



Arsenic removal from waste water by ozone oxidation combined with ferric precipitation

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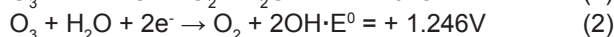
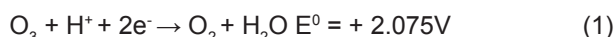
Abstract: The oxidation of As(III) to As(V) followed by precipitation and adsorption is thought to be the most effective process for removal of arsenic in industrial wastewater. In this work, the oxidation of As(III) to As(V) with ozone was carried out in an acidic solution. After oxidation, arsenic was removed by precipitation in an iron (III) sulfate system under ambient pressure at 90°C in acid. Batch experimental results show that ozone is quite effective in oxidizing As(III) at low pH. And more than 90% of 5g/l As(III) was removed from the acidic solution by precipitation with $\text{Fe}_2(\text{SO}_4)_3$ in 7-8 hours.

Key words: Arsenate, Arsenite, Ozone, Oxidation, Precipitation

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INTRODUCTION

Recently, the toxic behavior of arsenic is receiving increased attention as the arsenic pollution has been reported worldwide. Arsenic is a common element which is widely distributed throughout the rock, soil, natural water and marine environments and associated with some base and precious metals in the sulfide ores [1-3]. Hereupon, the mining and metallurgical industries have expended considerable research efforts to develop environmentally acceptable methodologies for the arsenic removal from waste water. Under natural conditions As is mostly found in inorganic forms as trivalent arsenite (As(III)) or as oxy-anions of pentavalent arsenate (As(V)). In comparison with As(V), As(III) is high mobile and more difficult to be removed from the aqueous solution. All of the arsenic precipitation work carried out involved both ferric iron and pentavalent arsenic in solution, based on the substantially correct premise [2, 4]. It is necessary to oxidize the trivalent arsenic to its pentavalent state before the arsenic removal. A lot of researchers focused on the methods for oxidation of As(III) to As(V) using different oxidants [5-7,8]. In several studies, ozone applications have been reported for treatment of wastewater and water, but very few studies are for oxidation of As [6-10]. The most characteristic chemical properties of ozone are its strong oxidizing and high standard redox potential according to the reaction conditions. It is strong oxidizing nature and its tendency to transfer an O atom with coproduction of O_2 [4]. The standard redox potentials in acid (1) and in alkaline (2) solutions are the following reactions.



In some cases, free radicals are formed from the ozone reaction as shown in reaction 2. The free radicals propagate themselves through the mechanisms of elementary steps to yield hydroxyl radicals. These hydroxyl radicals are extremely reactive with any organic and inorganic [11]. Khuntia *et al.* have oxidized As(III) using ozone microbubbles in the pH range of 5-9 and the oxidation was fast at pH 6 and slow at pH 7. They observed that the independent relative of pH in the range of 5-9 on the rate of As (III) oxidation. Therewith, the roles of $\cdot\text{OH}$ radical found to be effective in the oxidation of As(III) by using 2-propanol as the $\cdot\text{OH}$ radicals scavenger at pH 5 and 6 respectively. At pH 5 and 6, the reaction of As(III) likely occurred with both $\cdot\text{OH}$ radical and molecular ozone [11-12]. Kim and Nriagu have shown the effectiveness of ozone on oxidation of arsenic under ambient conditions in both groundwater and samples in neutral solutions [7]. In addition, the pH of the solution is also important in determining the arsenic speciation. However, the exact mechanism of the $\cdot\text{OH}$ radical generation under strong acidic condition is precisely not known. Li *et al.* investigated the generation of hydroxyl radicals by microbubbles at acidic pH and confirmed the generation of hydroxyl radicals at pH 2 [13]. On the other hand, another brief description of ozone is catalytic ozonation using metalion and it is a promising method to enhance the hydroxyl generation from ozone. For example Mn(II), Fe(II), Fe(III), Zn(II), Co(II), Ni(II) and Cu(II) have identified to be of a higher catalytic ozonation efficiency than ozone alone. These metal catalysts increase the hydroxyl radical generation and the oxidation of the compound occurs both directly and indirectly [14]. Khuntia *et al.* have reported that hydroxyl radicals were generated by the use of (Cu(II)), and the trend was $\text{Fe(III)} < \text{Fe(II)} < \text{Mn(II)} < \text{Cu(II)}$ [12]. The conversion of As(III) to As(V) by different oxidants especially with ozone is well documented except the

