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Effect of controlled parameters in lab-scale system of iron treatment from simulated groundwater with ozone

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ABSTRACT

Dissolved ozone ($O_{3(aq)}$) and residual ozone in groundwater under differently controlled parameters are two important outcomes in a lab-scale system of ferrous treatment with ozone, but they have not been well investigated yet. In this study, several preliminary parameters of ozone generation, types of diffusers, hydraulic retention time, and the pH in an ozone system of laboratory treatment were examined and evaluated statistically. The results showed that a venturi injector coupled with a bubble diffuser increased $O_{3(aq)}$ concentration to 9.05±0.28 mg/L corresponding to its diffusive coefficient of 0.195 min^{-1}, 2.6 times higher than the bubble diffuser only. The $O_{3(aq)}$ decay constant in the presence of ferrous was 4.88 times higher than that in its absence. The mole stoichiometry of ($\Delta[O_{3(aq)}]/\Delta[Fe^{2+}]$) in synthetic water during ozonation was 1.21, corresponding to its mass ratio of 1.04 mg $O_{3(aq)}$/mg Fe^{2+}. The highest efficacy of ozone on ferrous removal was achieved at pH4.0, followed by that at pH6.0; the residual iron concentration at pH6.0 was 0.230±0.149 mg/L, falling below the WHO standard for drinking water. The residual ozone at pH 4.0 and 6.0 was not statistically different and may take 186 and 300 hrs. to achieve EPA and FDA regulations, respectively. The obtained results may provide a system and information of ozone conditions applied in the treatment of iron to meet the maximum standards of iron and ozone in water.

1. Introduction

Various pollutants currently influence the contamination of groundwater; iron contaminant is a common issue, and a clear burden on drinking water, especially in the rural areas of Vietnam [1,2]. Its presence in potable water can create discomfort for the user through nausea and stomach and skin problems, as well as the aesthetic aspect. The World Health Organization (WHO) has set the maximum limit of iron in drinking water at 0.3 mg/L, which can help to assure safe consumption of these water types [3]. There are a lot of current and widely used technologies to remove iron from groundwater,

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such as ventilation, lime, chlorination, or the usage of a strong oxidant. Each technology has its advantages and disadvantages; however, groundwater not only deals with aesthetics but also disinfection problems. Ozone not only possesses all the chemical properties of oxygen but also is a compound with strong oxidation. As a result, ozone can often accomplish many objectives, such as carcinogenic compounds removal [4,5], disinfection [6,7], improved water aesthetics [8], and color [9]. In this study, dissolved ozone ($O_{3(aq)}$) can oxidize ferrous ions to form a precipitate of iron hydroxide that is removed from water through filtration following this reaction:

$$2Fe^{2+}_{(aq)} + O_{3(aq)} + 5H_2O \rightarrow 2Fe(OH)_{3(s)} \downarrow + O_2 + 4H^+ \quad (1)$$

The first application of ozone technology on iron removal at acidic conditions showed that the reaction between oxygen, which was produced from $O_{3(aq)}$ and Fe^{2+}, resulted in ferry ion (FeO^{2+}). The decomposition of FeO^{2+} occurred with an excess of Fe^{2+}, thus making it difficult to form $Fe(OH)_{3(s)}$ as expected [10]. Ozone technology has also been applied for iron and manganese removal in simulated groundwater with various pH values and shows that increasing pH leads to enhanced iron removal, and an optimum pH value to remove 99% of 109 mg/L iron was 6.99 [8,11]. The difference in turbidity measurement after ozonation is evidence of ferric hydroxide formation [12]. Basically, iron is easily removed through filtration of the precipitate at pH8 without ozone but is more difficult in soft and slightly acidic water, possibly due to humid acids, which is a common case in natural water [13,14]. In addition, the above investigations focused on the effect of pH, hardness, and time but have not investigated $O_{3(aq)}$ under different-controlled parameters and residual ozone after ozone treatment. Effect of controlled parameters of hydraulic retention time and diffuser types on dissolved ozone for various contaminant removal from water has been investigated in many previous articles but their influence on dissolved ozone for iron treatment has not been examined yet [15-19]. Optimization of O_3 generation is also an important preliminarily step of ozone technology, especially in iron treatment [20-22]. Therefore, objective of this study was to investigate the influence of overall conditions in the lab-scale system, including rate of air flow on the ozone generation, type of diffusers, hydraulic retention time, pH on $O_{3(aq)}$, and residual ozone in water, corresponding to its iron removal efficiency. This study may provide useful information to enhance $O_{3(aq)}$ and reduce residual ozone to meet the regulations for setting up a lab-scale ozone system.

