Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.11428

58 (2017) 391–398
January

Study on 4-bromophenol degradation using wet oxidation *in-situ* liquid ferrate(VI) in the aqueous phase

Fajar Budi Laksono[a], Il-Kyu Kim[b,*]

[a]*Interdisciplinary Program of Marine Convergence Design, Pukyong National University, 599-1, Daeyeon3-dong, Nam-gu, Busan 608-737, Korea, Tel.+ 82-51-629-7831*
[b]*Department of Environmental Engineering, Pukyong National University, 599-1, Daeyeon3-dong, Nam-gu, Busan 608-737, Korea, Tel. +82 51 629 6528; email: ikkim@pknu.ac.kr (I-K. Kim)*

Received 23 December 2015; Accepted 9 May 2016

ABSTRACT

The study on 4-bromophenol (4-BP) removal using wet oxidation *in-situ* liquid ferrate(VI) has been conducted. The effects of pH, ferrate(VI) dose, 4-BP initial concentration and temperature on the 4-bromophenol degradation were investigated. In the various pH conditions, 4-BP has the highest removal efficiency in the neutral condition (pH = 6.8). A removal efficiency of 65.79% has been observed after a reaction period of 30 s, and 84.1% after a reaction period of 10 min. A ferrate(VI) dose of 0.467 mM was sufficient to remove most of the 4-bromophenol with the efficiency of 96.71% and k_{app} value of 1596 $M^{-1}s^{-1}$. Increasing the molar ratio ([ferrate(VI)]/[4-BP]) enhanced the reaction rate of 4-BP removal. However, the reaction rate decreased when the molar ratio was more than 140:1. The optimal temperature has been observed at 25°C. The activation energy obtained was 29.25 kJ/mol. The 4-BP degradation was proposed through an oxidative pathway which involves the formation of phenoxy radical with isobutyraldehyde as the non-aromatic degradation product.

Keywords: Wet oxidation method; Liquid ferrate(VI); 4-bromophenol; Degradation pathway

---

1. Introduction

Ferrate(VI) is a versatile compound which contains a hyper-valent species of iron, Fe^{6+}. Ferrate(VI) can perform as the disinfectant [1], coagulant [2] and oxidant [3] simultaneously. The oxidation power of ferrate(VI) in the acidic condition is the highest among other oxidants (Table 1). Iron, unlike chromium and manganese, is considered non-toxic. Hence, ferrate(VI) is a suitable compound to remove contaminants in water and wastewater. In recent years, ferrate(VI) has attracted many researchers to employ it as an oxidizing agent for the organic contaminants removal, especially phenolic compounds.

Bromophenols are the phenolic compounds generally used as the flame retardants. Moreover, bromophenols are also used as polymers materials, resorcinol precursors and pesticide components [5,6]. Bromophenols production volume was estimated to be 9,500 tons per year worldwide in 2001. Furthermore, bromophenols are also found in the environment from the production of some organisms [7]. On the other hand, bromophenols are listed as the primary pollutants by US EPA. Bromophenols accumulation in the environment has led to harmful effects for organisms and the environment [8]. These problems encourage the researchers to establish an effective method to remove bromophenols. One of the hazardous bromophenols which is exemplified in this paper is 4-bromophenol (4-BP).

Several studies related to the degradation of 4-bromophenol have been conducted. Sahoo and Pakshirajan investigated the degradation of 4-bromophenol using *Arthrobacter chlorophenolicus* A6 [9]. In addition, Levy et al. also studied 4-bromophenol oxidation by the recombinant fused protein cellulose-binding domain-horseradish peroxidase immobilized on cellulose [10]. Further research regarding 4-bromophenol removal using direct photolysis was reported by Kochany [11]. However, problems still exist

---

[*] Corresponding author.

Presented at the 2015 International Environmental Engineering Conference (IEEC 2015) October 28–30, 2015, Busan, Korea.

1944-3994/1944-3986

Table 1
Redox potential of oxidants/disinfectants in water and wastewater treatment [4]

Disinfectant/ oxidant	Reaction	E°, V
Chlorine	$Cl_2(g) + 2e \leftrightarrow 2Cl^-$	1.358
	$ClO^- + H_2O + 2e \leftrightarrow Cl^- + 2OH^-$	0.841
Hypochlorite	$HClO + H^+ + 2e \leftrightarrow Cl^- + H_2O$	1.482
Chlorine dioxide	$ClO_2(aq) + e \leftrightarrow ClO_2^-$	0.954
Perchlorate	$ClO_4^- + 8H^+ + 8e \leftrightarrow Cl^- + 4H_2O$	1.3989
Ozone	$O_3 + 2H^+ + 2e \leftrightarrow O_2 + H_2O$	2.076
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2e \leftrightarrow 2H_20$	1.776
Dissolved oxygen	$O_2 + 4H^+ + 4e \leftrightarrow 2H_2O$	1.229
Permanganate	$MnO_4^- + 8H^+ + 3e \leftrightarrow MnO_2 + 2H_2O$	1.679
	$MnO_4^- + 8H^+ + 5e \leftrightarrow Mn^{2+} + 4H_2O$	1.507
Ferrate(VI)	$FeO_4^{2-} + 8H^+ + 3e \leftrightarrow Fe^{3+} + 4H2O$	2.2

in the application of those methods due to the low removal efficiency and expensive operation costs. On the other hand, the study concerning 4-bromophenol removal using liquid ferrate(VI) is limited. Liquid ferrate(VI) has been reported as an oxidizing agent for organic contaminants which has high removal efficiency [12] and low operational costs [13]. Consequently, liquid ferrate(VI) is expected to be one of the best available technologies to remove 4-bromophenol.