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oxidation of As(III) to As(V) by ozone in acidic condition. However, the significant requirement for fixation of arsenic from the As contaminated water by precipitation process is the As should be in arsenate form (+5 state) in acidic solution. Therefore, the objective of this study is to determine the effectiveness of ozone for oxidizing As(III) to As(V) in an acidic condition. The optimal conditions have been determined including experimental temperature, pH of the solution, an initial concentration of As(III) and reaction time for oxidation of As(III). After the oxidation process, arsenic was removed by the precipitated with ferric (Fe^{3+}) under acidic conditions (pH 1-2).

EXPERIMENTAL

Chemicals: All the reagents were of analytical grade and used without further purification. All solutions were prepared with deionized water. Ozone gas was used as oxidizing agent. Sodium arsenite (NaAsO_2) was used as the source of As(III).

Oxidation of As(III) by ozone: Ozone was produced through electronic discharge directly from an ozone generator with air. Then ozone gas was injected into the reaction mixture under stirring for mass transfer and dissolution. When the reaction takes place at 90°C , solution was indirectly electrically heated. The Eh and pH of solutions were measured by Mettler Toledo FE20 and EL20 pH/mV with dual electrode inputs. And pH was adjusted by adding (1:1) H_2SO_4 or 1N NaOH.

Separation of As(III) and As(V): As(III) and As(V) were

Determination of arsenic concentration: Residual As(III) concentration in the solution was measured by using inductively coupled plasma atomic emission spectroscopy (ICP) (Perkin Elmer Optima 5300DV).

Experimental procedure: The source of As(III) as arsenite was prepared from NaAsO_2 which was dissolved in water with different initial concentrations. An appropriate amount of arsenic (III) solution was measured and placed in the beaker and H_2SO_4 or NaOH was added to adjust the desired pH of a solution. The total volume was adjusted to 0.5 l by adding deionized water. For the high temperature, the reaction solution was heated under stirring. When the temperature reached 95°C , the ozone gas was injected into the mixture to start the oxidation reaction. At the set time intervals, 10 ml of samples were taken out of the flask reactor for the profile of As. The pH and the Eh of each sample were measured by Mettler Toledo FE20 and EL20 pH/mV with dual electrode inputs. The experimental equipment is described in Figure 1. The amount of oxidized As was determined by the difference between the final concentration of As(III) in solution and the initial concentration of As(III).

Precipitation process: The solution after oxidation was poured into the glass reactor. Then the required ferric sulfate was added with water to make the total volume 700 ml as described by Fujita *et al.* [16, 17]. Then the glass reactor was heated by an indirect heater and stirred until it reached 95°C . The air was introduced while stirring. The samples slurry was cooled to 60°C before measuring