2. Materials and methods

2.1. Materials

The experiments were conducted with tap and synthetic-water samples which was spiked 25 mg/L of ferrous ions (Fe^{2+}ions). The ferrous solution was made from ferrous sulfate heptahydrate ($FeSO_4.7H_2O$). The potassium iodide (KI), phosphate buffer (Na_2HPO_4 and NaH_2PO_4), sulfuric acid (H_2SO_4), sodium thiosulfate ($Na_2S_2O_3$), starch, iodine (I_2), N, N-diethyl-p-phenylenediamine (DPD), hydroxylamine solution ($NH_2OH.HCl$), ammonium acetate buffer solution pH5.0 (CH_3COONH_4, CH_3COOH), and phenanthroline were of analytical grade. The ozone generator (model OBM-O005) was made by the OBM Environmental Company, Vietnam. Other equipment used were a UV-Vis spectrophotometer (Hatch, USA) and a pH meter (YSI, USA).

2.2. Experimental design

The lab-scale system of iron treatment with ozone is shown in Figure 1. The schematic one includes the following: an ozone generator with PSA technology and air flow control (0-3.5 lpm) to purify O_2 from air and generate gaseous ozone; an ozone flow control (0-5.0 lpm) made from glass to measure gaseous flow out of the ozone generator; a 10 cm length of venturi mixer made from PVDF material and a 30 mm diameter of spherical gas stone diffuser to distribute ozone into water; a 0.425m(h) x 0.06m(d) contact column made from glass to let the reaction occur; an absorbing column to absorb residual gaseous ozone from the semi-batch reactor; a fume hood to remove residual gaseous ozone from the absorbing column; a peristaltic pump with flow control to pump water and control water flow rate.

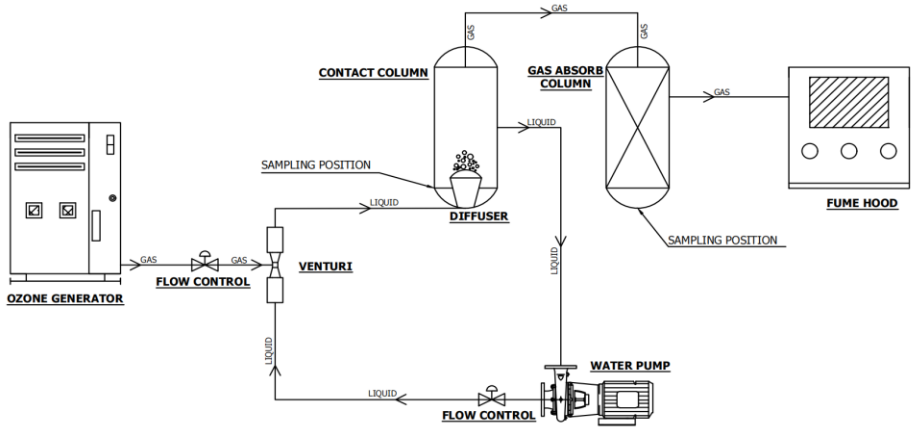

Fig.1. Schematic representation of the experimental setup.

2.2.1. Effect of air flow on ozone production

Oxygen is a precursor of ozone production via corona discharge and purified via PSA technology from air. Stability of the input ozone generation, corresponding to ozone concentration in the KI solution, was carried out to choose the optimal condition of ozone generator. Rates of air flow from 0.5 to 3.0 lpm were investigated for 21 mins of ozonation. The generated ozone was diffused through a spherical air stone diffuser and trapped in 500 mL of KI solution (1%) buffered with pH7 solution. The trapped ozone in KI solution (1%) was sampled and measured every 3 mins during 21 mins with the iodometric titration method [22]. These values were used to calculate the ozone generation (g/h), corresponding to the ozone concentration (g/L) in the KI solution. All experiments were carried out at room temperature (25°C).

2.2.2. Effect of diffuser types, water-flow rate and hydraulic retention time (HRT) on dissolve ozone in tap water

Ozone mass transfer corresponding to ozone mass transfer coefficient is a process of gaseous ozone transportation into the liquid phase and a critical factor in the design of operational parameters in any treatment system. In this primarily lab-scale study, the following systems were chosen to investigate the effect of the diffuser types, HRTs, and water flow rate on $O_{3(aq)}$ concentration and its mass transfer: (1) a bubble diffuser (BD) with a water-flow rate of 0.5 lpm and a hydraulic retention time (HRT) of 2.4 minutes, denoted as BD0.52.4; (2) a bubble diffuser coupled with a venturi diffuser (VD) at water flow rates of 0.5 lpm and HRTs of 2.4 mins and 2.8 mins, symbolized as BD0.52.4 and VD0.52.8, respectively; and (3) a bubble diffuser coupled with a VD at water flow rates of 2.0 lpm and HRTs of 2.5 mins, noted as VD2.02.5. The coefficient of the ozone mass transfer (k_{La}) is represented for transferring ozone into water and is a crucial parameter for designing the treatment system with ozone. This coefficient is developed from the ozone mass balance in the liquid phase [18]:

$$k_{La} \times \mathrm{V_L} \times (\mathrm{C_L^*} - \mathrm{C_L}) \times \mathrm{dt} = \mathrm{V_L} \times \mathrm{dC_L} + \mathrm{k_c} \times \mathrm{C_L} \times \mathrm{V_L} \times \mathrm{dt} \tag{2}$$

