太田 未也来‡, 大川 浩一, 加藤 貴宏, 菅原 勝康 (秋田大院 理工)

1. Introduction

Arsenic ions [As(III), As(V)] are toxic substance for human body. Therefore, it is necessary to remove arsenic ions from solution before discharge. As(V) is able to be removed by the coprecipitation method using iron hydroxide [$Fe(OH)_3$] and the adsorption method using iron compounds. As(III) is also able to be removed using same treatment of As(V) after oxidation treatment of As(III) to As(V). Therefore, oxidation process is necessary to remove As(III) in the solution. Futhermore, the toxicity of As(V) is lower than that of As(III). Therefore, it is crucial to efficiently oxidize As(III) to As(V). Oxidation methods of As(III) using ultrasound irradiation are reported.[1] OH radicals (OH·), which is generated by thermal decomposition of water [Eq. (1)] by ultrasound irradiation, can oxidize As(III) because the redox potential of OH· (E° = 2.60 V vs. Ag/AgCl) is higher than that of As(III) (E° = 0.36 V vs. Ag/AgCl).

$$H_2O \rightarrow OH\cdot + H\cdot \quad (1)$$

Recently, it is reported that Pb compounds can remove As(V) from solutions.[2] As (V) is removed by the synthesis of mimetite [$Pb_5(AsO_4)_3Cl$] by the adding of Pb compound into the solution containing As(V) and Cl^-. The mimetite has high chemical stability for the pH range of natural waters. Therefore, we consider that combination of Pb and ultrasound may be able to remove As(V) which is oxidized from As(III) by ultrasound irradiation. Furthermore, we used a Pb plate as a cathode electrode to control pH values of solutions and the concentration of residual Pb ion.

In this study, we performed removal of As(III) from the solution using Pb compound generated by ultrasound irradiation and electrochemical reaction. In this paper, we introduce that As can be removed from As(III) solution using Pb cathode and 200 kHz ultrasound.

2. Experimental procedure

m8018106@s.akita-u.ac.jp

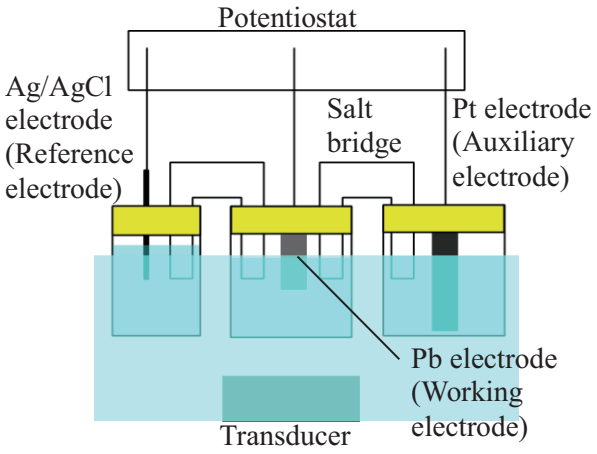

Fig.1 Experimental apparatus.

Fig. 2 Appearance of the solution treated by ultrasound for 30 min in the presence of a lead electrode.

As(III) solution (10 ppm, pH 4.6, 50 mL) containing 20 mM KCl was prepared using arsenic standard solution (1,000 ppm, Wako), KCl (99.5%, Wako) and ion-exchange water. We evaluated oxidation capacity of ultrasound from As(III) to As(V) and removal capacity of Pb electrode. Experimental apparatus is shown in **Fig. 1**. Pb electrode as cathode was immersed in As(III) solution (10 ppm, pH 4.9, 50 mL) containing 20 mM of KCl. Pt electrode as anode was immersed in H_2SO_4 solution (pH 2.0, 50 mL). Ag/AgCl electrode in saturated KCl solution was used as reference electrode. Pb electrode was separated using salt bridge from the Pt and Ag/AgCl electrodes. Before sonication, Ar gas was injected into the As(III) solution at a rate of 100 mL/min for 30 min to remove dissolved air. Potential of Pb electrode was set at −0.7 V vs. Ag/AgCl using potentiostat (Hokuto, HA-301) and sonication was performed

using ultrasonic generator (Kaijo, TA-4021). Ultrasound power and frequency were set at 200 W and 200 kHz. The temperature of reaction solution during sonication was controlled about 25 °C using water bath. A precipitate was generated in treated solution (**Fig. 2**). After standing for 1 day, the precipitate was filtered through a 0.2 μm membrane filter. The concentration of As(III) in the filtrate was measured by colorimeter method using ultraviolet-visible spectrophotometer (UV–vis, JASCO Corporation, V-630). The residual concentration of As [As(III) + As(V)] and Pb^{2+} was measured using an inductively coupled plasma optical emission spectrometry (ICP-OES, SSI nanotechnology, SPS5510). We also performed oxidation of As(III) using ultrasound without Pb electrode.