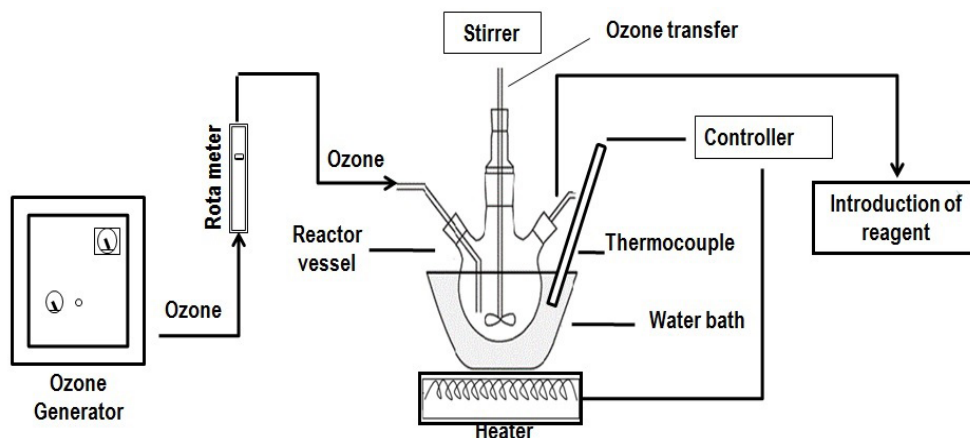


Fig.1. Schematic of the experiment setup

separated by using Analytic grade AG® 1x8 100-200 mesh resin (acetate form) by the method described by Ficklin [15]. The resin was packed into a glass column of 10 cm height and 12mm diameter. Before running the sample, the resin was converted into the acetate form. About 5 ml of 0.1M NaOH was passed through the resin, followed by 20 ml water and 8 ml of 1.0mol/l acetic acid, at a flow rate of $1.0 \text{ ml}\cdot\text{min}^{-1}$, the mini-column was washed with 100 ml of deionized water. Then an aqueous solution of 3 ml containing As(III) and As(V) was passed through the column at a flow rate of $1 \text{ ml}\cdot\text{min}^{-1}$, followed by 7 ml deionized water. As (V) was retained in the column while As(III) was collected from the effluent in clean sample bottles. A solution of 0.12 mol/l of HCl was used to elute As(V) from the column. The eluted As(V) was collected in other flasks. After each run, the column was washed with 2.0 mol/l HCl and then with 50 ml water.

pH and Eh with time intervals. After measurement of pH and Eh, 10 ml sampled slurry was passed through a $0.2\mu\text{m}$ membrane filter to separate the solid and liquid. The precipitate was washed with distilled water. All the residual solutions were collected into a 50 ml bottle for determining the concentration of total As and As(III).

RESULTS AND DISCUSSION

Effect of reaction time: The effect of reaction time on oxidation of As(III) with ozone at pH 1 and 20°C is shown in Figure 2. The ozone oxidation was effective in an acidic solution and the concentration of As(III) decreased whereas the concentration of As(V) increased in the solution after oxidation. 60% of 5 g/l As(III) oxidized below 10 min and more than 99% of As(III) was oxidized within 25 min in an acidic solution.

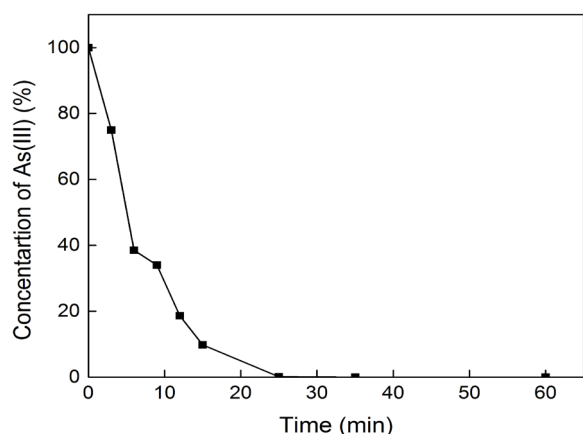


Fig. 2. Effect of oxidation time at low initial concentration (50mg/l), pH 1 and T=20°C

Fig.3. illustrates the function of oxidation time at three different initial concentrations of As(III). The results are the three identical experiments performed at the same conditions. The amount of oxidized As(III) in the solution decreased to less than 0.0001 g/l when the reaction time is 120 min at 5 g/l, about 90 min at 2.5 g/l and 75 min at 1.5 g/l with the initial pH of 0.5 (acidic media). These results show that the oxidation of As(III) with ozone is quite dependent on the reaction time.

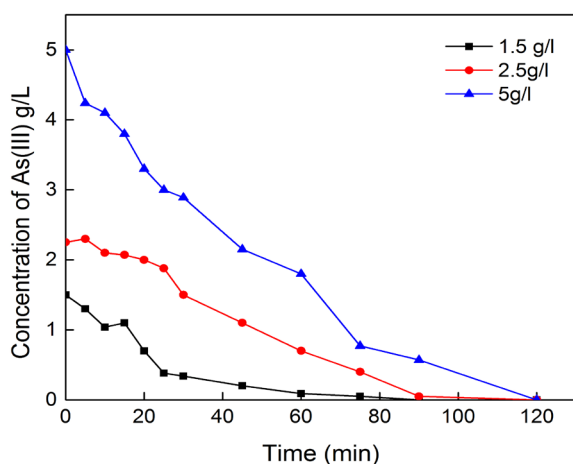


Fig. 3. Oxidation of As(III) to As(V) with different initial concentrations (pH 0.5, 20°C)

Effect of initial pH of the solution: The unique feature of ozone is its decomposition in an aqueous solution. pH is one of the most important factors for the ozone decomposition and controlling arsenic speciation in aqueous systems [18]. In this study, the batch experiment results indicate that the ozone is very effective on the oxidation of As(III) at pH from 0.5 to 2. When the pH of the solution was 0.5, 50 mg/l As(III) was completely oxidized in 20 min as shown in Figure 2. The final pH values of solutions, after the oxidation reactions were slightly lower than that initial pH values of solutions. For example, when initial pH was 0.5, the final pH reached 0.34 in 120 minutes.