By rearranging and isolating the above equation, the linear equation (3) is obtained:

$$\ln\left(C_L^* - C_{L(t)}\right) = (k_c + k_{La}) * t + b \tag{3}$$

where C_L^*: concentration of ozone in water at equilibrium with the gas phase (mg/L), $C_{L(t)}$: dissolved ozone ($O_{3(aq)}$) concentration in the solution measured at sampled time t (mg/L), k_c: ozone decay constant (min^{-1}), k_{La}: ozone mass transfer coefficient (min^{-1}), and t: ozonated time (min). The dissolved ozone ($O_{3(aq)}$) concentration at equilibrium based on Henry's Law is [18,23].

$$\mathrm{C_L}^* = \frac{\mathrm{C_{gin}}}{1{,}59 \times e^{(0{,}0437 \times T)}} \tag{4}$$

where C_{gin}: concentration of inlet gaseous O_3 ($g\ m^{-3}$) and T: temperature (K).

Coefficients of determination (R^2) and p-values of the Fisher test in the linear model of Eq. 3 were evaluated statistically. If the p-value is smaller than the significant level of 0.05, this linear model is fitted well with the experimental data. The mass transfer coefficient (k_{La}) of ozone into the water was estimated by subtracting k_c from the slope of the linear equation (Eq. 3). The ozone decay constant (k_c) is described in the following formula:

$$r = k[O_3][OH^-] = k_C[O_3] = d[O_3]/dt \quad (5)$$

where $k_C=k[OH^-]$ due to constant $[OH^-]$, k_C: decay rate constant (min^{-1}), and t: decay time (min). Eq. 6 is obtained by rearranging and isolating from Eq. 5.

$$\ln\frac{[O_3]_t}{[O_3]_o} = k_c t + \text{const} \quad (6)$$

Correlation coefficients corresponding to p-values of the Fisher test in two linear models of Eq. 6 were evaluated statistically to test their model fitness with the experimental data. The p-value is smaller than the significant level of 0.05, and the slope of k_c can be used to estimate constant of decay rate.

2.2.3. Consumption of dissolve ozone by ferrous ions and its half-lives after ozonation

Amount of dissolved ozone ($O_{3(aq)}$) consumed by 01 mg of ferrous ions and the half-lives of residual ozone in water after ozonation is also important to design the ozonation system and achieve the regulations. In this experiment, ozone was introduced into the tap and the tap and synthetic water under the optimal conditions examined in part 2.2.2; the ozonated water samples were collected every 3 mins for 15 mins. Ozonation of these two water types was stopped after 15 mins, but sampling continued every 3 mins for an additional 15 mins. The residual ozone ($O_{3(aq)}$) and ferrous ions in water during and after ozonation were sampled and analyzed in the following section 2.2.5.

2.2.4. Effect of pH on iron treatment and residual ozone in water

The pH influenced the activity of the ferrous species, both in the formation of the hydroxide complexes and the precipitation of solid hydroxides. pH is also one of the factors strongly affecting ozone solubility and decomposition. Thus, the effect of different pH values at 2, 4, 6, and 8 on the efficiency of iron removal and residual ozone from the synthetic water was investigated. The ozonated water was sampled continuously every 3 mins at the optimal conditions examined in part 2.2.2. Two samples of the synthetic water were carried out parallelly in one experimental batch. One sample was not ozonated, and the ferrous species were oxidated and precipitated with dissolved oxygen; then, the remaining ferrous ions in the filtrate were analyzed and denoted as C_{O2P} (mg/L). Another sample was ozonated, and the ferrous species in the sample were oxidated and precipitated with dissolve ozone; then, the residual ferrous ions in the filtrate were analyzed and denoted as C_{O3P} (mg/L).

Ferrous removal due to ozonation (%) was calculated using the following equation:

$$H_{O3} = \frac{C_{O2P} - C_{O3P}}{C_O} * 100 \quad (7)$$

Ferrous removal (mg/L) via ozonation was calculated via the following equation:

$$m = C_{O2P} - C_{O3P} \quad (8)$$

Total ferrous removal efficiency (%) was calculated with the following equation:

$$H_{total} = \frac{C_o - C_{O3P}}{C_o} * 100 \quad (9)$$

where C_o: initial ferrous concentration (mg/L)

2.2.5. Analytical methods

The residual ozone in water was analyzed with the DPD method. $O_{3(aq)}$ was absorbed in a 1% solution of KI at a pH 6.8±0.2 of phosphate buffered solution and produced the liberated iodine, which then reacted with the DPD to form the pink compound. This pink solution was determined spectrophotometrically at 540 nm, and its intensity was proportional to the ozone concentration [24]. The residual ferrous after reactions with ozone was analyzed with the 1,10-phenanthroline method. The 1,10-phenanthroline reacted with the ferrous ions to form a reddish-orange complex, which was measured spectrophotometrically at 508 nm [24].