Previous studies have focused on the examination of the ferrate(VI) possibility as an agent of disinfection and coagulation. Only a limited amount of research has been conducted on the application of ferrate(VI) for the 4-bromophenol removal. One of them was conducted by Lee et al. which used solid ferrate(VI) (K_2FeO_4) to remove 4-bromophenol [14]. However, that study only focused on the determination of phenolic endocrine disruptor and 4-bromophenol k_{app} value at the neutral pH condition. However, this paper presented information concerning the application of liquid ferrate(VI) for 4-bromophenol removal in various conditions. The parameters such as pH, ferrate(VI) dose, 4-BP initial concentration, and temperature were investigated. Degradation pathways have been proposed using GCMS analysis. Furthermore, this research also employed *in-situ* liquid ferrate(VI) which has never been used for the removal of 4-bromophenol.

2. Materials and methods

2.1. Materials

The chemicals such as $FeCl_3.6H_2O$, NaOCl and NaOH for the liquid ferrate(VI) production were purchased from Junsei Company (Ltd., Japan) with extra pure grade quality. The buffer solution for the determination of ferrate(VI) concentrations contained $Na_2B_4O_7.10H_2O$ and $Na_2HPO_4.12H_2O$. These chemicals and HCl were purchased from Crown (Ltd., Japan). The 4-bromophenol was obtained from Sigma-Aldrich with 98% purity. Stock of 4-bromophenol was prepared in a stirred glass flask, which was sealed with a Teflon-covered rubber stopper to prevent organic vapor from escaping.

2.2. Experimental procedures

2.2.1. Synthesis of ferrate(VI)

The preparation of the sodium ferrate(VI) was based on Thompson et al. (1951) wet oxidation method with some modifications. The modification of method was conducted to enhance the yield. It will be useful because the liquid ferrate(VI) will be used directly after the synthesis. The first step to synthesis liquid ferrate(VI) was the addition of 31 g NaOH into 60 mL of NaOCl. Afterward, the mixture was stirred until a homogeneous solution formed. After a homogeneous solution was formed, 4 g of $FeCl_3.6H_2O$ was added into the solution. The mixing process was carried out over a period of 11 min. Lastly, spectrophotometer UV-Vis technique at the multi wavelengths of 254, 390, 505 and 680 nm was used to determine the concentrations of ferrate(VI) [15].

2.2.2. Degradation of 4-BP

Reactions between 4-bromophenol and liquid ferrate(VI) were performed using a closed zero-head space glass reactor with a port for sampling, pH probe, thermometer, and ferrate(VI) inlet. The ferrate(VI) solutions used in the experiments were produced from the synthesis processes. After the addition of ferrate(VI), the solution in the reactor was stirred and then 3 ml of samples were taken at certain time intervals. Afterward, the samples were extracted by n-hexane using the liquid-liquid extraction method. The extracted 4-bromophenol samples were then analyzed 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°C/min ramp until a final temperature of 250°C was reached. The experiments were performed in duplicate.

2.2.3. Intermediate study and degradation pathway

The gas chromatography/mass spectrometry (GC/MS) technique was used to analyze intermediate products. To stop further degradation reaction, a quenching process using sulfuric acid had been conducted. GC/MS analysis was performed with Mass Spectrometer Systems (GC/MS-QP2010Plus, Shimadzu, Japan) and an AT-1 capillary column (60 m × 0.32 mm I.d × 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°C/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)

$FeCl_3.6H_2O$ performed as the iron (Fe) source in the ferrate(VI) production. A red purplish color was formed as a result of the reaction between iron source ($FeCl_3.6H_2O$) with NaOH and NaOCl. Ferrate(VI) (FeO_4^{2-}) has been successfully produced with the concentration 42,000 ppm (Fe) after 11 min of reaction time. The ferrate(VI) was the result of the conversion of $FeCl_3$ into $Na_2FeO_4$with the yield of 86.1%. The concentration of liquid ferrate(VI) achieved in this experiment was considered high. It was because in the previous study by Batarseh et al. the yields of sodium liquid ferrate synthesized by the wet oxidation method was only 70%. The ferrate(VI) formation followed the reaction below.

$$2FeCl_3 + 3NaOCl + 10NaOH \rightarrow 2Na_2FeO_4 + 9NaCl + 5H_2O + 4O_2 \qquad (1)$$

3.2. *Effect of pH*

Ferrate(VI) is a powerful oxidant in the entire pH range [16]. However, the oxidation power of ferrate(VI) is dependent on the pH condition [17]. The experiments have been carried out at pH 3.2, 6.8 and 10.2. Ferrate(VI) has the highest redox potential in acidic condition. However, acidic condition led to the self-decomposition of ferrate(VI) into Fe (III) and oxygen. At its basic condition, ferrate(VI) is very stable due to the oxygen ligand of ferrate(VI) exchange which is very slow with water [16,18]. Therefore, a decrease in the removal efficiency has been observed at the acidic and basic condition. As a result, the highest degradation efficiency has been achieved in the neutral condition. The results of pH effect on 4-BP degradation were shown in Fig. 1.