Figure 4. shows that the effect of initial pH on the ozone oxidation of As(III) at ambient temperature. Under this condition, about 99% of As (III) was completely oxidized in 35 minutes. The oxidation was similar at both pH 1 and pH 2. It can be interpreted by direct and indirect reaction mechanisms [19-21]. The reaction of As(III) with

$\cdot\text{OH}$ radicals forms the As(IV) intermediate, which further oxidizes As(III) to As(V). The reaction mechanism is speculated as follows [5, 22, 23].

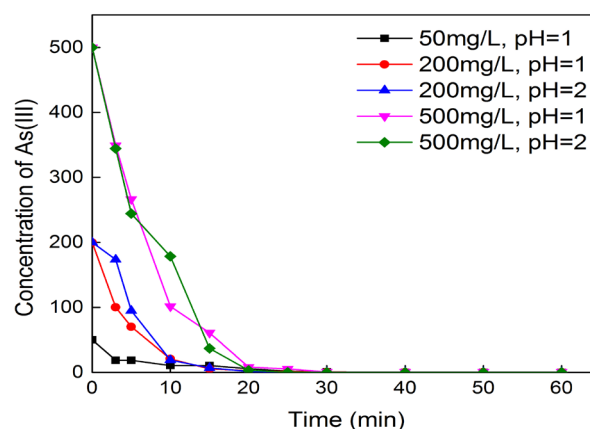
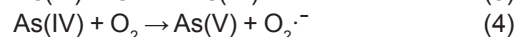
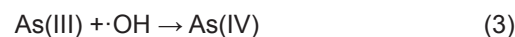
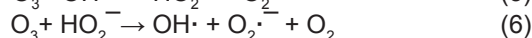


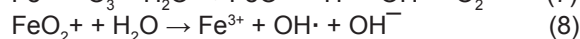
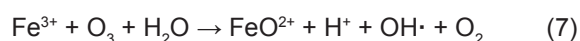
Fig. 4. Effect of pH on As(III) oxidation with ozone at 20°C

Effect of temperature and Fe^{3+} : In our work, the experiment was carried out for testing the effect of temperature on oxidation of As(III) with ozone in an acidic solution at its low (50 mg/l) and high initial (5 g/l) concentrations. Experiment results show that at 25°C the ozone oxidation was efficient but at 90°C there was no difference in the concentration of As(III) in the solutions between initial and after reactions at pH 1 and 2 as shown in Table 1 in absence of Fe^{3+} . Whereas, in presence of Fe^{3+} , 5 g/l As(III) was oxidized 97.2% and 90.6% at pH 2 and 1, respectively, in 2 hours as shown in table 1, which depicts the comparison of the presence and absence of Fe^{3+} on the oxidation of As(III).

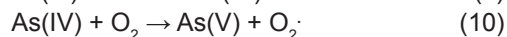
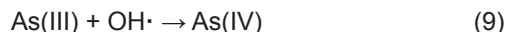
During ozonation of aqueous solution, part of the ozone normally decomposes to OH radicals. The elementary reaction mechanism of decomposition of ozone in aqueous solution is as follows.



The radicals that are produced during reaction (6) can introduce other reactions with ozone, causing more OH· radicals to be formed [4]. On the other hand, metal catalysis increases the hydroxyl radical generation from ozone in aqueous solution. Several effectual reports suggested the catalytic oxidation reactions [11-14]. Khuntia et al. (2013) determined the enhancement of OH· radical generation from ozone for the catalytic ozonation using four common metal ions. In their findings, the catalytic ozonation was more efficient than that the ozonation alone by increasing OH· ($\text{O}_3 < \text{O}_3 + \text{Fe(III)} < \text{O}_3 + \text{Fe(II)} < \text{O}_3 + \text{Mn(II)} < \text{O}_3 + \text{Cu(II)}$). Also, many researchers have been determined that the Fe(III) catalytic ozonation was more effective in degradation of organic and inorganic compounds than the ozone alone, due to the generation of OH· radicals [5, 8, 12, 24, 28].