3. Results and discussion

3.1. Effect of air flow rate on ozone production

Ozone production under various rates of air flow from 0.5 to 3.0 lpm during 21 mins is described as ozone generation (g/h) and ozone concentration (g/L) in the KI solution shown in Figure 2, respectively.

The ozone generation (g/h) was in the range of 1.30–5.10 g/h and decreased with increasing operating time, possibly due to reducing adsorptive capability of zeolite column in PSA. It was enhanced with air flow from 0.5 to 2.0 lpm but reduced slightly at 3.0 lpm. O_3 concentrations passaging in 15 mins were in the range of 0.064–0.642 g/L and achieved the pseudo saturated levels at 0.246 g/L, 0.271 g/L, and 0.461 g/L after 15 mins at 0.5, 1.0 and 3.0 lpm, respectively. However, the saturation of O_3 concentration at 2.0 lpm was not observed after 15 mins. These results have also been observed in previous studies [12,24,25] and explained by chemical chains of O_3 production from O_2 described in the following reactions from (10) to (15):

$$O_2 + e^- \rightarrow O + O + e^- \quad (10)$$

$$O_2 + e^- \rightarrow O_2^* + e^- \quad (11)$$

$$\mathrm{O} + \mathrm{O}_2 + \mathrm{M} \rightarrow \mathrm{O}_3 + \mathrm{M} \quad (12)$$

$$O_2^* + O_2 \rightarrow O_3 + O \quad (13)$$

$$O_3 + O \rightarrow 2O_2 \quad (14)$$

$$O + O \rightarrow O_2 \quad (15)$$

The air contains 21% of O_2 gas, which is purified by PSA technology. Increasing the air flow from 0.5 to 2.0 lpm led to the enhancement of the O_2 volume and amount, resulting in an increase of O_3 generation as well as O_3 concentration according to chemical reactions from (10) to (13) and (15). However, an increase in O_2 concentration at the higher flow rate (3.0 lpm) gave a shorter stay and time in the corona discharge tube. In addition, an excess of inlet O_2 amount may accumulate in the tube or produce lots of O atoms corresponding to reaction (10), resulting in the consumption of O_3 with O atom followed the chemical reaction (14). Thus, O_3 production decreased as observed at a flow rate of 3.0 lpm. The air flow of 1.0 lpm and interval period of 21 mins should be selected to investigate the lab-scale purpose and assure operational stability; O_3 generation at this flow rate was 3.17±0.29 g/h.

3.2. Effect of diffuser types, water-flow rate, and hydraulic retention time (HRT) on dissolve ozone in water

The results in Figure 3 show that the dissolved ozone of the four systems rises sharply in 12 minutes and reaches the following saturation values: 3.48±0.21 mg/L for BD0.52.4, 5.07±1.80 mg/L for VD0.52.4, 9.05±0.28 mg/L for VD0.52.8, and 10.99±0.96 mg/L for VD2.02.5.

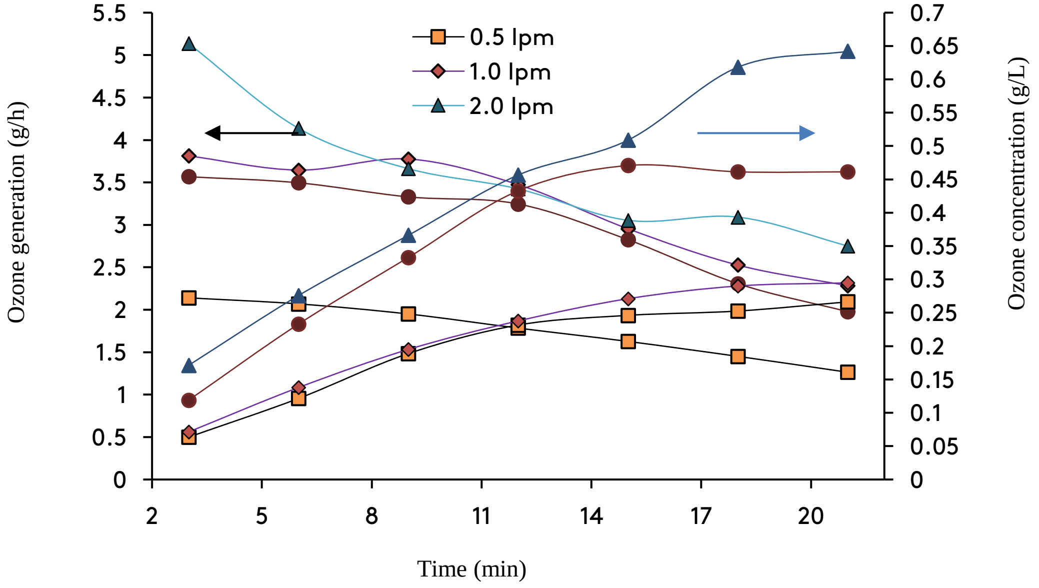

Fig. 2. Effect of air flowrates on ozone production denoted as ozone generation and ozone concentration in KI solution with time. *(Experimental conditions: T=25°C, P=1atm, 500 mL of KI solution (1%)+ pH7 of buffered solution, spherical gas stone diffuser).*

