

## **Removal of 2-Bromophenol by Advanced Oxidation Process with *In-situ* Liquid Ferrate(VI)**

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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 2-bromophenol treatment. The study on 2-bromophenol (2-BP) removal using wet oxidation in-situ liquid ferrate(VI) has been conducted. The effects of molar ratio and temperature on the 2-bromophenol removal were investigated. In the various of molar ratio, increasing the molar ratio ([ferrate(VI)]/[2-BP]) enhanced the reaction rate of 2-BP removal. However, the reaction rate decreased when the molar ratio was more than 42.7. The optimal temperature has been observed at 25°C. The activation energy of 2-bromophenol removal was 17.815 KJ/mol. The 2-bromophenol degradation occurred through an oxidative pathway which involves the formation of phenoxy radical and production of isobutyraldehyde as a non-aromatic degradation product.

**Keywords:** liquid ferrate(VI), 2-bromophenol, oxidation, intermediates

### **1. Introduction**

Bromophenols are the phenolic compounds generally used as the flame retardants. Moreover, bromophenols are also used as polymers materials, resorcinol precursors and pesticide components [1], [2]. 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 [3]. On the other hand, bromophenols are listed as the primary pollutants by U.S. EPA because its accumulation in the environment has led to harmful effects for the organisms and the environment [4]. These problems encourage the researchers to establish an effective method to remove bromophenols.

One of the hazardous bromophenols exemplified in this paper was 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 [5]. Furthermore, Knight et al. (1999) studied 2-bromophenol degradation using phenol-degrading microbial consortia [6]. The results of those researches showed good removal efficiency. However, 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 [7]. Ferrate(VI) has shown great potential as a multi-functional water and wastewater treatment chemical for coagulation, disinfection, and oxidation [8–10]. 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 [11].

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Therefore, ferrate(VI) is an appropriate compound to remove hazardous contaminants in the water and wastewater including heavy metal and organic contaminants [9].

Applications of ferrate(VI) for the water and wastewater treatments have been well acknowledged. However, challenges have existed for the implementation of ferrate(VI) technology in the water and wastewater treatment. These problems were caused by either the instability property of ferrate(VI) solution or the high preparation cost of solid ferrate(VI) [10]. To overcome these problems, research has been directed to the production and application of *in-situ* liquid ferrate(VI) [11]. Liquid ferrate(VI) has been reported as the great oxidizing agent for the pollutants including organic contaminants [12]. Consequently, liquid ferrate(VI) has been 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.

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 2-bromophenol removal. This paper presented information concerning the application of liquid ferrate(VI) for 2-bromophenol removal in various conditions. The parameters such as molar ratio and temperature were investigated due to the importance of both parameters on the real application of liquid ferrate(VI). Furthermore, this research also employed *in-situ* liquid ferrate(VI) which has never been used for the removal of 2-bromophenol. Degradation pathways have been proposed using GCMS analysis.

## 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  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NaOCl}$ ,  $\text{NaOH}$ ,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  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 M $\Omega$  Milli-Q cm water purification system.

### 2.2. Methods

#### 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 [13]. 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 grams  $\text{NaOH}$  into 60 mL of  $\text{NaOCl}$ . Afterward, the mixture was stirred until a 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 a period of 11 minutes. Lastly, spectrophotometer UV-Vis technique at the multi wavelengths of 254 nm, 390 nm, 505 nm and 680 nm was used to determine the concentrations of ferrate(VI) [14].

#### 2.2.2. Synthesis of Ferrate(VI)

Reactions between 2-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 2-bromophenol samples were then analysed using gas chromatography (Technologies Co. 4890D) equipped with Rxi-5 ms column ( $L = 30$  m, internal diameter = 0.25  $\mu\text{m}$ ), 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.

### 3. Results and Discussions

#### 3.1. Synthesis of Ferrate(VI)

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  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 ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) with NaOH and NaOCl. Ferrate(VI) ( $\text{FeO}_4^{2-}$ ) has been successfully produced with the concentration 42,000 ppm (Fe) after 11 minutes of reaction time. The ferrate(VI) was the result of the conversion of  $\text{FeCl}_3$  into  $\text{Na}_2\text{FeO}_4$  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. (2007), the yields of sodium liquid ferrate synthesized by the wet oxidation method was only 70% [15]. The ferrate(VI) formation followed the reaction below.