The initial concentration (C_o) of 4-BP in this experiment was 1 mg/L with the ferrate(VI) concentration ± 0.23 mM. The highest removal was observed at the neutral condition with the efficiency of 84.1%. The results also showed that the lowest efficiency was observed at the basic condition. These results were caused by the combination effects between Ferrate(VI) speciation and halogenated phenol speciation. Ferrate(VI) is a stronger oxidant upon protonation and speciation. Thus, the reaction rate to remove contaminants is expected to increase [19,20]. The ferrate(VI) speciation compounds were H_2FeO_4 (Eq. (2), Rush et al.) and $HFeO^{4-}$ (Eq. (3), Sharma et al.). These two compounds have great oxidation power and exist in pH acid and neutral.

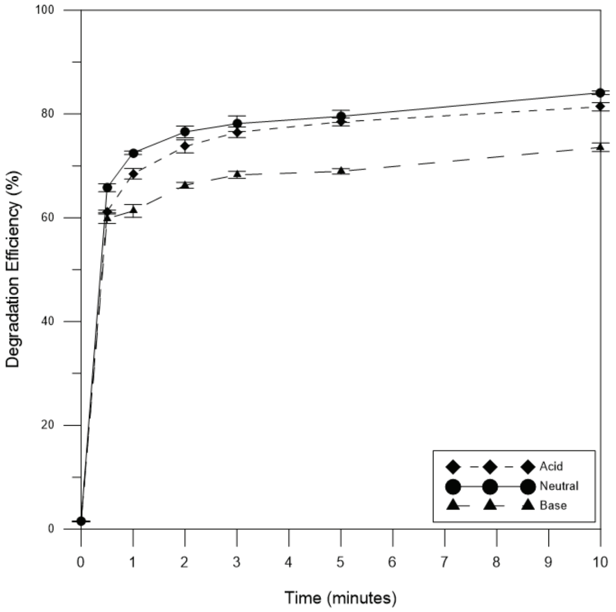


Fig. 1. Results of 4-BP degradation (%) in the various pH condition, C_o = 1 ppm, ferrate(VI) concentration 0.23 mM, temperature 25°C.

$$H_2FeO_4 \leftrightarrow HFeO^{4-} + H^+,\ pKa,\ H_2FeO_4 = 3.50 \qquad (2)$$

$$HFeO^{4-} \leftrightarrow FeO_4^{2-} + H^+,\ pKa,\ HFeO^{4-} = 7.23 \qquad (3)$$

From the removal efficiency data, k_{app} values can be determined using the second order reaction rate equation. The reaction of ferrate(VI) with an organic compound is the second order reaction rate [21]. The second order reaction rate law can be described by Eq. (4).

$$-d[\text{4-BP}]/dt = k_{app}[FeO_4^{2-}][\text{4-BP}] \qquad (4)$$

Eq. (4) was rearranged and $d[\text{4-BP}]/dt$ was integrated to become Eq. (5).

$$\ln(4-\mathrm{BP}]/[4-\mathrm{BP}]_0) = -k_{app}\int_0^t \left[FeO_4^{2-}\right]dt \qquad (5)$$

where $\int_0^t \left[FeO_4^{2-}\right]dt$ was the level of ferrate(VI) exposure, the time integrated concentration of ferrate(VI) (was?) due to the instability [20,22]. The values of k_{app} which were the apparent of second-order rate constant have been achieved by plotting the natural logarithm of 4-BP concentration ($\ln C/C_o$) with the ferrate(VI) exposure (Fig. 2). From this plotting, the rate of oxidation reaction can be determined.

In the previous research conducted by Lee et al., the k_{app} value of solid ferrate(VI) (K_2FeO_4) at pH 7 to remove 4-bromophenol was 86 $M^{-1}\ s^{-1}$ with the ferrate dose 2 mg/L [14]. However, the k_{app} value of *in-situ* liquid ferrate(VI) at pH 6.8 to remove 4-bromophenol from this experiment was 896.74 $M^{-1}\ s^{-1}$ with the ferrate(VI) dose 28 mg/L. Even though both of these experiments used different kinds of ferrate(VI), the ratio of the k_{app} value and ferrate(VI) doses (k_{app}/ferrate(VI) dose) from both experiments were only slightly different. The difference might be caused by the different pH condition and ferrate(VI) dose. However, further investigation needed to be conducted to confirm this hypothesis.

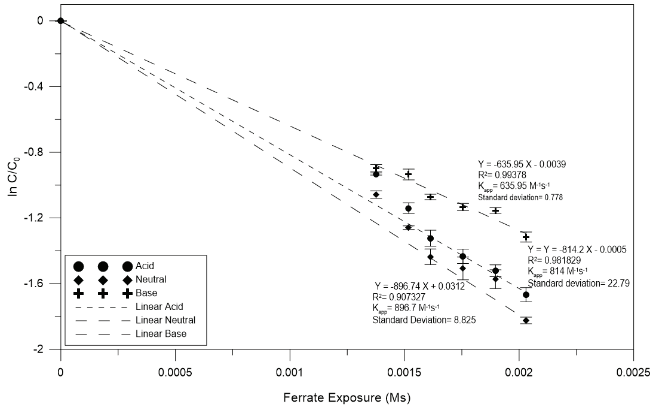


Fig. 2. Plot of ferrate(VI) exposure and ln C/C_o in the determination of k_{app} value of 4-BP's degradation by ferrate(VI).