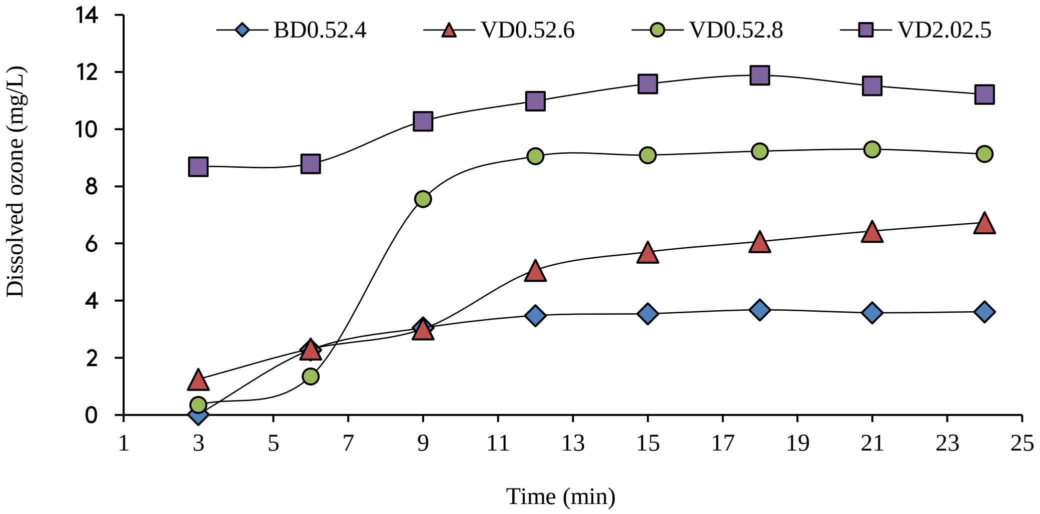

Fig. 3. Effect of diffusers and water flowrates, HRT on dissolved ozone in water *(Experimental conditions: T=25°C, P=1atm,* Q_g*=1.0 lpm,* V_L*=1.2 L, Ozone generation=3.17±0.29 g/h,* $[Fe^{2+}]_o$*=25 mg/L)*.

Size distribution and Zeta potential are two factors of a bubble diffuser regarding the mass transfer efficiency of ozone. The smaller diameter of the bubble distributor indicates that its internal pressure is higher, and mass transfer rates are more rapid [19]. Venturi diffuser works on the principle of pressure difference through the throat of the venturi system. The amount of ozone sucked in forms bubbles in the water, and microbubbles are created due to a large decrease in pressure cavitation inside the venturi, thus producing an emulsion of fine ozone bubbles. The bubble size derived from the system coupled with venturi was observed to be smaller than that from only a bubble diffuser. Consequently, the dissolved ozone of VD0.52.4 was 1.5 times higher than that of BD0.52.4. This observation was in agreement with [26] and [27], who also showed enhancement of the dissolved ozone in venturi system up to 9 and 6 times compared to that of only the bubble diffuser, respectively. In addition, an increase in HRTs and water flow rates helped the ozone to remain in contact with the water if possible and decreased pressure at an orifice, resulting in ozone dissolved well in the water. Consequently, dissolved ozone in the system of VD2.02.5 (10.99±0.96 mg/L) was observed as the highest one, followed by that in VD0.52.8 (9.05±0.28 mg/L), and finally VD0.52.6 (5.07±1.80 mg/L).

Table 1. Calculated data of the diffusive coefficients.

	BD0.52.4	**VD0.52.4**	**VD0.52.8**	**VD2.02.5**
Linear equation	y=-0.175x+1.243	y=-0.186x+2.703	y=-0.208x+2.518	y=-0.108x+1.389
R^2	0.794	0.928	0.808	0.565
p-value	0.002939	0.00012	0.002375	0.03135
k_{La} (min^{-1}) (This study)	0.162	0.173	0.195	0.095
k_{La} (min^{-1}) [17]	0.100–0.160			
k_{La} (min^{-1}) [25]	0.087-0.0978			

