

Oxidation of arsenite using a combination of sonochemical reaction and electrochemical reaction

超音波化学反応と電気化学反応を併用した亜ヒ酸の酸化

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 (秋田大学院 理工)

1. Introduction

Arsenic [As(III), As(V)] is a toxic substance for human body. Therefore, it is necessary to remove arsenic ions from solution before discharge. Considering the removal of As by the coprecipitation method using iron hydroxide [Fe(OH)₃], oxidation treatment is required. Because the removal ratio of As(V) using Fe(OH)₃ is much higher than that of As(III). Furthermore, As(V) is lower toxicity than As(III). Therefore, it is crucial to efficiently oxidize As(III) to As(V). OH· radicals (OH·) generated by ultrasound irradiation can oxidize As(III),¹⁾ because redox potential of OH· (E° = 2.18 V vs. Ag/AgCl) is higher than that of As(III) (E° = 0.36 V vs. Ag/AgCl). However, H₂O₂ generated by ultrasound irradiation (2OH· → H₂O₂) doesn't work as the oxidant of As(III) in acid solution. Therefore, we challenged to generate OH· from H₂O₂ generated by ultrasound irradiation using electrochemical reduction. Electrochemical reaction was applied to generate OH· from H₂O₂ at the cathode of -0.2 – -0.8 V vs. Ag/AgCl.²⁾ The chemical reaction formula is shown below.



In this study, we performed enhanced oxidation from As(III) to As(V) using combination of ultrasound irradiation and electrochemical reaction.

2. Experimental procedure

As(III) solution (10 ppm, pH 6.0, 50 mL, KCl 20 mM) was prepared using arsenic standard solution (1000 ppm), KCl, NaOH and ion-exchange water. At first, we evaluated the oxidation ratio of As(III) to As(V) using ultrasound irradiation. As(III) solution was sonicated at air or argon (Ar) atmosphere for 30 min using ultrasound generator (Kaijo, TA-4021) at the output of 200 W and the frequency of 200 kHz. The temperature of reaction solution during sonication was controlled about 25 °C. After treatment, concentration of As(V) was measured using colorimetry method. Concentration of H₂O₂ generated by ultrasound irradiation was

also measured using colorimetry method. Experimental apparatus for oxidation of As(III) using ultrasound irradiation and electrochemical reaction is shown in **Fig. 1**.

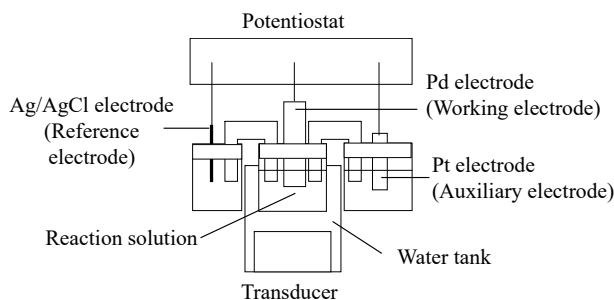


Fig. 1 Experimental apparatus

Secondly, we evaluated the oxidation ratio of As(III) to As(V) using combination of ultrasound irradiation and electrochemical reaction. In this study, we expected to oxidize As(III) using OH· generated by ultrasound irradiation and electrochemical reduction, therefore we evaluated oxidation ratio of As(III) at cathode electrode. Anode electrode was separated from the cathode electrode in the reaction solution, because anode can oxidize As(III) to As(V) on the electrode.³⁾ Pb electrode was immersed as cathode in As(III) solution (10 ppm, pH 6.0, 50 mL) containing 20 mM KCl and Pt electrode was immersed as anode in H₂SO₄ solution (pH 2.0, 50 mL). Ag/AgCl (saturated KCl) electrode was used as reference electrode. Potential of Pb electrode was set at -0.7 V vs. Ag/AgCl using potentiostat (Hokuto, HA-301). Oxidation of As(III) using a combination of ultrasound irradiation and electrochemical reaction was carried out at air or Ar atmosphere for 30 min. After treatment, As(III) and H₂O₂ concentration were measured by colorimetry method and effect of electrochemical reaction was studied.

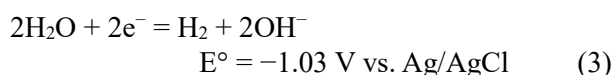
3. Results and Discussion

Oxidation ratio from As(III) to As(V) and concentration of H₂O₂ using ultrasound irradiation at air or Ar atmosphere are shown in **Fig. 2**. Oxidation ratios of As(III) were changed by atmosphere conditions, air was 33% and Ar was

49%. Under air and Ar atmosphere conditions, concentrations of H₂O₂ were 1.5 and 5.4 ppm, respectively. pH values were decreased from 6.0 to 3.8 (air) or 4.4 (Ar), because generations of HNO₃ by sonication in air and H⁺ by the reaction of Eq. (2) in air and Ar.