3.3. Effect of ferrate(VI) dose

One of the important parameters that affects removal efficiency is ferrate(VI) dose [20]. The ferrate(VI) dose experiments were carried out with the dosages of 0.1167, 0.23, 0.35 and 0.467 mM. The ferrate(VI) dose effect on the 4-BP removal was shown in Fig. 3.

The ferrate(VI) dose of 0.467 was sufficient to remove most of the 2-bromophenol in the reactor with the efficiency of 96.714%. The k_{app} values of ferrate(VI) in the various doses were calculated graphically in Fig. 4. The k_{app} values have a proportional relationship with the increasing of ferrate(VI) doses. Fig. 5 showed the correlation between ferrate(VI) doses and k_{app} values. Removal efficiency increased because increasing the ferrate(VI) doses increased the amount of ferrate(VI) available to initiate oxidation reaction.

3.4. Effect of 4-BP initial concentrations

Identifications of 4-BP initial concentrations effect toward removal efficiency have been conducted. The 4-BP concentrations used in these experiments started from 0.578, 0.867, 1.156, 1.445, 2.89, 5.78 and 8.67 μM with the ferrate(VI) dose 0.23 mM. The results of the experiments were shown in Fig. 6.

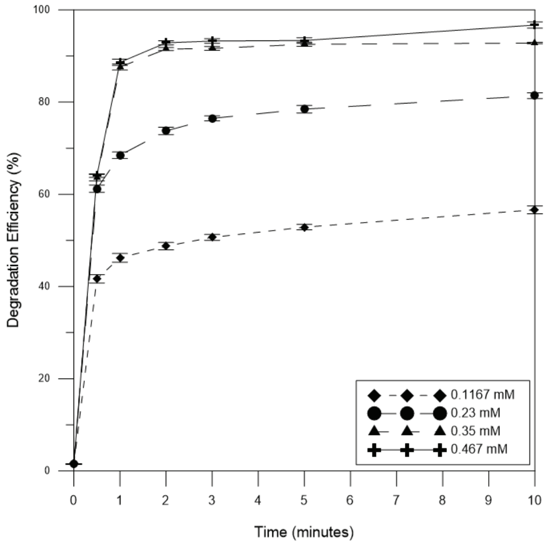


Fig. 3. Result of 4-BP degradation (%) in the various ferrate(VI) doses, pH = 3.2 with 1 ppm initial concentration temperature 25°C.

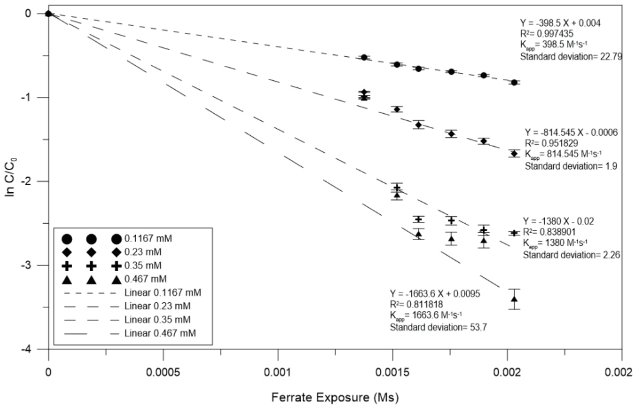


Fig. 4. Ferrate(VI) exposure and ferrate(VI) doses plot in the determination of 4-BP degradation k_{app} value.

The removal efficiency of 4-BP were strongly dependent on the ratio of ferrate(VI) dose and the target compound initial concentration in the reactor [23]. However, an excess amount of ferrate(VI) led to the decreasing of removal efficiency. This is due to the fact that an excess of ferrate(VI) induced the self-decomposition of ferrate(VI). The optimal ratio can be observed from the k_{app} values shown in Table 2.

Jiang and Lloyd in their review suggest that the optimal removal of various compounds achieved with the ratio of

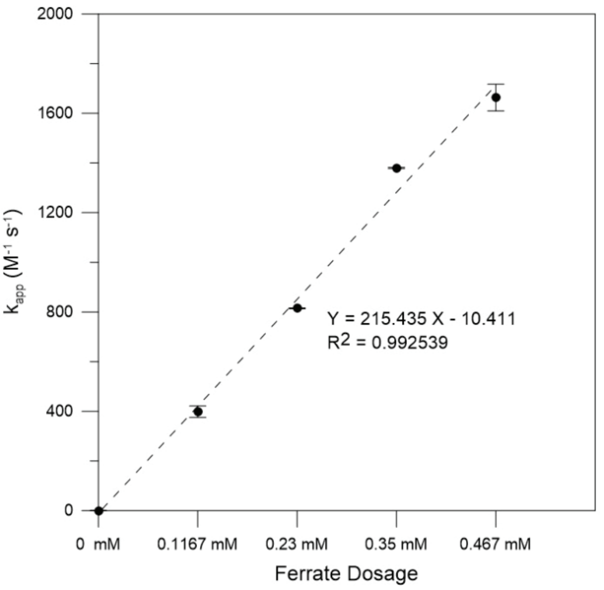


Fig. 5. Plot of ferrate(VI) dose and k_{app} value showed linier trend.