Eq. 2 was applied to estimate the ozone mass transfer coefficients in different systems. The linear correlation between the natural logarithm of the dissolved ozone concentrations and time of Eq. 2 was evaluated and are described in Table 1. From Table 1, the coefficients of determination (R^2) of the linear models (Eq. 2) in the BD0.52.4, VD0.52.4, VD0.52.8, and VD2.02.5 systems were 0.794, 0.928, 0.808, and 0.565, respectively. These results indicates that the equilibrium state between the ozone gas and aqueous phases can be achieved in the system of VD0.52.4, followed by VD0.52.8, then BD0.52.4, and finally VD2.02.5. However, all p-values of the Fisher test for the four linear models smaller than 0.05 demonstrate that these models can be used to describe the experimental data statistically. Thus, diffusive coefficients of BD0.52.4, VD0.52.4, VD0.52.8, and VD2.02.5 were estimated as 0.162, 0.173, 0.195, and 0.095, respectively. The VD0.52.8 system of 0.5 lpm and 2.8 min^{-1} was selected to conduct the experiments of iron treatment due to its highest diffusive coefficient (k_{La}, 0.195) and relatively high correlation coefficient (R^2, 0.808) corresponding to the equilibrium state achieved in the system. The diffusive coefficient of the bubble diffuser in this study (BD0.52.4) was relatively similar to the result of Yao et al. [17] but higher than that of Ratnawati et al. [25], possibly due to lower HRT and higher gas flow rate compared to the investigated HRT and gas flow rate in this study.

3.3. Consumption of dissolved ozone by ferrous ion and its half-lives after ozonation

Figure 4 showed that $O_{3(aq)}$ concentrations in the tap and synthetic water for 15 minutes ozonation were witnessed an uptrend and achieve the maximum values of 9.82 mg/L and 1.92 mg/L, respectively whereas removal of ferrous concentrations via ozonation were of 30.23±0.23%, corresponding to7.54±0.082 mg/L.

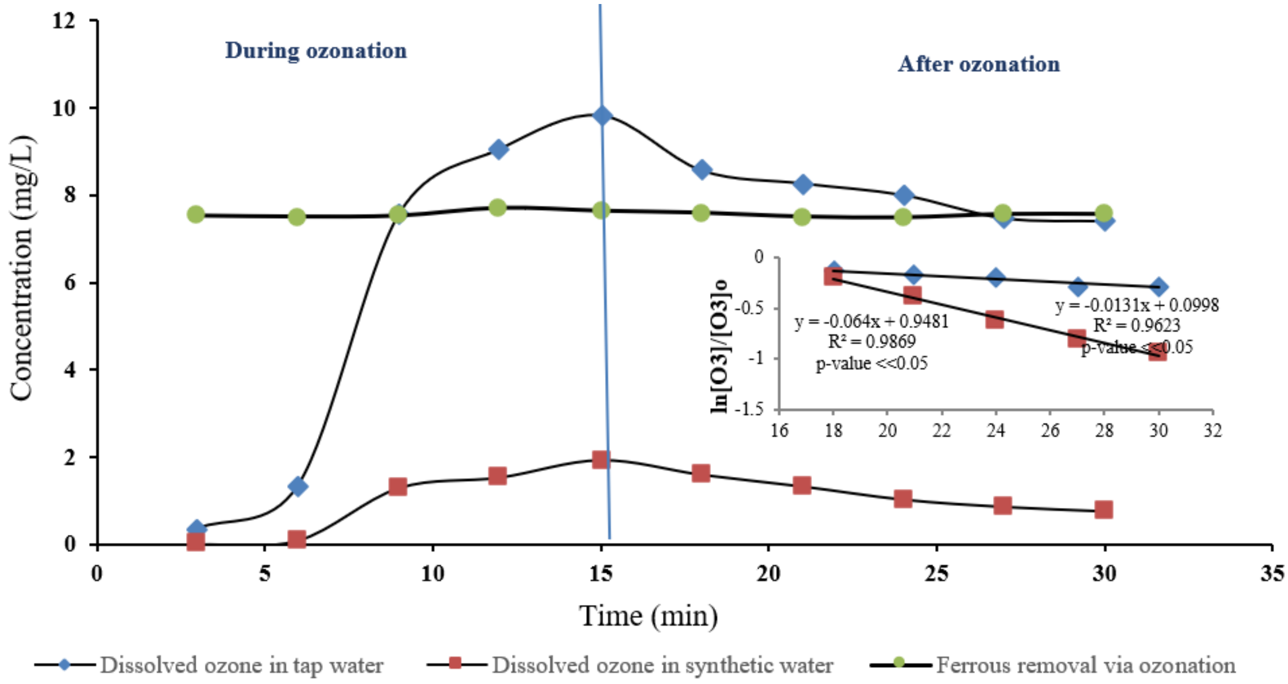

Fig. 4. Consumption of dissolved ozone by ferrous ions and half-life of residual $O_{3(aq)}$ after ozonation *(Experimental conditions: T=25°C, P=1atm, Q_g=1.0 lpm, V_L=1.2 L, Ozone generation=3.17±0.29 g/h, $[Fe^{2+}]_o$=25 mg/L, VD0.52.8).*