Oxidation ratio from As(III) to As(V) and concentration of H₂O₂ using a combination of ultrasound irradiation and electrochemical reaction are shown in **Fig. 3**. Oxidation ratios of As(III) under air and Ar atmosphere were increased by the addition of electrochemical reaction from 33 to 65% and 49 to 90%, respectively. pH values of solutions after sonication were 10.1 in air and 10.3 in Ar. We considered that pH was increased by OH⁻ generated by electrochemical reduction of H₂O₂ [Eq. (1)] or electrolysis of H₂O [Eq. (3)].



To confirm increase of pH by electrolysis of H₂O, Pb electrode in H₂O₂ solution (100 ppm, pH 5.7, 50 mL) containing 20 mM of KCl or in KCl solution (20 mM, pH 5.8, 50 mL) was set at -0.7 V vs. Ag/AgCl for 30 min. From those results, pH values increased from 5.7 to 10.4 in 100 ppm of H₂O₂ solution and from 5.8 to 10.2 in KCl solution. At pH 6, theoretical value of electrolysis of H₂O is -0.56 V vs. Ag/AgCl. Therefore, main factor of pH increase may come from the electrolysis by applying -0.7 V vs. Ag/AgCl. Therefore, we performed oxidation of As(III) using a combination of ultrasound irradiation and electrochemical reaction > -0.56 V vs. Ag/AgCl to inhibit pH rise. And we also evaluated the oxidation ratio of As(III) using OH⁻ at various pH values, 2, 4 and 8, of the solution.

4. Conclusion

We performed enhanced oxidation from As(III) to As(V) using combination of ultrasound irradiation and electrochemical reaction. The combination is successfully enhanced oxidation ratio of As(III) from 33% (ultrasound irradiation only) to 65% at air atmosphere and from 49% to 90% at Ar atmosphere.

References

1. R. Hosokawa, T. Saito, and H. Okawa: *Jpn. J. Appl. Phys.* **50** (2011) 07HE11.
2. K. Imamura, Y. Tada, H. Tanaka, T. Sakiyama, and K. Nakanishi: *J. Colloid Interf. Sci.* **250**

(2002) 409.

3. M. A. Hasnat, M. M. Hasan, N. Tanjila, M. M. Alam, and M. M. Rahman: *Electrochim. Acta* **225** (2017) 105.

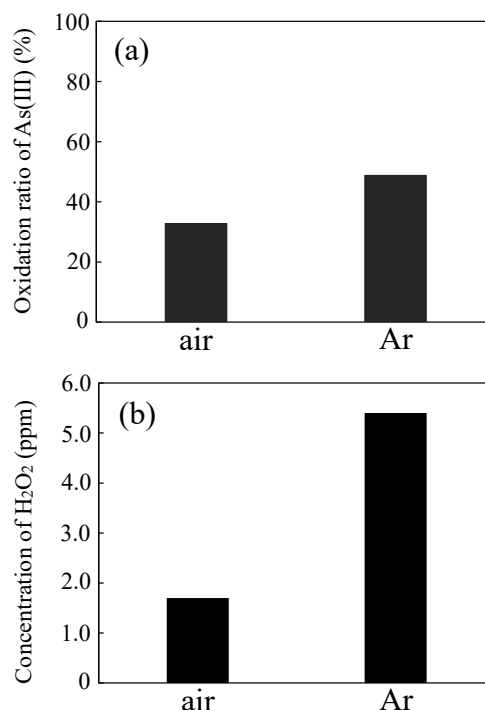


Fig. 2 (a) Oxidation ratio of As(III) to As(V), (b) concentration of H₂O₂ after ultrasound irradiation for 30 min at air or Ar atmosphere.

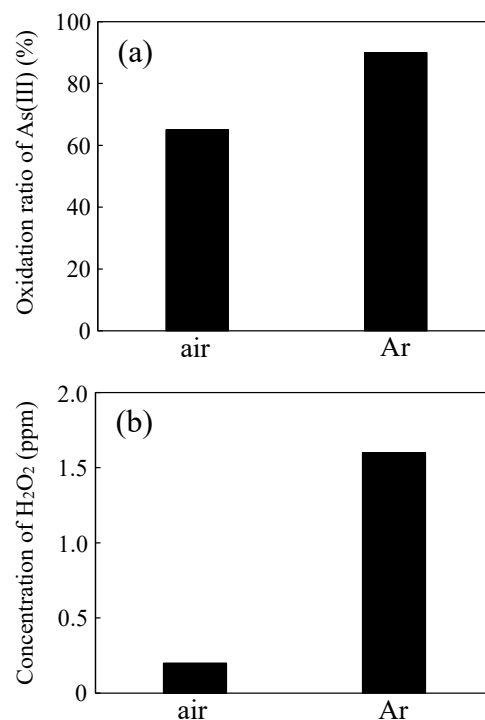


Fig. 3 (a) Oxidation ratio of As(III) to As(V), (b) concentration of H₂O₂ using combination of ultrasound irradiation and electrochemical reaction for 30 min at air or Ar atmosphere.