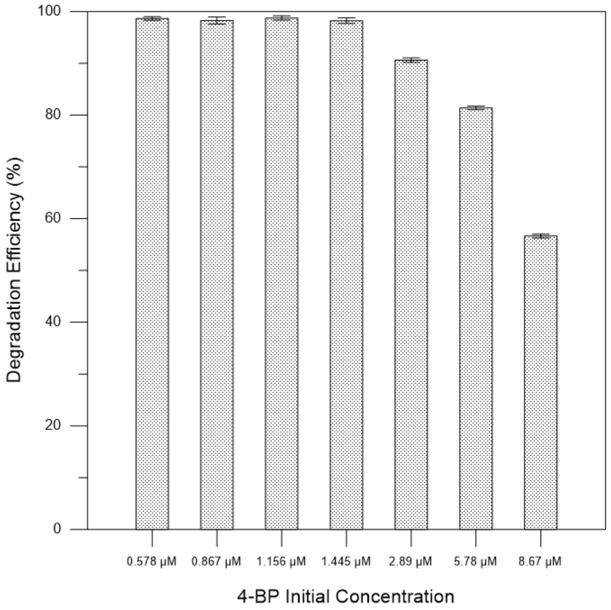


Fig. 6. 4-BP degradation (%) in various 4-BP initial concentrations, pH = 3.2, 0.23 mM ferrate(VI) dose, and temperature 25°C.

Table 2
k_{app} value of 4-BP degradation using liquid ferrate(VI) in the various 4-BP initial concentration

4-BP Initial concentration (μM)	k_{app} ($M^{-1}s^{-1}$)			Standard deviation
	1	2	Average	
0.578	1047.7	1064.5	1056.1	11.87939
0.867	1082.29	1068.71	1075.5	9.60251
1.156	1338.88	1368.72	1353.8	21.10007
1.445	1228.84	1203.56	1216.2	17.87566
2.89	864.11	832.69	848.4	22.2173
5.78	819	816.5	817.75	1.767767
8.67	605.3	609.73	607.515	3.132483

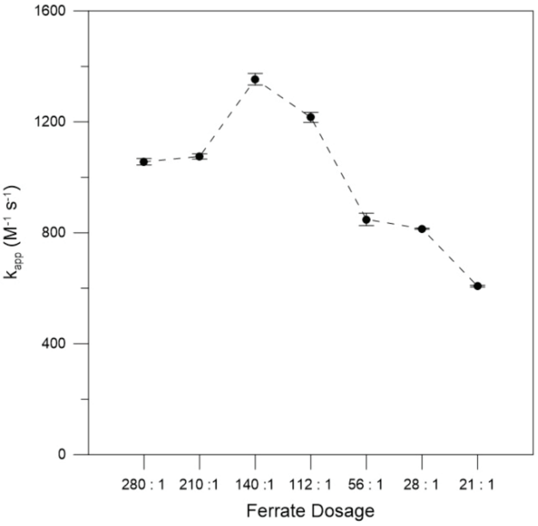


Fig. 7. Plot of ferrate(VI) dose and 4-BP initial concentration ratio and k_{app} value.

ferrate(VI) dose and target compound initial concentration ranged between 3:1 and 15:1. However, further research regarding the relationship between ferrate(VI) doses and 4-BP initial concentrations needs to be conducted. The optimal k_{app} value 1358 $M^{-1}s^{-1}$ was observed from this experiment (Fig. 8). In the investigation of molar ratio, significant improvement of rate reaction occurred in the ratio of 21:1 until 140:1 (Fig. 7). After reaching the optimal ratio, the removal efficiency slightly decreased.

3.5. Effect of temperature

Temperature was one of the important parameters that affects ferrate(VI) stability. The purpose of this experiment was to observe the effect of temperature on the removal efficiency. Therefore, the optimal temperature condition to remove 4-bromophenol will be established. The experiments were conducted with temperatures 10, 25, 35 and 45°C. From the experimental results, the optimal temperature for the 4-BP removal was observed at 25°C with the efficiency of 81.4%. The results of 4-BP degradation in various temperatures were shown in Fig. 8.

The removal of 4-BP by ferrate(VI) in this experiment was established as a second order reaction. Fig. 9 shows the k_{app} in the temperature range from 10 to 45°C with the highest k_{app} value observed at a temperature of 25°C. It was caused by a slow reaction of ferrate(VI) at 10°C because of the low temperature. On the other hand, at 35 and 45°C ferrate(VI) decomposed rapidly due to the instability of ferrate(VI) at a high temperature. Decomposition kinetics of ferrate(VI) were enhanced when the temperature increased [24–26].

The Arrhenius equation can be used to determine activation energy. The activation energy for 4-BP degradation reaction was 29.252 KJ/mol. This result was obtained from the measurement using the Arrhenius equation (Eq. (6)). Where *ea* was activation energy; *R* was constant value (8.314 J K^{-1} mol^{-1}); and *T* is temperature (*K*).

$$\ln\frac{rate_1}{rate_2} = -\frac{ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{6}$$

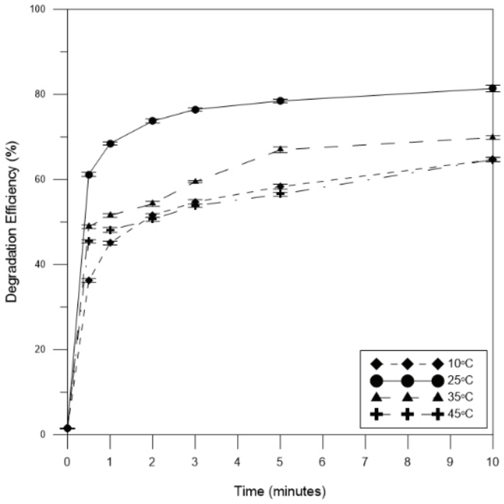


Fig. 8. 4-BP degradation (%) in various temperatures, acid condition, 1 ppm initial concentration and 0.23 mM ferrate(VI) concentration.