Difference in dissolved ozone concentration ($\Delta[O_{3(aq)}]$) among the two cases was 7.90 mg/L at 15 minutes, which was supposed mainly for ozone consumption on ferrous removal from water. A ratio of the experimental mole of $\Delta[O_{3(aq)}]/\Delta[Fe^{2+}]$ was 1.21, corresponding to its mass ratio of 1.04 mg O_3/mg Fe^{2+}. This experimental mole ratio was higher than the stoichiometric reaction of ozonation and the values reported by the O_3 manufacture with the mole ratio and mass ratio of 0.51 and 0.48 mg $O_{3(aq)}$/mg Fe^{2+}, respectively. If this mole ratio was 0.5, corresponding to the stoichiometry, intermediate species of a ferrous-ozone complex, or so-called ferry ions (FeO^{2+}) [27] might form; these ferry ions cannot be analyzed with 1,10-phenanthroline and may give erroneous results. Hence, the mole ratio of 1.21 used in this study can assure the promotion of the ozonation reaction shifting to the right completely and avoid intermediate formation. After ozonation, $O_{3(aq)}$ decreased in a downtrend to 7.40 mg/L and 0.75 mg/L at 30 minutes in the two cases of the absence and presence of iron in the in water, respectively. Hydroxide ions (OH^-) were a reactant in the formation of the hydroxyl radical ($^{\bullet}OH$) and the main initiator of the chain reactions (16) & (17) for ozone decomposition [29].

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad (70\ M^{-1}s^{-1})\ (16)$$

$$O_3 + HO_2^- \rightarrow \cdot OH + \cdot O_2^- + O_2 \qquad (2.8*10^6\ M^{-1}s^{-1})\ (17)$$

The decay constants of ozone after ozonation in these two cases were developed from reaction (8) due to the slow rate, which controlled all reactions between the O_3 and OH^- ions. The relationship was built between the natural logarithm dissolved ozone and the decay time of Eq. 6 and is presented in the small figure 4. The determinate coefficients of two linear models in the cases of iron presence and absence were 0.986 and 0.962, respectively; the p-values of the Fisher test smaller than 0.05 indicated that these two linear models of Eq. 5 could be applied to estimate decay constant. Thus, the decay constant of $O_{3(aq)}$ in the presence of iron was 0.064 min^{-1}, 4.88 times higher than in its absence (0.013 min^{-1}). The half-lives of $O_{3(aq)}$ in the two cases were 11 minutes and 53 minutes, respectively, which were in a range of 17-833 minutes reported in the review article of Gardoni et al. [29]. However, residual ozone concentration after ozonation in the synthetic water was 1.9 mg/L, above the EPA standard of 0.4 mg/L and the FDA regulation of 0.1 mg/L as a good manufacturing practice for bottled water. Therefore, the respective decay times of 24.50 minutes and 46.17 minutes were required to meet the EPA and FDA standards.

3.4. Effect of pH on ferrous treatment and residual ozone in water

Impact of pH on the total ferrous removal efficiency, ferrous removal via ozonation and residual ozone in the synthetic water is depicted in Figure 5. Figure 5a illustrates that the efficiency of the total ferrous removal increases dramatically from 32.84±2.97% to 99.58±0.47%, while that of ozonation is in the range of 7.19±0.45% and 38.96±1.17% with an increase of pH from 2 to 8. The concentration of residual $O_{3(aq)}$ was also observed in the opposite trend from 8.52±4.81 to 0.33±0.64 mg/L.

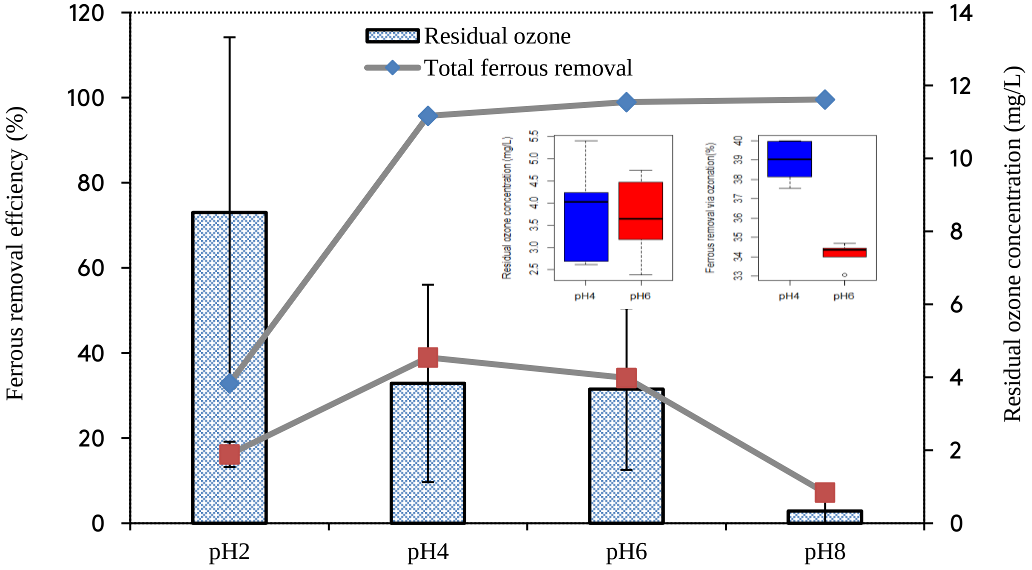

Fig. 5. Influence of pH on iron removal efficiency *(Experimental conditions: T=25°C, P=1atm, Q_g=1.0 lpm, V_L=1.2 L, Ozone generation=3.17±0.29 g/h, $[Fe^{2+}]_o$=25 mg/L, VD0.52.8, mean±t*SEM)*.

