



Application of *in situ* Liquid Ferrate(VI) for 2-Bromophenol Removal

2-브로모페놀 제거를 위한 액상 페레이트 적용 연구

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ABSTRACT

The concern over the risk of environmental exposure to brominated phenols has been increased and has led the researchers to focus their attention on the study of bromophenol treatment. In this study, the effects of pH and ferrate(VI) dose on the degradation of 2-bromophenol were investigated. The results indicated that the oxidation of 2-bromophenol by liquid ferrate(VI) was found to be highly sensitive to the pH condition. Furthermore, the highest removal efficiency was observed at the neutral condition with the removal efficiency of 94.2%. In addition, experimental results showed that 2-bromophenol removal efficiency increased with increasing of ferrate dosage. Ferrate(VI) dose of 0.23 mM was sufficient to remove most of the 2-bromophenol with the efficiency of 99.73% and kapp value of 2982 M⁻¹s⁻¹. Seven compounds were identified as the intermediate products by the GC/MS analysis.

Key words: liquid ferrate(VI), 2-bromophenol, oxidation, intermediates

주제어: 액상페레이트, 2-브로모페놀, 산화, 중간생성물

1. Introduction

In the last decade, the concern over the risk of environmental exposure to brominated phenols has been increased. Bromophenols are flame retardant compounds which are quite toxic and slowly degraded in the environment. Bromophenols are usually used as the precursors to resorcinol and pesticide materials. Moreover, bromophenols are also used in the production of polymers (Rhee et al., 2003; Uhnáková et al., 2009). The production volume of bromophenols is estimated to be 9,500 tons per year worldwide in 2001. Furthermore, bromophenols are also observed in

nature because they are produced by some organisms in the environment (Vetter & Janussen, 2005). U.S. EPA listed bromophenols as the priority pollutants. Therefore, these problems have led many researchers to focus their attention on the study of bromophenol removal (Dell'Erba et al., 2007).

One of the hazardous bromophenols exemplified in this paper is 2-bromophenol. In order to find out the effective removal method, several experiments to degrade 2-bromophenol have been conducted. 2-bromophenol is a fire retardant component which is usually treated using high-temperature pyrolysis. However, according to the research conducted by Evans and Dellinger (2005), treatment of 2-bromophenol using high-temperature pyrolysis led the production of a hazardous compound like dioxin.

Received 19 November 2015, revised 14 December 2015, accepted 15 December 2015

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Furthermore, Knight et al. (1999) studied 2-bromophenol degradation using phenol-degrading microbial consortia. The results of those researches showed good removal efficiency, but the degradation processes were very slow. It took 28 days to degrade 200 μM of 2-bromophenol. On the other hand, only few studies have been reported regarding the usage of ferrate(VI) for the removal of organic contaminants, especially 2-bromophenol.

Ferrate(VI) is a supercharged iron molecule in which iron is in the +6 oxidation state (Yang et al., 2012). Ferrate(VI) has shown great potential as a multi-functional water and wastewater treatment chemical for coagulation, disinfection, and oxidation (Jiang, 2007; Li, et al., 2008; Sharma, 2002). Ferrate(VI) oxidation power is greater than ozone and it is the strongest among all the oxidants/disinfectants used in the application for water and wastewater treatment (Jiang, 2014). Therefore, ferrate(VI) is an appropriate compound to remove hazardous contaminants in the water and wastewater including heavy metal and organic contaminants (Sharma, 2002).

Applications of ferrate(VI) for water and wastewater treatment have been well acknowledged. However, challenges have existed to the implementation of ferrate(VI) technology in water and wastewater treatment. These problems were caused by either the instability property of a ferrate(VI) solution or a high preparation cost of a solid ferrate(VI) (Jiang, 2007). To overcome these problems, research has been directed to the production and application of *in-situ* liquid ferrate(VI) (Jiang, 2014). Liquid ferrate(VI) has been reported as the great oxidizing agent for the pollutants including organic contaminants (White & Franklin, 1998). Consequently, liquid ferrate(VI) is expected to be a good oxidizing agent for 2-bromophenol and it can be one of the best available technologies to remove bromophenols from water and wastewater.