#### 3.2. Effect of Molar Ratio

In order to investigate molar ratio effect, several ratios of ferrate(VI) and 2-BP initial concentration (6.4, 12.8, 25.6, 42.7, 64) were applied with a fixed ferrate(VI) dose at room temperature (25 °C). The 2-bromophenol initial concentrations used were 0.578  $\mu\text{M}$ , 0.867  $\mu\text{M}$ , 1.445  $\mu\text{M}$ , 2.89  $\mu\text{M}$ , and 5.78  $\mu\text{M}$  at the ferrate(VI) doses 0.23 mM. The removal efficiency increased with the decreasing of 2-bromophenol initial concentration. However, 2-bromophenol initial concentration less than 0,867  $\mu\text{M}$  caused decreasing of removal efficiency (Fig. 1).

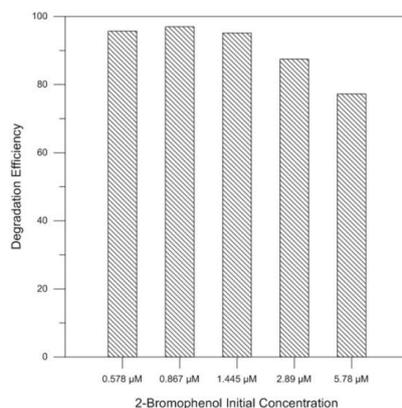


Fig. 1: 2-BP degradation (%) using ferrate(VI) in various 2-BP initial concentrations, acid condition, 0.04668 mM ferrate(VI) dose, and temperature 25°C.

Reaction rate was determined from the  $k_{\text{app}}$  value using second order reaction rate equation. The reaction of ferrate(VI) with an organic compound is the second order reaction rate [16]. The second order reaction rate law can be described by eq. (2).

$$-d[2\text{-BP}]/dt = k_{\text{app}}[\text{FeO}_4^{2-}][2\text{-BP}] \quad (2)$$

Eq. (2) is rearranged and  $d[2\text{-BP}]/dt$  is integrated to become

$$\ln(2\text{-BP})/[2\text{-BP}]_0 = -k_{\text{app}} \int_0^t [\text{FeO}_4^{2-}] dt \quad (3)$$

where,  $\int_0^t [\text{FeO}_4^{2-}] dt$  denotes level of ferrate(VI) exposure and  $k_{\text{app}}$  is the apparent second order reaction rate constant [17], [18]. The value of  $k_{\text{app}}$  had been achieved by plotting the natural logarithm of 2-BP concentration ( $\ln C/C_0$ ) with the ferrate(VI) exposure. From this plotting, the rate of degradation process can be determined.

The removal efficiency of 2-bromophenol were strongly dependent on the ratio of ferrate(VI) dose and target compound initial concentration ( $[\text{Fe(VI)}]/[2\text{-BP}]$ ) [16]. The higher molar ratios induced the increasing of ferrate(VI) quantity available to initiate degradation reaction. However, excess ferrate(VI) induced decomposition of ferrate(VI). Hence, excess amount of ferrate(VI) caused the decreasing of removal efficiency. Maximum ratio of ferrate(VI) dose and 2-BP initial concentrations can be determined from the  $k_{\text{app}}$  value showed in Table I.

Compound	Molar Ratio		$k_{app}$ ( $M^{-1} s^{-1}$ )
	Fe(VI)/[Target compound]		
2-Bromophenol	6.4		817.64
	12.8		1039.1
	25.6		1524.6
	42.7		1824.2
	64		1622.8

Table I: Degradation of 2-BP by various molar ratio, pH acid (3.5) and temperature 25°C

The review by Jiang and Lloyd (2002) suggest that the maximum removal efficiency of various compounds using ferrate(VI) achieved with the molar ratio 3:1 to 15:1 [19]. However, research related molar ratio effect [ferrate(VI) dose] and [2-BP initial concentration] has never been conducted. The optimal  $k_{app}$  value observed from this experiment was  $1622.8 M^{-1} s^{-1}$ . In the investigation of molar ratio, significant improvement of rate reaction were observed in the ratio of 6.4 : 1 until 42.7 : 1. After molar ratio 42.7: 1, the degradation efficiency decreased (Fig.2).