3. Results and Discussion

We performed oxidation of As(III) using ultrasound without Pb electrode. We also performed removal of As using Pb electrode of –0.7 V vs. Ag/AgCl during ultrasound irradiation. Residual concentrations of As(III) and As(V) in treated solutions were shown in **Fig. 3**. When the condition of ultrasound irradiation without Pb electrode for 30 min, As(III) concentration decreases from 10 to 3.6 ppm and As(V) concentration increases from 0 to 6.4 ppm by oxidation effect of 200 kHz ultrasound. Residual As concentration in the solution treated by ultrasound decreased in the presence of Pb electrode. By comparison between these results, ultrasound treatment with Pb decrease not only As(V) concentration but also As(III) concentration. When ultrasound irradiates into the solution in the presence of Pb electrode, white color precipitate was appeared. Therefore, it is suggested that generated Pb compounds can remove As(III) and As(V). The pH value of solution treated by ultrasound irradiation without Pb electrode decreased from 4.6 to 3.9, it is because that H^+ concentration increased by the reaction of Eq. (2).

$$H_3AsO_3 + 2OH\cdot \rightarrow H_2AsO_4^- + H_2O + H^+ \qquad (2)$$

The pH value of the solution treated by ultrasound irradiation with Pb electrode increased from 4.6 to 6.4, it is because of OH^- generated by the electrochemical reduction of water [Eq. (3)] and oxidation of Pb by $2OH\cdot$ [Eq. (4)].

$$2H_2O + 2e^- = H_2 + 2OH^-$$
$$E = -0.49 \text{ V vs. Ag/AgCl (pH 4.9)} \qquad (3)$$

$$Pb + 2OH\cdot = Pb^{2+} + 2OH^- \qquad (4)$$

Residual Pb^{2+} concentration in the filtrate was only 0.2 ppm. Potential-pH diagram of Pb-H_2O is shown in **Fig. 4**. PbO may be generated at pH 6.4 and 336 mV vs. Ag/AgCl and residual Pb^{2+} concentration decreased in the solution on the generation of Pb compounds and the concentration of As in the solution.

In the future, we confirm effect of frequency of ultrasound, applying potential of electrode, and initial pH of solution. We perform qualitative analysis of generated Pb compound and clarify the reaction between As and Pb during ultrasound.

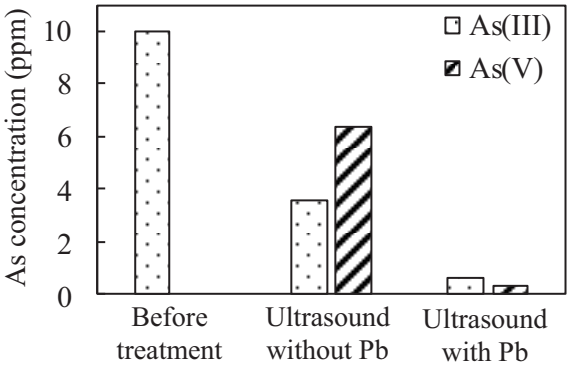

Fig. 3 Residual As(III) and As(V) concentrations before and after treatment using ultrasound with or without Pb electrode which is applied potential of –0.7 V vs. Ag/Ag/Cl.

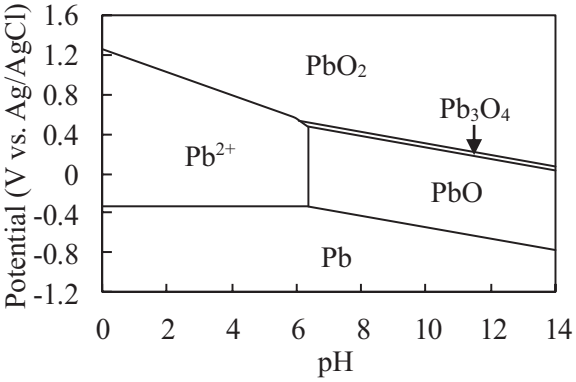

Fig. 4 Potential-pH diagram of Pb.

4. Conclusion

We performed removal of As(III) using Pb precipitated from Pb electrode by ultrasound irradiation under applying at –0.7 V vs. Ag/AgCl in Ar atmosphere for 30 min. Residual As concentration in the filtrate decreased from 10 to 0.9 ppm. Additionally, generated Pb compound can remove both As(V) and As(III) from the solution.

References

1) R. Hosokawa, T. Saito, and H. Okawa: Jpn. J. Appl. Phys. **50** (2011) 07HE11.
2) H. Long, Y. Zheng, Y. Peng, G. Jin, W. Deng, and S. Zhang: Hydrometallurgy **183** (2019) 199.