Arsenite oxidation by ultrasound combined with UV-C in aqueous solution

Seban Lee[1†], Mingcan Cui[1], Seungmin Na[1], Min Jang[2], Jeehyeong Khim[1*]
([1]School of Civil Environmental and Architecture Engineering, Korea University;
[2]Korea Mine Reclamation Corporation, Institute of Mine Reclamation Technology)

1. Introduction

Arsenic appears in its inorganic state as oxyanions of trivalent arsenite, As(III), or pentavalent arsenate, As(V), in aquatic phase [1]. Among these two, As(III) is significantly more mobile, because As(III) is less strongly adsorbed than As(V) to all sorts of sorbents, and 25-60 times more toxic [2]. Immobilization, therefore, can be improved by oxidation of As(III) to As(V) [2]. Hence, oxidation of As(III) is essential for increasing the removal efficiency of total arsenic.

Many studies have been reported for oxidation of As(III), however, all of these methods have their limitations. In order to conform to the new restriction of 10 μg L^{-1}, it is necessary to consider more rapid and environmentally friendly approach for the oxidation of As(III) rendering a powerful oxidation of As(III) to As(V) without additional oxidants and with reasonable costs [3]. Meanwhile, reports on oxidation of As(III) by hydroxyl radical of a powerful oxidant using ultrasound (US) within short time have been found out [4], and some researches were successfully performed using ultraviolet-C (UV-C), in the range of 254 nm giving the similar effective production of hydroxyl radicals as gamma-radiolysis or electron beam [3]. However combining these two wave energies namely, ultrasonic dynamic wave energy and electromagnetic wave, assessing the synergistic effects of hydroxyl radical have not been done so far.

With the aim of meeting the criteria of not using additional chemicals and making the experiment cost effective a comparative analysis for calculating the kinetic data and synergistic effects under different pH conditions were performed.

2. Materials and Methods

The system comprises of a Pyrex reactor with 1.5 L capacity and an ultrasonic cup-horn type transducer (Mirae Ultrasonics Tech.) coupled with a single piezoelectric transducer (PZT, Tamura corp.). The ultrasonic frequency of 450 kHz which is highly effective in decomposing heavy metals was selected [4]. An 8 W mercury lamp with a maximum

----
hyeong@korea.ac.kr

intensity at 254 nm (Sankyo Denki), having 19 cm length and 2.2 cm diameter which can be installed up to four in the reactor was used. The inner wall of the reactor is dual structured and the temperature was maintained at 20±2℃ constantly by water cooling system. The initial pH value was set at 7.1 and 10.9 respectively. Sodium (meta)arsenite ($NaAsO_2$, Sigma-Aldrich, 94%) was used as the source of As(III) for the research and 0.2 mg L^{-1} was taken as initial concentration.
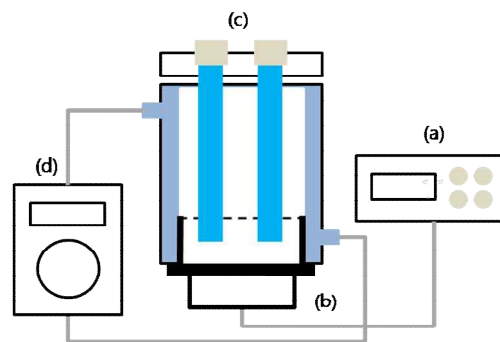

Fig. 1 Schematic diagram of the experimental setup: (a) ultrasonic controller, (b) coupon type transducer, (c) UV-C lamps, and (d) cooling system.

Furthermore, hydrogen peroxide produced during sonication of deionized water was investigated by the iodometric method and the occurrence of hydroxyl radical was measured by KI method, (99.5% potassium iodide, Junsei) [5]. The concentration of I_3^- was detected by UV-vis spectrophotometer (Analyticjena, SPECORD 40). To separate As(III) and As(V), an anion cartridge (Supelclean LCSAX SPE 3mL) filter has been used. Finally, As(III) concentration was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES; Perkinelmer 5300DV).

3. Results and Discussion

Fig. 2 represents the comparative study on the generation rate of hydrogen peroxide and triiodide ion which is directly proportional to hydroxyl radical production. It showed that US process had highest rate of hydrogen peroxide as 2.192 mg $L^{-1} \cdot min^{-1}$ by the time. But, in the US/UV-C processes production rate of hydrogen