The reaction mechanism for the oxidation of As(III) by $\text{OH}\cdot$ described by Hoigne *et al.*



Therefore, the generation of hydroxyl radicals by the Fe^{3+} catalyst increase the oxidation of As(III). So it can be hypothesized that the existence of Fe^{3+} in the ozonation process increases the efficiency of As(III) oxidation at 90°C in an acidic solution.

CONCLUSIONS

In our study, we aimed to determine the conversion of As(III) to As(V) by ozone oxidation under acidic conditions and showed ozone is a strongest oxidant. The experimental results illustrate that the oxidation of As(III) in the acidic solution by ozone was fast. The pH values of solutions were slightly decreased after the ozonation process and temperature was quite dependent on oxidation reaction. At increased temperature (90°C) ozone was not effective on As(III) oxidation however, in presence of ferric ions, ozone oxidation reaction of As(III) was effective at 90°C.

Table 1. Effect of Fe(III) on oxidation of As(III)

Reactions	Reaction conditions				As(III) in the solution g/l	
	pH	Time	T°C	Eh (mV)	Initial	After reaction
Presence Fe(III)	2	2 (h)	90°C	646	5g/l	0.12
	1			660		0.47
Absence Fe(III)	2	1		391		5.03
	1			491		5.007

Table 2. Oxidation and precipitation of As

After reactions	Reaction conditions				As concentration in the solution (g/l)		Removed As g/l
	T°C	Time	Eh (mV)	pH	Total	As(III)	
Oxidation	25	2 (h)	446	2	5.250	1.004	-
Precipitation	90	5 (h)	900	2	0.271	0.27	4.98

Once the effectiveness of Fe^{3+} in oxidation process with As(III) has been identified, the precipitation process of As occurred according to the operational procedures for the ferric arsenate (scorodite) precipitation [16, 17, 25].

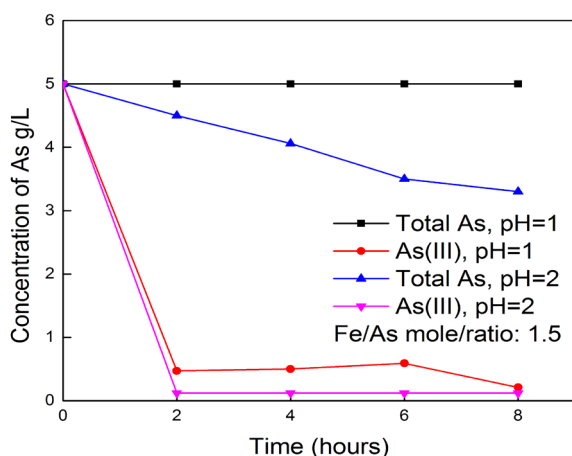


Fig. 5. Effect of Fe^{3+} on oxidation of As(III) (5 g/l) (T-90°C)

As shown in Figure 5, with the increase in the reaction time at pH 2, 97.6% of 5 g/l As(III) and 35% of total As were removed from the solution in 8 hours. At pH 1, 95.8% of 5 g/l As was oxidized in 8 hours but the solid products did not form.

The precipitation test of As with the addition of $\text{Fe}_2(\text{SO}_4)_3$ at pH 2 and 90°C was carried out after oxidation reaction of As(III) to As(V) at 25°C. The result is shown in Table 2. 0.27 g/l As(III) was in the residual solution, for As(III) is not absorbed the surface of $\text{FeO}(\text{OH})$ [9, 26, 27].

Therefore Fe^{3+} might be acting as a catalyst in the oxidation of As(III) by ozone due to the use of metal ion catalysts increase the hydroxyl radical generation in ozonation reaction. After the oxidation process with additional $\text{Fe}_2(\text{SO}_4)_3$ for 7-8 hours, more than 90% As(III) was removed from the solution. Insofar as ozone has been found to be effective for the oxidation of As(III) under acidic condition, As can be removed by producing crystalline scorodite.

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