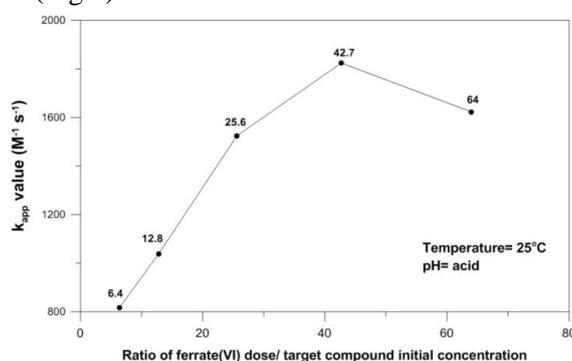


Fig. 2: Relationship between molar ratio and  $k_{app}$  with ferrate(VI)'s concentration 1 ppm.

### 3.3. Effect of Temperature

Temperature is one of important factors affecting ferrate(VI) removal efficiency [11]. The experiments were conducted with temperatures of 10 °C, 25 °C, 35 °C and 45 °C. The results showed the optimal temperature of 2-BP degradation was 25°C with removal efficiency 90.3% (Fig. 3).

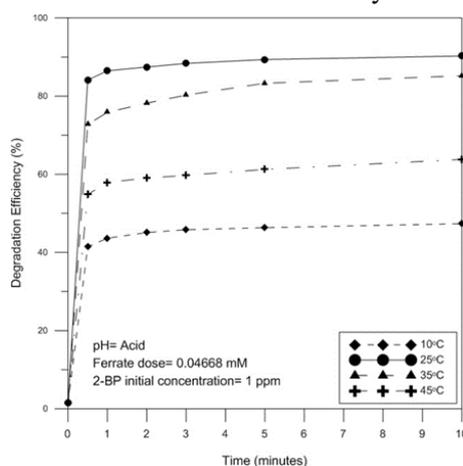


Fig. 3: 2-BP degradation (%) in various temperatures condition.

Degradation of 2-BP using ferrate(VI) was established as a pseudo second order reaction. The  $k_{app}$  values were determined with plotting ferrate exposure and  $\ln C/C_0$ . Table II shows the  $k_{app}$  in the temperature range from 10°C to 45°C with the highest value  $1175.7 M^{-1} s^{-1}$ . Spontaneous decomposition of ferrate(VI) will be enhanced when temperature increased [20]–[22].

Ferrate(VI) at 10°C reacted slowly due to the low temperature condition and kinetic energy. In contrast, ferrate(VI) decomposed rapidly at the temperatures 35°C and 45°C due to its instability in the high

temperature (Fig. 4). Therefore, ferrate(VI) was a suitable material for organic contaminants removal because it did not need to spend more energy to maintain its optimal temperature.

Compound	[Fe(VI)]	$k_{app}$ ( $M^{-1} s^{-1}$ )			
		10°C	25°C	35°C	45°C
2-Bromophenol	0.04468 mM	322.42	1175.7	930.9	500.03

Table II: Degradation of 2-BP the various temperatures

Arrhenius equation of experiment data was used to determine activation energy (eq. 4), where  $ea$  is activation energy;  $R$  is constant value ( $8.314 J K^{-1} mol^{-1}$ ); and  $T$  is temperature (K). From the calculation, the activation energy for 2-BP degradation reaction was 17.815 KJ/mol.

$$\frac{\ln rate_1}{rate_2} = -\frac{ea}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4)$$

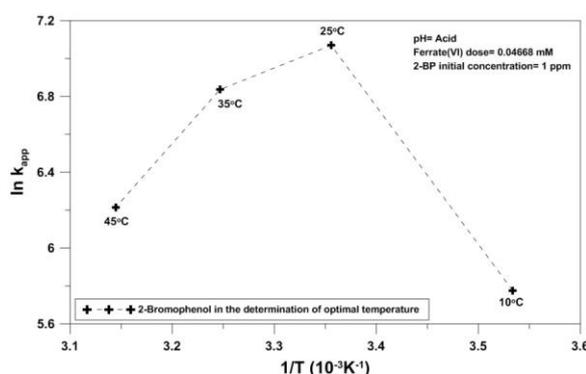


Fig. 4: Relationship between  $1/T$  and  $k_{app}$  value in the determination of optimal temperature.

### 3.4. Degradation Pathway

The degradation pathway of 2-BP has been proposed in this experiment. The intermediates products was identified using GCMS analysis. The degradation of the phenolic compounds by ferrate(VI) usually started by oxygen transfer and proton addition [22], [23].