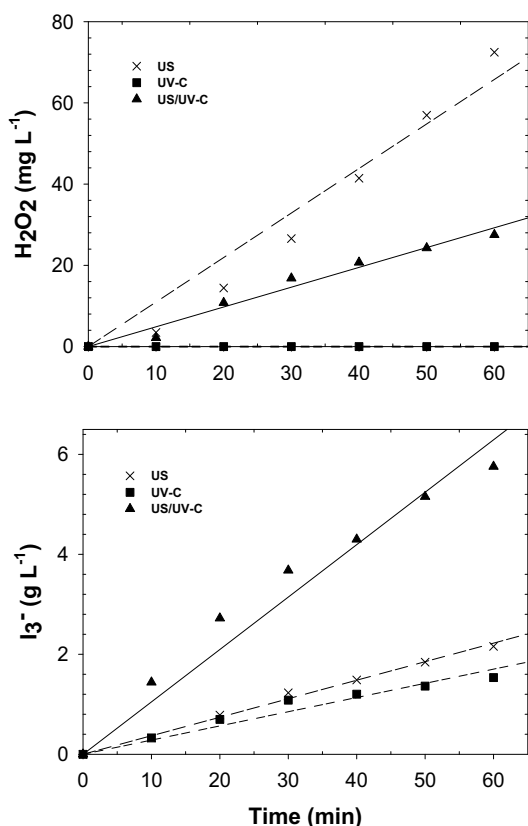peroxide was 0.974 mg L^{-1}·min^{-1}, it was decreased bv 55.6%.

Fig. 2 Concentrations of hydroxyl radical and hydrogen peroxide by US (450 kHz, 26.27 W L^{-1}), UV-C (254 nm, 21.26 W L^{-1}), US/UV-C processes

To explain this result, the generation rate of hydroxyl radical has been carried out. The I$_3^-$ concentrations were measured for this. As a result, the production rate of hydroxyl radical was 37.03, 28.37 and 104.86 mg L^{-1}·min^{-1} by US, UV-C and US/UV-C. Thus, in this study a synergistic effect has been interpreted that the value of rate constant of combined system is divided by total of rate constants of each independent process [6]. The synergistic effect value of hydroxyl radical in US/UV-C process was approximately 1.60.

$$Synergy = \frac{k_3(Combined)}{k_1(US) + k_2(UVC)} \qquad (1)$$

Fig. 3 indicates the highest power intensity of 26.27 and 21.26 W L^{-1} respectively, used in each processes. Subsequently, synergistic effect by two combined processes of US/UV-C was studied. After 60 min of reaction time, first order rate constants of each reaction were found to be 1.65×10^{-4}, 3.65×10^{-4} and 8.31×10^{-4} S^{-1} respectively. In the process of US/UV-C, synergistic effect was 1.57 from which the change of hydrogen peroxide to hydroxyl

radical was confirmed as a function of direct photolysis. This result was in accord with in Fig. 2.

In the neutral state As(III) exists in nonionic, condition, however, above pH 9.2 it exists as an anion [3]. And in the present study, the rate with different pH attributed to existing form of arsenic species and to production of hydroxyl radical. The rate constant, k at pH 10.9 was found to be 1.94×10^{-3} and 8.31×10^{-4} S^{-1} at pH 7.1 which is about 2.3 times faster than the latter.
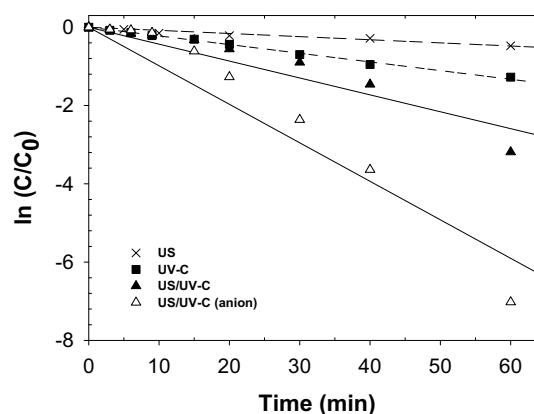

Fig. 3 Degradations of As(III) by US (450 kHz, 26.27 W L^{-1}), UV-C (254 nm, 21.26 W L^{-1}), US/UV-C processes

4. Conclusion

The study investigated the oxidation of As(III) using synergistic effect of hydroxyl radicals. The combination process of US/UV-C had synergistic effect of 1.57. Also, the oxidation rate of the anionic form with pH 10.9 was 2.3 times faster than that of nonion with pH 7.1, the rate constant value was 1.94×10^{-3} S^{-1}. The US/UV-C process did not use any additional catalysts or oxidants, which will give an effective technique for the oxidation of As(III) to As(V).

References
1. P. L. Smedley, H. B. Nicolli, D. M. Macdonald and A. J. Barros: Appl. Geochem. **17** (2002) 259.
2. N. Bhandari, R. J. Reeder and D. R. Strongin: Environ. Sci. Technol. **45** (2011) 2783.
3. S. Yoon, J. Lee, S. Oh and J. Yang: Water Research **42** (2008) 3458.
4. M. Cui, S. Lee, M. Jang, B. Kweon, H. Jo and J, Khim: Jpn. J. Appl. Phys. **50** (2011) 07HE13-02.
5. M. A. Beckeet, I. Hua; J. Phys. Chem. **105** (2001) 3796.
6. E. Selli: Phys. Chem. Chem. Phys. **4** (2002) 6123.