1. Introduction

In the nature, arsenic species exists in two different oxidation states, +III (arsenite) and +V (arsenate). Removal of the As(III) is much harder than removing the As(V). Once As(III) is oxidized into As(V), the removal by adsorption becomes much easier. This is the reason that the oxidation of As(III) into As(V) has to be preceded in order to have an effective removal system for arsenic. In previous studies, many methods have been used the oxidation of acutely toxic As(III) to the less toxic As(V), including advanced oxidation processes (AOPs) such as photocatalysis, zero-valent iron, Fenton’s reaction, ozonation, etc.

Among the different AOPs, application of ultrasound is the environment friendly technique which does not use additional chemicals or catalysts. Also, it is attractive since the sonication reactor can be used semi-permanently. The mechanism of ultrasound is to be classified into two ways of physical and chemical. This paper focuses on chemical methods by using the OH radicals which are the dominant factors among lots of radicals like O₂-, H radical, etc. The redox potential of OH radicals estimated 2.7 V, and it is considered to be the most powerful oxidizing agent. Stoichiometry of the oxidation reactions of As(III) by using OH radicals are expressed in the following equation.

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\begin{align*}
\text{AsO}_2^{3-} + \text{OH} & \rightarrow \text{HAsO}_4^{3-} \quad (1) \\
\text{HAsO}_4^{3-} + \text{OH} & \rightarrow \text{AsO}_4^{3-} + \text{H}_2\text{O} \quad (2) \\
2\text{AsO}_3^{3-} + 2 \cdot \text{O}_2^- + 4\text{H}^+ & \rightarrow 2\text{HAsO}_4^{3-} + \text{H}_2\text{O}_2 \quad (3) \\
2\text{HAsO}_4^{3-} + \text{O}_2^- & \rightarrow 2\text{AsO}_4^{3-} + 2\text{OH}^- \quad (4)
\end{align*}
\]

In this study, the effect of frequency and the power in the oxidation of As(III) to As(V) using ultrasound were analyzed. Also, the kinetics of the As(III) oxidation with the obtained frequency was studied as well.

2. Materials and Methods

A cylindrical pyrex vessel was submerged in a bath type and cup-horn shaped sonoreactor (Mirae Ultrasonic Tech.) equipped with transducers. As(III) solution (0.2 mgL⁻¹) prepared with a stock solution of sodium arsenite (NaAsO₂, 94%, Samchun) was used for the study. All liquid used in this study was DI water. The pH is maintained at 7 because of under typical anoxic groundwater conditions at a near neutral pH of 7. The capacity of the reactor was 500 mL and the double-wall of the reactor enabled to maintain the system at 20±2 °C through using a cooling system.

An anion-exchange cartridge (Supelclean LCSAX SPE 3mL) was used as a filter to separate As(III) and As(V) (the anion-exchange cartridge keeps As(V) while leaving As(III) in the filtrate). After separation, ICP-AES was used to measure the level of arsenic species. To find out the effect of frequency on the oxidation of As(III) into As(V), different frequencies such as 35 to 935 kHz were used with 80 W input power. Based on the frequency estimated, the oxidation kinetics were monitored through sampling every 10 minutes for 60 minute sonication.

3. Results and Discussion

The preceding experiment was conducted by using potassium iodide (KI) solution. Input power was fixed at 80 W and tests were carried out at the frequency of 35, 72, 110, 170, 283, 450, and 935 kHz, respectively. The pH was fixed at 7, and temperature was maintained at 20±2 °C and reaction time was 40 minutes. The concentration of the KI solution was 10 gL⁻¹. As shown below, at frequency
283kHz, 450kHz is higher than others to occur OH radicals, and the highest concentration of OH radicals was observed at 450 kHz (Figure 2).

![Graph showing the effect of ultrasonic frequency on OH radicals](image1)

Fig. 2 Effect of ultrasonic frequency on the OH radicals. Experimental conditions: KI solution concentration 10 gL⁻¹, ultrasonic power 80 W, pH 7, temp. 20±2°C, reaction time 40 min

The sonication for the As(III) solutions was carried out and the results were shown at Figure 3. The highest efficiency of oxidation was shown at 450 kHz. Through observing the production of OH radicals, it can be inferred that the oxidation efficiency at 450 kHz was higher than that at 283 kHz. Thus, the oxidation efficiency exactly corresponds to the result of OH radicals production in KI solution (Figure 2). The OH radicals produced during acoustic cavitations readily oxidize As(III) to As(V) in an aqueous environment.

![Graph showing the effect of ultrasonic frequency on arsenite oxidation to arsenate](image2)

Fig. 3 Effect of ultrasonic frequency on the oxidation of As(III) to As(V). Experimental conditions: ultrasonic power 80 W, As(III) 0.2 mgL⁻¹, pH 7, temp. 20±2°C, reaction time 40 min

As another test, both 283 and 450 kHz frequencies at 80 W were used to find the As(III) kinetics. The results are shown at Figure 4. Reaction time was faster at 450 kHz than at 283 kHz. The oxidation efficiency of 283 kHz was 92 % and that of 450 kHz was 99 % at 40 minutes, respectively. The second-order rate constants, K, had been calculated to observe for the oxidation rate of As(III) to As(V). It was 2388.4 M⁻¹S⁻¹ and the half-life was 156 sec⁻¹ at 450 kHz.

![Graph showing oxidation kinetics of As(III) to As(V)](image3)

Fig. 4 Oxidation kinetics of As(III) to As(V). Experimental conditions: ultrasonic frequency 283 and 450 kHz, ultrasonic power 80 W, As(III) 0.2 mgL⁻¹, pH 7, temp. 20±2°C, reaction time 60 min

4. Conclusion

In this study, the oxidation process using ultrasonication for the highly-toxic As(III) was conducted. The results showed that 450 kHz at 80 W was the optimal conditions to occur OH radicals with 40 minutes. In terms of kinetics, it was 99 % of oxidation efficiency under the same terms. The experimental data will be useful to applying pre-treatment process for the combination environment of As(III) and As(V) in groundwater.

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References