In this study, liquid ferrate(VI) was applied to investigate the influence parameters for the 2-bromophenol removal. Previous studies have focused on the examination of the possibility of the ferrate(VI) as an agent of disinfection and coagulation. Only few researches have been conducted on the application of ferrate(VI) for the 2-bromophenol removal. Moreover, this research employed *in-situ* liquid ferrate(VI)

which has never been used for the removal of 2-bromophenol. In particular, this paper evaluated the efficiency of *in-situ* liquid ferrate(VI) for the 2-bromophenol removal in the various pH and ferrate(VI) doses. Moreover, intermediate products were identified in this study to investigate the mechanism of 2-bromophenol removal by *in-situ* liquid ferrate.

2. Materials and Methods

2.1 Materials

Ferrate(VI) in these experiments was produced in the laboratory by the wet oxidation method. The principal reagents used in the experiments were analytical grade and used without further purification. These reagents included $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NaOCl , NaOH , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ from Junsei Company (Ltd., Japan). The 2-bromophenol reagent in the experiment was obtained from Sigma-Aldrich with the purity 99%. The solutions were prepared using water that had been filtrated and passed through an 18 $\text{M}\Omega$ Milli-Q cm water purification system.

2.2 Experimental Section

2.2.1 Synthesis of Ferrate(VI)

Liquid ferrate(VI) in these experiments was produced on site and was synthesized by the wet oxidation method. Typically, the first step to synthesize liquid ferrate(VI) was the addition of 31 grams NaOH into 60 mL NaOCl . Afterward, the mixture was stirred until homogeneous solution formed. After a homogeneous solution was formed, 4 grams of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added into the solution. The mixing process was carried out over the period of 11 minutes. At last, the concentrations of ferrate(VI) were measured by spectrophotometer UV-Vis using several wavelengths which were 254 nm, 390 nm, 505 nm and 680 nm.

2.2.2 Degradation Experiments

The oxidation experiments were performed in a closed zero-head space glass reactor with port for sampling, pH probe, thermometer, and ferrate(VI) inlet. The 3 mL samples

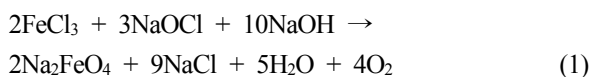


were taken and extracted using liquid-liquid extraction method with n-hexane. Afterward, the 2-bromophenol concentrations were measured using gas chromatography (Technologies Co. 4890D) equipped with Rxi-5 ms column ($L = 30$ m, internal diameter = 0.25 μm), and an electron capture detector (ECD). The temperatures of the injection port and detector were 250 and 300°C , respectively. The temperature program began at 50°C , followed by a $50^\circ\text{C}/\text{min}$ ramp until a final temperature of 250°C was reached. The gas chromatography/mass spectrometry (GC/MS) technique was used to analyze intermediate products. To stop further degradation reaction, quenching process using sulfuric acid was conducted. GC/MS analysis was performed with Mass Spectrometer Systems (GC/MS-QP2010Plus, Shimadzu, Japan) and an AT-1 capillary column (60 m \times 0.32 mm I.d \times 1.0 μm film thickness). The injection port temperature was 300°C and the column temperature, initially 100°C , was held constant for 5 min, followed by $50^\circ\text{C}/\text{min}$ ramp until a final temperature of 250°C was reached and held for 7 min.

3. Results and Discussion

3.1 Synthesis of Ferrate(VI)

In the ferrate(VI) synthesis, oxidizing agents such as NaOCl, O_3 and H_2O_2 can be used to oxidize iron (Fe) from low oxidation states (+3) to the highest oxidation states (+6) (Chengchun et al, 2008). In this experiment, the iron (Fe) source for the ferrate(VI) production was $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. Red purplish color was formed as the result of oxidation reaction between iron ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and NaOCl (Eq. (1)) (Williams & Riley, 1974). The color development indicated that the ferrate(VI) was successfully established. Ferrate(VI) (FeO_4^{2-}) was successfully produced with the iron (Fe) concentration of $42,000$ mg/L for 11 minutes of reaction time. The ferrate(VI) yield in this experiment was 86.1% .



3.2 Effect of pH

Ferrate(VI) is a powerful oxidant in the entire pH range

(Sharma, 2002). However, its oxidation power is dependent on pH condition (Thompson et al., 1951). Among 3 values of pH chosen from 3.2 , 6.8 , and 10.2 , the highest 2-bromophenol removal extent was observed at pH 6.8 with the removal efficiency of 94.2% (Fig. 1).