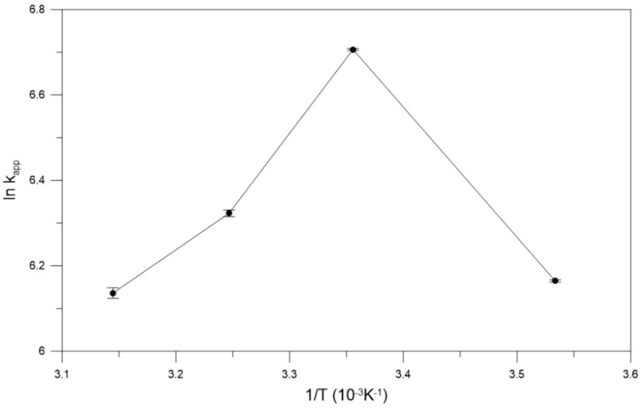


Fig. 9. k_{app} value in temperature variation acid condition, 1 ppm initial concentration and 0.23 mM ferrate(VI) concentration.

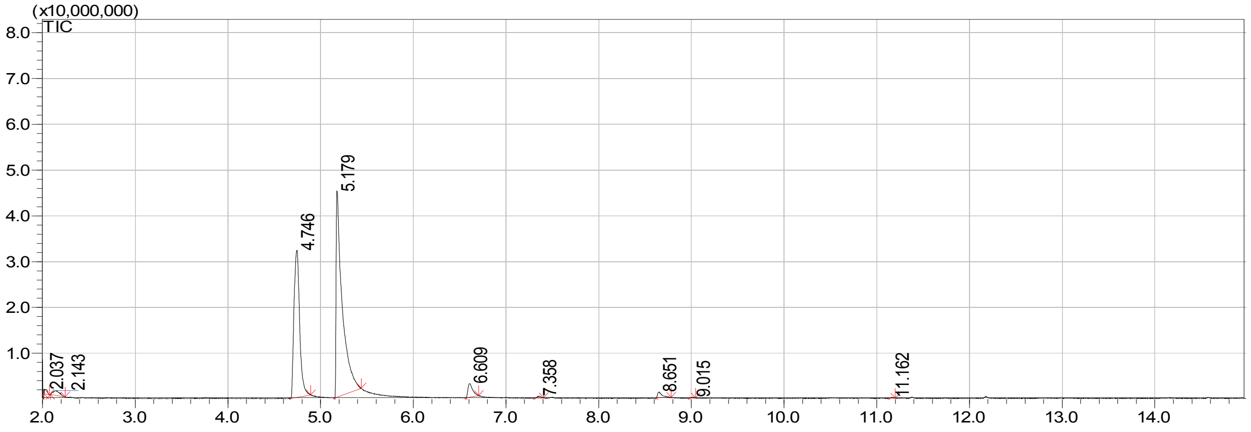


Fig. 10. GCMS spectra from the degradation of 4-bromophenol by liquid ferrate(VI).

3.6. Intermediate study and degradation pathway

The degradation mechanism of 4-BP has been observed in this experiment. The degradation of the phenolic compounds by ferrate(VI) usually started with the oxygen transfer and proton addition [27,28]. The GCMS results from this experiment were shown in Fig. 10.

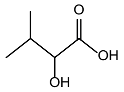
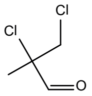
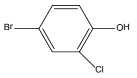
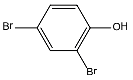
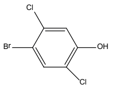
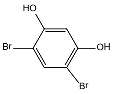
The oxidation reaction mechanisms of 4-BP by ferrate(VI) can be described using the distribution of reaction products and the differentiation between the primary and non-primary in the GCMS results. The oxidation of 4-bromophenol was proposed through an oxidative pathway which involves the formation of phenoxy radical [29]. A 2,4-dibromophenol compound has been detected as the primary reaction product. On the other hand, several non-primary products were also detected in the GCMS results. The detected non-primary intermediate products were 2-hydroxy-3-methyl-butanoic acid; 4,6-Dibromobenzene-1,3-diol; 1-Hepten-3-ol and 2,3-dichloro-2-methyl-propanal (Table 3). The proposed degradation pathway was shown in Fig. 11.

Also, a color change was detected during the mixing process between 4-bromophenol and ferrate(VI). The color of the solution changed into yellow after the addition of liquid ferrate(VI) in the acidic condition. This result supported the mechanism given in Fig. 11. The color change was caused by the complex formation between ferric(III) and phenoxy radical [29]. The reaction is initiated with the scavenging of phenol by FeO_4^{2-} to form the phenoxy radical and FeO_4^{3-}.

The intermediates detected in the experiment were not only bromophenol but also bromo-chlorophenol. The formation of bromo-chlorophenol was caused by 4-bromophenol chlorination reaction. The Cl radical presented in the solution caused the reaction of 4-bromophenol into 4-bromo-2-chlorophenol and further chlorination into 4-bromo-2,5 dichlorophenol. The reaction mechanism was shown in Fig. 12.