An increase in pH from 2.0 to 8.0 led to a shift into the right of ozonation reactions with quantitative equilibrium constants of redox ($\log K_{O2,Fe2+}$, 36 -83; $\log K_{O3,Fe2+}$, 45 – 69), thus enhancing the efficiency of the total ferrous removal from 32.84±2.97% to 99.58±0.45%. Whereas the removal efficiency due to ozonation was promoted from 16.18±2.97% to 38.96±1.17% with an increased pH from 2.0 to 4.0, then reduced slightly to 34.16±0.61% and significantly to 7.19±0.45% at pH6.0 and 8.0, respectively. This phenomenon could be explained by the self-decomposition of ozone in the synthetic water explained by reactions (8) and (9). As a result of these processes, residual $O_{3(aq)}$ in the synthetic water decreased when OH^- concentration increased. However, Figure 5a shows that the removal efficiency due to ozonation and concentration of residual $O_{3(aq)}$ at pH 4.0 and 6.0

cannot be discriminated; therefore, boxplots of effect pH 4.0 & 6.0 on residual $O_{3(aq)}$ and ozonation were employed for further analysis and are shown with a small b in Figure 5. Figure 5b indicates that ranges of residual $O_{3(aq)}$ concentration at pH4.0 and 6.0 were 2.61–5.41 mg/L and 2.38–4.74 mg/L, respectively, whereas removal efficiency due to ozonation at pH4.0 and 6.0 was 37.54–40.00 mg/L and 33.07–34.71 mg/L, respectively. Due to the non-normal distribution of these data, the Wilcoxon test was applied to compare the two samples of pH4.0 and 6.0 for residual $O_{3(aq)}$ and ozonation. There was no statistical difference between residual $O_{3(aq)}$ at pH4.0 and pH6.0 (p-value=0.8182>0.05) while ozonation efficiency at pH 4.0 was significantly higher than that of pH6.0 (p-value=0.002165 <0.05). Therefore, pH4.0 was an optimal value for iron removal due to ozonation. The residual iron concentration at pH4.0 was 0.811±0.035 mg/L, which was greater than that of WHO regulation [3]. In contrast, the residual iron concentration at pH6.0 was 0.230±0.149 mg/L, falling below the iron standards of the WHO for drinking water. Meanwhile, the concentration of residual $O_{3(aq)}$ in the synthetic water at pH4.0 and pH6.0 was 3.833±2.706 mg/L, higher than the EPA standard (0.4 mg/L) and FDA regulation (0.1 mg/L) for bottled water. These residual $O_{3(aq)}$ may take 186 and 300 hrs. to self-decompose and achieve EPA and FDA regulations, respectively.

4. Conclusions

The optimization of ozone solubility in water is a preliminary and important step in setting up an ozone technology for water treatment. The optimal conditions for ozone performance in this study were a gaseous flow rate of 1.0 lpm and an ozone generation of 3.17±0.29 g/h, corresponding to an ozone concentration of 0.246 g/L in the KI solution. In addition, the venturi system coupled with spherical air stone diffusers, an HRT of 2.8 minutes, and a water flow rate of 0.5 lpm were selected to carry out the experiments of ferrous removal because of its highest diffusive coefficient (k_{La}, 0.195 min^{-1}). The stoichiometry of ($\Delta[O_{3(aq)}]/\Delta[Fe^{2+}]$) in the synthetic water during ozonation was 1.21, corresponding to its mass ratio of 1.04 mg $O_{3(aq)}$/mg Fe^{2+}. Also, the decay constant of $O_{3(aq)}$ in the presence of ferrous ions was 0.064 min^{-1}, 4.88 times higher than that in the tap water (k_c, 0.013 min^{-1}). Ferrous removal due to ozonation was active in a wide pH range of 2.0-8.0 but was strongest at pH 4.0 with ozonation, and the total removal efficiencies were 38.96±1.17% and 95.76±1.17%, respectively. Residual $O_{3(aq)}$ concentrations at pH 4.0 and 6.0 in the synthetic water after ozonation were not statistically different (p-value >>0.05) and their value was 3.83±2.71 mg/L. This $O_{3(aq)}$ concentration is much higher than the EPA (0.4 mg/L) and the FDA (0.1 mg/L) regulations for bottled water. The residual ferrous concentrations at pH 4.0 and pH 6 were 0.81±0.035 mg/L and 0.23±0.15 mg/L, respectively which are above the WHO guidelines for iron in drinking water quality for the first case and below for the latter one.

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