This result agreed with other studies on the oxidation of phenolic compounds; for the example, an optimum pH range of 7 to 9.2 has been reported by Graham et al. (2004) on the oxidation of phenol and chlorophenol. Ferrate(VI) has highest oxidation power in acidic condition. However, acidic condition led ferrate(VI) self-decomposition (Abduly & Sharma, 2014). At basic condition ($\text{pH} > 10$), ferrate(VI) is very stable because its oxygen ligands exchange very slowly with water (Sharma, 2002, 2010). Consequently, both conditions reduced the reaction rate of ferrate with 2-bromophenol (Sharma & Bielski, 1991; Sharma et al., 2000).

Ferrate(VI) and 2-bromophenol speciation also play a significant role in the effect of pH. The 2-bromophenol only has phenolate anion as its speciation product (eq. (2)). On the other hand, Ferrate(VI) has triprotonated (H_3FeO_4^+), diprotonated (H_2FeO_4), monoprotated (HFeO_4^-), and deprotonated (FeO_4^{2-}) species existed in the acidic to basic

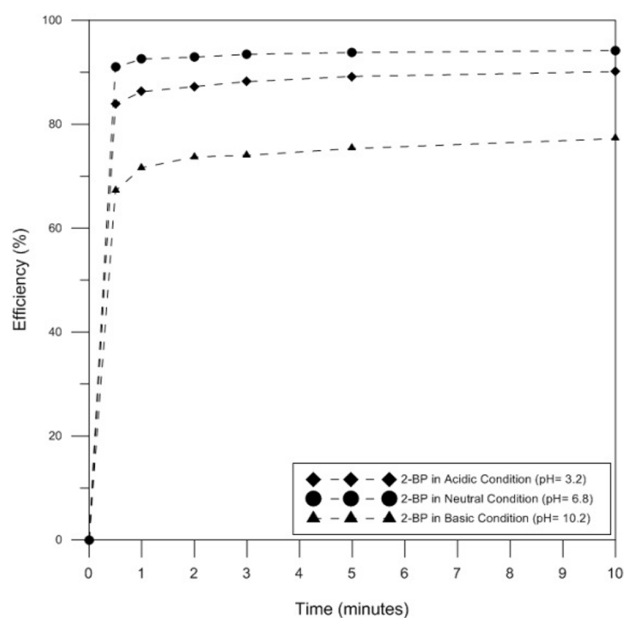
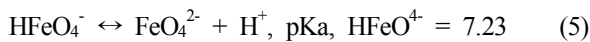
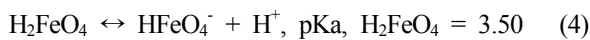
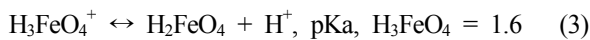
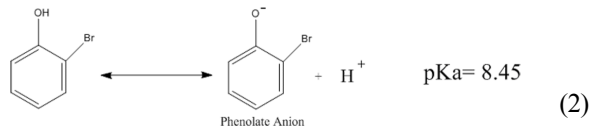


Fig. 1. Effect of pH on the removal of 2-bromophenol by ferrate(VI). (Experimental conditions: $C_0 = 1$ mg/L, $[\text{FeO}_4^{2-}] = 0.04668$ mM, Temp. = $25 \pm 1^\circ\text{C}$.)

pH range (Eqs. (3–5)) (Rush et al., 1996; Sharma et al., 2001; Sharma, 2011). The diprotonated and monoprotated species have high oxidation power and exist in the acidic and neutral conditions. As the result, the highest removal efficiency was observed at the neutral condition (pH= 6.8).



Reaction rate was determined from the kapp value using second order reaction rate equation. The reaction of ferrate(VI) with an organic compound is the second order reaction rate (Yang et al., 2011). The second order reaction rate law can be described by eq. (6).

$$-d[2\text{-BP}]/dt = k_{\text{app}}[\text{Fe(VI)}]_{(\text{tot})}[2\text{-BP}]_{(\text{tot})} \quad (6)$$

$[\text{Fe(VI)}]_{(\text{tot})}$ represented the total concentration of Ferrate (VI) species, and $[2\text{-BP}]_{(\text{tot})}$ represented the total concentration of 2-bromophenol species. Ferrate(VI) has different speciation products in the various pH conditions (Fig. 2). The pH dependency of ferrate(VI) species and 2-bromophenol species could be quantitatively modeled by eq. (7) (Lee & Gunten, 2005; Sharma, 2013).