The source of the detected chloride radical in the GCMS result was from $FeCl_3$ and NaOCl. These two compounds were used to synthesize ferrate(VI). Since the ferrate(VI) used in this experiment was *in-situ* liquid ferrate(VI), liquid ferrate(VI) taken directly from the reactor contained Cl (chlorine radical) as the side product of the reaction.

Table 3
GCMS Result from the degradation of 4-bromophenol by liquid ferrate(VI)

Compound name	Structure	Ret time
Butanoic acid, 2-hydroxy-3-methyl-		2.037
Propana1,2,3-dichloro-2-methyl-		2.143
Phena1, 4-bromo-2-chloro-		4.746
Pheno1, 2,4-dibromo-		6.609
Pheno1, 4-bromo-2,5-dichloro-		8.651
4,6-Dibromobenzene-1,3-diol		9.015

The intermediate study showed 4-bromo-2-chlorophenol as the dominant intermediate product. The 4-bromo-2-chlorophenol was categorized as acute health hazard chemicals so the productions of this intermediate product need to be minimalized. However, further investigation to determine concentration of 4-bromo-2-chlorophenol did not conducted since it did not become focus of this research. Therefore, the potency of the terminal degradation product, whether it was benign or harmful cannot be determined. In order to get better results, the alternative Cl free reagent such as Fe_2O_3 instead of FeCl3 and H_2O_2 instead of NaOCl can be used at the future study.

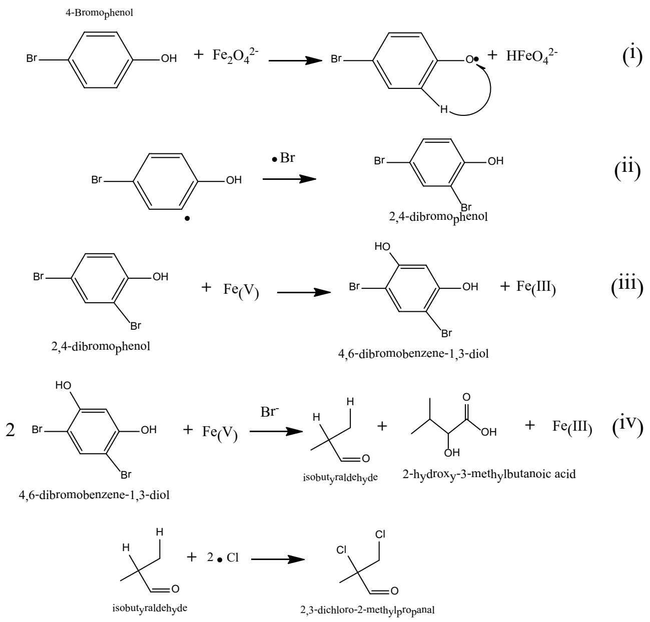


Fig. 11. Degradation pathway of 4-bromophenol by Ferrate(VI).

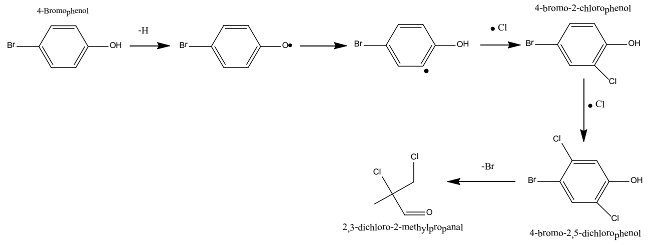


Fig. 12. Chlorination reaction of 4-BP by Cl radical.

4. Conclusion

The ability of ferrate(VI) to remove 4-BP has been investigated. In the various pH conditions, the neutral pH condition has been observed as the best condition with the 84.1% 4-BP degraded (k_{app} value 896.7 $M^{-1}s^{-1}$) compared to the acidic condition (81.4%) and the basic condition (73.6%). A higher ferrate(VI) dose increased the degradation efficiency of 4-BP. However, the degradation efficiency decreased when the ferrate(VI) ratio versus 4-BP initial concentration reached 140:1. In the observation of temperature effects, 25°C was the optimal temperature condition to degrade 4-BP with the k_{app} 814.545 $M^{-1}s^{-1}$ in acidic condition. The activation energy of 4-BP degradation using ferrate(VI) was 29.25 kJ/mol. The degradation reaction pathway was proposed based on intermediate products identified using GC/MS. The 4-BP's degradation occurs through an oxidative pathway which involves the formation of phenoxy radical.

Acknowledgement

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

References

[1] J.-Q. Jiang, Advances in the development and application of ferrate(VI) for water and wastewater treatment, J. Chem. Technol. Biotechnol., 89 (2014) 165–177.

[2] J.Q. Jiang, Research progress in the use of ferrate(VI) for the environmental remediation, J. Hazard. Mater., 146 (2007) 617–623.

[3] C. Li, X.Z. Li, N. Graham, A study of the preparation and reactivity of potassium ferrate, Chemosphere, 61 (2005) 537–543.

[4] J. Jiang, B. Lloyd, Progress in the development and use of ferrate (VI) salt as an oxidant and coagulant for water and wastewater treatment, Water Res., 36 (2002) 1397–1408.

[5] S.K. Rhee, D.E. Fennell, M.M. Häggblom, L.J. Kerkhof, Detection by PCR of reductive dehalogenase motifs in a sulfidogenic 2-bromophenol-degrading consortium enriched from estuarine sediment, FEMS Microbiol. Ecol., 43 (2003) 317–324.