$$\begin{aligned}
 k_{\text{app}}[\text{Fe(VI)}]_{(\text{tot})}[2\text{-BP}]_{(\text{tot})} \\
 = \sum_{i=1,2,3,4} k_{ij} \alpha_{ij} \beta_{ij} [\text{Fe(VI)}]_{(\text{tot})}[2\text{-BP}]_{(\text{tot})} \quad (7)
 \end{aligned}$$

Where $[\text{Fe(VI)}]_{(\text{tot})} = [\text{H}_3\text{FeO}_4^+] + [\text{H}_2\text{FeO}_4] + [\text{HFeO}_4^-] + [\text{FeO}_4^{2-}]$, $[2\text{-BP}]_{(\text{tot})} = [2\text{-bromophenol}] + [2\text{-bromophenoxide}^-]$, α_{ij} and β_{ij} represented the respective species distribution coefficients for Fe(VI) and 2-BP, i and j represented each of four species of Fe(VI) and two species of 2-BP, and k_{ij} was the species-specific second-order rate constant for the reaction between the Ferrate(VI) species i with the 2-BP species j. Values of k_{ij} were calculated in the pH 3.2, 6.8,

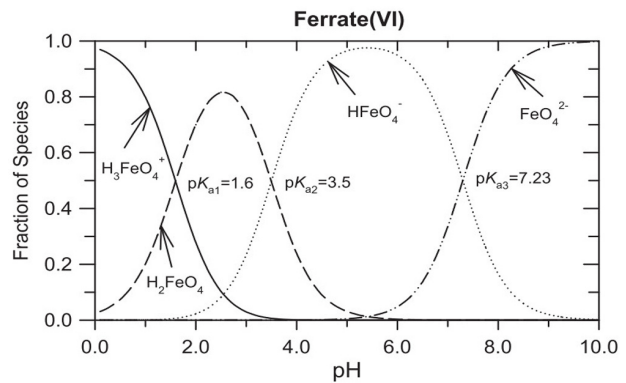


Fig. 2. Speciation of Ferrate(VI) in various pH conditions. (Sharma, 2013)

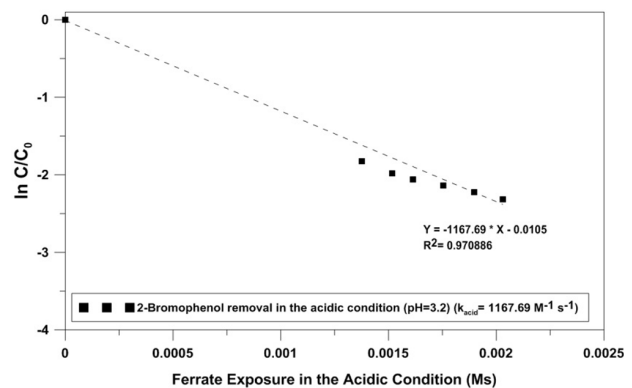


Fig. 3. Rate of 2-Bromophenol removal by ferrate(VI) in the pH 3.2 (Experimental conditions: $C_0 = 1 \text{ mg/L}$, $[\text{Fe(VI)}]_{(\text{tot})} = 0.04668 \text{ mM}$, $\text{Temp.} = 25 \pm 1^\circ\text{C}$).

and 10.2 (Figs. 3-5) based on the ferrate speciation (fig. 2) and 2-bromophenol speciation.

In the acidic condition (pH 3.2), ferrate(VI) dominant species was H_2FeO_4 with the fraction of species 0.75. The other species in this pH were H_3FeO_4^+ and HFeO_4^- with the fraction of species 0.03 and 0.22 respectively. In this condition, 2-bromophenol existed in the form of normal 2-bromophenol. From the eq. (6) and eq. (7), rate constant (k) in the acidic condition can be determined using eq. (8) and calculated graphically using figure 3. Where denotes level of ferrate(VI) exposure in acidic condition and kacid was the second order reaction rate constant in acidic condition (Sharma, 2013; Yang et al., 2014). The kacid value of $1167.69 \text{ M}^{-1} \text{ s}^{-1}$ was obtained in this experiment.

$$\begin{aligned}
 \text{Ln}(2\text{-BP})/[2\text{-BP}]_0 = & -k_{\text{acid}} \int_0^t [0.75[\text{H}_2\text{FeO}_4] \\
 & + 0.03[\text{H}_3\text{FeO}_4^+] + 0.22[\text{HFeO}_4^-]] dt \quad (8)
 \end{aligned}$$

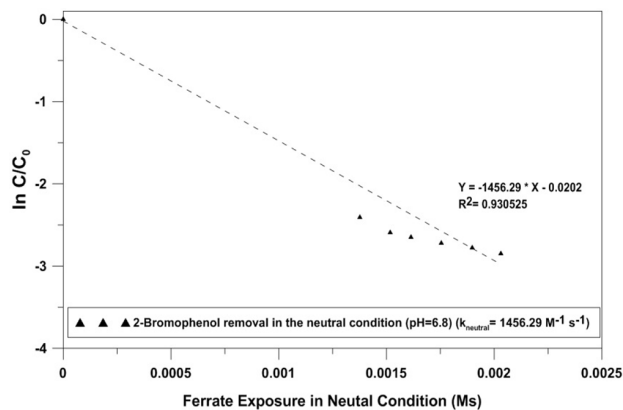


Fig. 4. Rate of 2-Bromophenol removal by ferrate(VI) in the pH 6.8 (Experimental conditions: $C_0 = 1$ mg/L, $[\text{Fe(VI)}]_{(\text{tot})} = 0.04668$ mM, Temp. = $25 \pm 1^\circ\text{C}$).

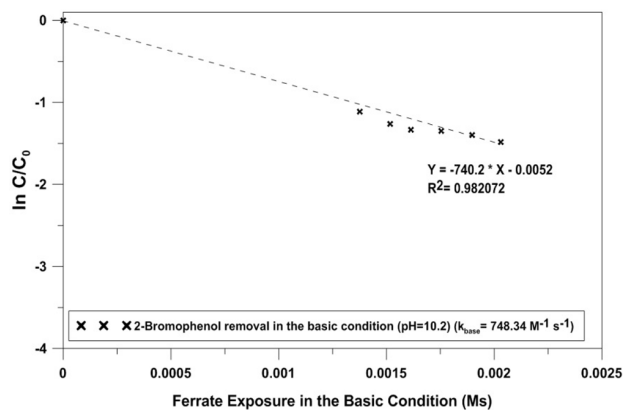


Fig. 5. Rate of 2-Bromophenol removal by ferrate(VI) in the pH 10.2 (Experimental conditions: $C_0 = 1$ mg/L, $[\text{Fe(VI)}]_{(\text{tot})} = 0.04668$ mM, Temp. = $25 \pm 1^\circ\text{C}$).

Table 1. k_{app} value in the variation of pH

Compound	ferrate(VI) dose	Kapp ($\text{M}^{-1}\text{s}^{-1}$)		
		Acid	Neutral	Base
2-Bromophenol	0.0467 mM	1167.69	1456.29	748.34

In the neutral condition (pH 6.8), ferrate(VI) species were HFeO_4^- and FeO_4^{2-} with the fraction of species 0.7 and 0.3 respectively. In this condition, 2-bromophenol also existed in the form of normal 2-bromophenol. Rate constant (k) in the neutral condition can be determined using eq. (9) and calculated graphically using figure 4. Where denotes level of ferrate(VI) exposure in the neutral condition and k_{neutral} is the second order reaction rate constant in the neutral condition. The k_{neutral} value of $1456.29 \text{ M}^{-1}\text{s}^{-1}$ of was obtained in this experiment.

$$\ln(2\text{-BP}]/[2\text{-BP}]_0) = -k_{\text{neutral}} \int_0^t [0.7[\text{HFeO}_4^-] + 0.3[\text{FeO}_4^{2-}]] dt \quad (9)$$

In the basic condition (pH 10.2), ferrate(VI) species was only existed in the form of FeO_4^{2-} . In this condition, 2-bromophenol existed in the form of 2-bromophenolate anion. Rate constant (k) in the basic condition can be determined using eq. (10) and calculated graphically using figure 5. Where denotes level of ferrate(VI) exposure in the basic condition and k_{base} is the second order reaction rate constant in the basic condition. The k_{base} value of $748.34 \text{ M}^{-1}\text{s}^{-1}$ was obtained in this experiment.