[6] B. Uhnáková, A. Petříčková, D. Biedermann, L. Homolka, V. Vejvoda, P. Bednář, et al., Biodegradation of brominated aromatics by cultures and laccase of Trametes versicolor, Chemosphere, 76 (2009) 826–832.

[7] W. Vetter, D. Janussen, Halogenated natural products in five species of antarctic sponges: compounds with POP-like properties?, Environ. Sci. Technol., 39 (2005) 3889–3895.

[8] A. Dell'Erba, D. Falsanisi, L. Liberti, M. Notarnicola, D. Santoro, Disinfection by-products formation during wastewater disinfection with peracetic acid, Desalination, 215 (2007) 177–186.

[9] N.K. Sahoo, K. Pakshirajan, P.K. Ghosh, Biodegradation of 4-bromophenol by Arthrobacter chlorophenolicus A6 in batch shake flasks and in a continuously operated packed bed reactor, Biodegradation, 25 (2014) 265–276.

[10] I. Levy, G. Ward, Y. Hadar, O. Shoseyov, C.G. Dosoretz, Oxidation of 4-bromophenol by the recombinant fused protein cellulose-binding domain-horseradish peroxidase immobilized on cellulose, Biotechnol. Bioeng., 82 (2003) 223–231.

[11] E. Lipczynska-Kochany, Direct photolysis of 4-bromophenol and 3-bromophenol as studied by a flash photolysis/HPLC technique, Chemosphere, 24 (1992) 911–918.

[12] D.A. White, G.S. Franklin, A preliminary investigation into the use of sodium ferrate in water treatment, Environ. Technol., 19 (1998) 1157–1161.

[13] W. Jiang, L. Chen, S.R. Batchu, P.R. Gardinali, L. Jasa, B. Marsalek, et al., Oxidation of microcystin-LR by ferrate (VI): kinetics, degradation pathways, and toxicity assessments, Environ. Sci. Technol., 48 (2014), 12164–12172.

[14] Y. Lee, J. Yoon, U. Von Gunten, Kinetics of the oxidation of phenols and phenolic endocrine disruptors during water treatment with ferrate (Fe(VI)), Environ. Sci. Technol., 39 (2005) 8978–8984.

[15] Y. Lee, M. Cho, J.Y. Kim, J. Yoon, Chemistry of ferrate (Fe (VI)) in aqueous solution and its applications as a green chemical, J. Ind. Eng. Chem., 10 (2004) 161–171.

[16] V.K. Sharma, Potassium ferrate(VI): An environmentally friendly oxidant, Adv. Environ. Res., 6 (2002) 143–156.

[17] G.W. Thompson, L.T. Ockerman, J.M. Schreyer, Preparation and purification of potassium ferrate. VI, J. Am. Chem. Soc., 73 (1951) 1379–1381.

[18] V.K. Sharma, Oxidation of inorganic compounds by ferrate (VI) and ferrate(V): One-electron and two-electron transfer steps, Environ. Sci. Technol., 44 (2010) 5148–5152.

[19] W.F. Wüst, R. Köber, O. Schlicker, A. Dahmke, Combined zero- and first-order kinetic model of the degradation of tce and cis-DCE with commercial iron, Environ. Sci. Technol., 33 (1999) 4304–4309.

[20] V.K. Sharma, Ferrate(VI) and ferrate(V) oxidation of organic compounds: kinetics and mechanism, Coord. Chem. Rev., 257 (2013) 495–510.

[21] B. Yang, G.G. Ying, L.J. Zhang, L.J. Zhou, S. Liu, Y.X. Fang, Kinetics modeling and reaction mechanism of ferrate(VI) oxidation of benzotriazoles, Water Res., 45 (2011) 2261–2269.

[22] B. Yang, G.-G. Ying, Z.-F. Chen, J.-L. Zhao, F.-Q. Peng, X.-W. Chen, Ferrate(VI) oxidation of tetrabromobisphenol A in comparison with bisphenol A, Water Res., 62 (2014) 211–219.

[23] N. Graham, C.C. Jiang, X.Z. Li, J.Q. Jiang, J. Ma, The influence of pH on the degradation of phenol and chlorophenols by potassium ferrate, Chemosphere, 56 (2004) 949–956.
[24] W.F. Wagner, J.R. Gump, E.N. Hart, Factors affecting stability of aqueous potassium ferrate(VI) solutions, Anal. Chem., 24 (1952) 1497–1498.
[25] K. Svanks, Oxidation of ammonia in water by ferrates (VI) and (IV), US DOI project report A-031-OHIO (1976), pp. 16–31.
[26] Z. Mácová, K. Bouzek, J. Híveš, V.K. Sharma, R.J. Terryn, J.C. Baum, Research progress in the electrochemical synthesis of ferrate(VI), Electrochim. Acta., 54 (2009) 2673–2683.
[27] H.Y. Jeong, H. Kim, K. F. Hayes, Reductive dechlorination pathways of tetrachloroethylene and trichloroethylene and subsequent transformation of their dechlorination products by Mackinawite (FeS) in the presence of metals, Environ. Sci. Technol., 41 (2007) 7736–7743.
[28] A.L. Roberts, Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe (0) particles, Environ. Sci. Technol., 34 (2000) 1794–1805.
[29] H. Huang, D. Sommerfeld, B.C. Dunn, E.M. Eyring, C.R. Lloyd, Ferrate (VI) oxidation of aqueous phenol: kinetics and mechanism, J. Phys. Chem., 105 (2001) 3536–3541.