$$\ln(2\text{-BP}]/[2\text{-BP}]_0) = -k_{\text{basic}} \int_0^t [\text{FeO}_4^{2-}] dt \quad (10)$$

Figures 3, 4, and 5 showed the relationship between ferrate exposure and 2-bromophenol decomposition (C/C_0) in the various pH conditions. The ferrate exposure is the time-integrated concentration of ferrate(VI) due to its instability (Yang et al., 2011). The reactions of ferrate(VI) with target compounds were characterized most commonly by (i) one electron transfer step from Fe(VI) to Fe(V), followed by a two electron transfer to Fe(III) as the reduced product ($\text{Fe(VI)} \rightarrow \text{Fe(V)} \rightarrow \text{Fe(III)}$), and (ii) two electron transfer steps ($\text{Fe(VI)} \rightarrow \text{Fe(IV)} \rightarrow \text{Fe(II)}$) (Sharma, 2013). The second order reaction rate (k) values in various pH conditions were shown in table 1. This method was used to determine all the second order reaction rate (k) value in the experiments.

3.3 Effect of Ferrate(VI) Dose

Ferrate(VI) dose is significant operational parameter which affected ferrate(VI) performance to remove organic contaminants (Sharma, 2013). The 2-bromophenol removal efficiency increased with an increase of ferrate(VI) doses. In the solution contained 1 mg/L of 2-bromophenol, the removal efficiency ranged from 77.23 to 99.73% at the ferrate(VI) dosage range from 0.04668 to 0.23 mM (Fig. 6).

In the previous studies, It has been reported that the removal efficiency increased with increasing of ferrate(VI) dose and the removal of 2-bromophenol strongly depended on the dose of ferrate(VI) added to the reactor (Sharma & Bielski, 1991; Sharma et al., 2000; Yu et al., n.d.). Ferrate(VI) dose

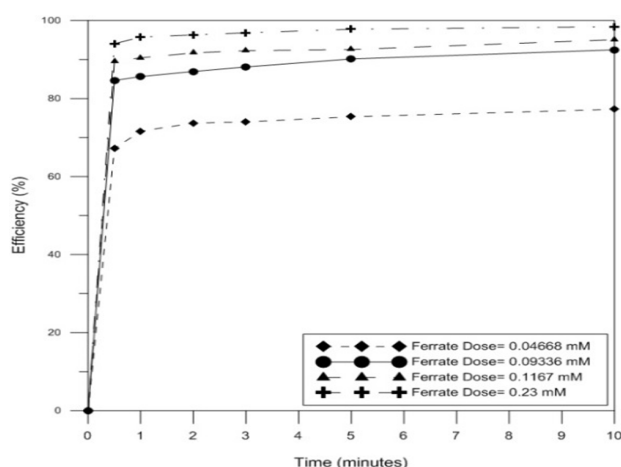


Fig. 6. Effect of the ferrate $[\text{FeO}_4^{2-}]$ dose on the removal of 2-bromophenol. (Experimental conditions: $C_0 = 1$ mg/L, pH = 3.2, Temp. = $25 \pm 1^\circ\text{C}$.)

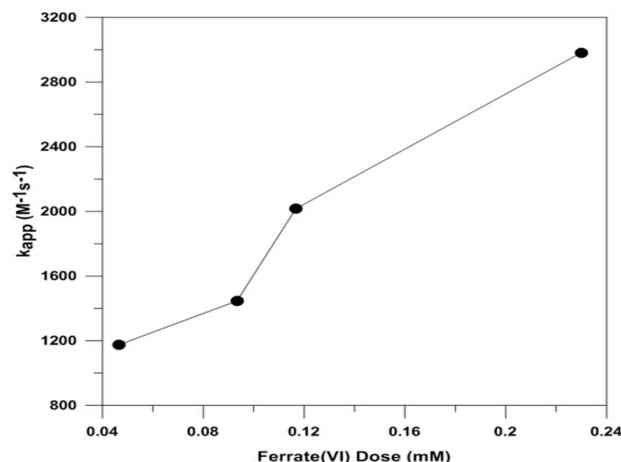


Fig. 7. k_{app} of 2-bromophenol removal by ferrate(VI) in the various ferrate(VI) doses. (Experimental conditions: $C_0 = 1$ mg/L, pH = 3.2, Temp. = $25 \pm 1^\circ\text{C}$.)

Table 2. k_{app} value of 2-BP in the various ferrate(VI) doses (initial concentration of the target compound 1 mg/L, pH acid (3.2), and temperature 25oC)

Compound	Ferrate(VI) Dose	k_{app} value ($\text{M}^{-1}\text{s}^{-1}$)
2-Bromophenol	0.04668 mM	1157.7
	0.09336 mM	1445.8
	0.1167 mM	2016.9
	0.23 mM	2982

of 0.23 mM was sufficient to remove most of the 2-bromophenol in the reactor with the efficiency of 99.73%.

The k_{app} values in the various ferrate(VI) doses were calculated and shown in the Table 2. The observed rate constants (k_{app}) increased proportionally with increasing

of ferrate(VI) doses (Fig. 7). These results indicated that ferrate(VI) ion followed the simple stoichiometric reaction with 2-bromophenol. Removal efficiency increased because increasing ferrate(VI) doses increased the amount of ferrate(VI) available to initiate degradation reaction.

3.4 Identification of Intermediate Products

The intermediate products were identified using GC/MS analysis. The result of GC/MS analysis was shown in Fig. 8. The mass spectra were examined with the computer database of the National Institute of Science and Technology mass spectral library. The degradation of the phenolic compounds by ferrate(VI) usually started by oxygen transfer and proton addition (Jeong & Kim, 2007; Roberts, 2000).

Table 3. Reaction Intermediates of 2-bromophenol degradation by liquid ferrate(VI)

Intermediates Name	Structure	Ret. Time
2,3-dichloro-2-methylpropanal		2.139 min
2-bromo, p-benzoquinone		3.463 min
2-bromo-4-chlorophenol		4.618 min
2,4-dibromophenol		6.646 min
2,6-dibromophenol		7.213 min
ethane-1,2-diol		8.607 min
2,6-dibromobenzene-1,4-diol		9.02 min

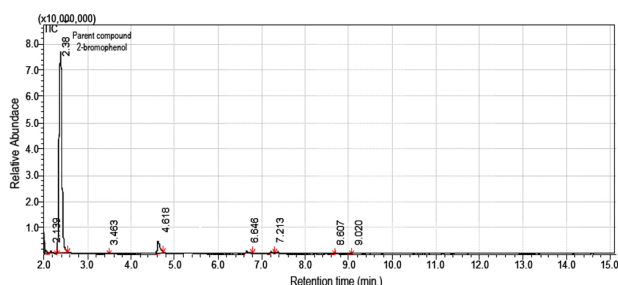


Fig 8. GC/MS chromatogram of 2-bromophenol degradation by Ferrate(VI).

Intermediate products of 2-bromophenol degradation by ferrate(VI) can be classified as the primary and non-primary reaction products. The 2-bromophenol intermediate products detected in the GC/MS chromatogram were 2,6-dibromophenol and 2,4-dibromo-phenol as the primary reaction products. The non-primary reaction products were 2,3-dichloro-2-methyl-propanal, 2-bromo-p-benzoquinone, 1,2-ethanediol, and 2,6-dibromohydroquinone [Table. 3].

The oxidation of 2-bromophenol was proposed to occur through an oxidative reaction which involved the formation of phenoxy radical. It was based on the previous experiment by Huang et al. (2001) which studied intermediate products of phenol degradation by ferrate(VI) using EPR. A similar intermediate product was observed in the experiment. The similar intermediate product was p-benzoquinone.

4. Conclusions

The efficiency of ferrate(VI) for the 2-bromophenol removal has been investigated. In the effect of pH, the neutral pH condition has been observed as the best condition to remove 2-bromophenol with the removal efficiency of 94.2% (kapp value $1469.5 \text{ M}^{-1}\text{s}^{-1}$), while acidic condition 90.11% and basic condition 77.23%. In the case of ferrate(VI) dose effect, the removal efficiency was increased along with the increasing ferrate(VI) doses. The 99.73% of 2-bromophenol has been successfully removed using ferrate(VI) dose of 0.23 mM. Seven compounds were identified as the intermediate products from the GC/MS analysis. From the intermediate products, 2-bromophenol degradation was proposed through an oxidative reaction which involves the formation of phenoxy radical.

Acknowledgements

The authors gratefully acknowledge financial support from the BK21 plus MADEC Human Resource Development Group.

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