Degradation pathway of 2-BP using ferrate(VI) can be described using the distribution and differentiation between primary and non-primary reaction products of the GCMS results. The oxidation of 2-bromophenol occurred through an oxidative pathway which involves the formation of phenoxy radical. This proposed pathway was based on the previous experiment by Huang (2001) which studied intermediate products of phenol degradation by ferrate(VI) using EPR [24]. A similar intermediate result was found in this experiment. Those similar intermediate result was p-benzoquinone. The 2-bromophenol intermediates detected in the GCMS spectra were 2,6-dibromo-phenol 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-Ethenediol; and 2,6-Dibromohydroquinone. The degradation pathway was showed in Fig. 5.

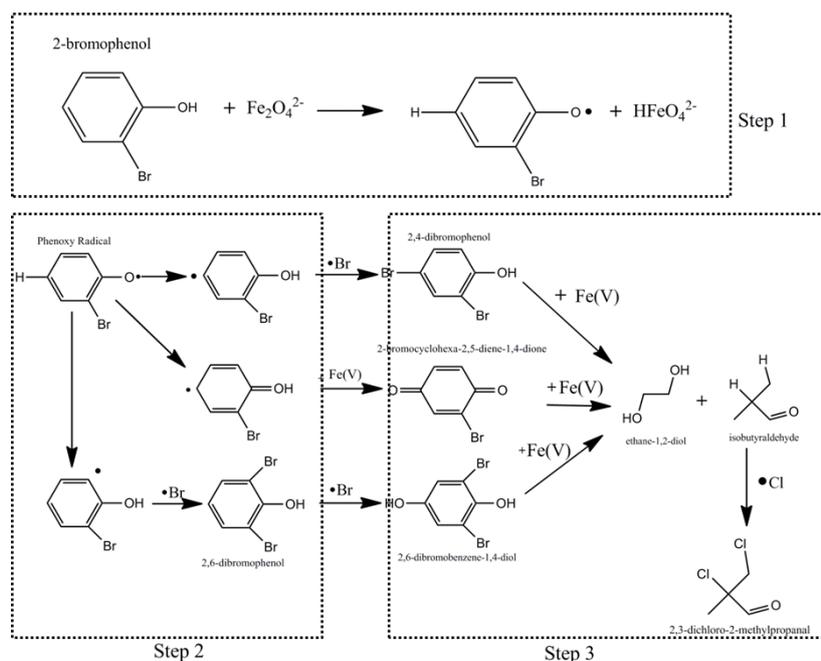


Fig. 5: Degradation pathway of 2-bromophenol removal using liquid ferrate(VI).

The observed color changes during the mixing of phenol and  $\text{FeO}_4^{2-}$  corresponded nicely with the results of the present research and support the mechanism given in Fig. 5. The reaction is initiated with the phenol uniting with  $\text{FeO}_4^{2-}$  to form the phenoxy radical and  $\text{FeO}_4^{3-}$  shown in step 1. The color of the solution was changed into yellow after liquid ferrate(VI) had been put in acidic condition. This phenomenon can be explained by the complex formation between ferric(III) and phenoxy radical [24]. In the step 2, phenoxy radical was encountered electron configuration which generated 3 different products. Finally, aromatic compounds breaking process was occurred. After that, in the step 3, aliphatic compounds which in the further degradation process become  $\text{CO}_2$  and  $\text{H}_2\text{O}$  had been produced.

The intermediate products in the experiment were not only in the form of bromophenol but also in bromo-chlorophenol. The formation of bromo-chlorophenol was caused by 2-bromophenol chlorination reaction. The radical presented in the solution including Cl radical initiates the reaction of 2-bromophenol into 2-bromo-4-chlorophenol and further chlorination and oxidation into 2,3-dichloro-2-methylpropanol. The occurred reaction mechanism was shown in Fig. 6.

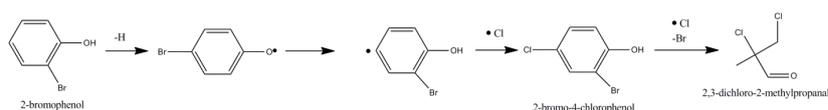


Fig. 6: Chlorination reaction of 2-bromophenol.

The source of the detected chloride radical in the GCMS result was from  $\text{FeCl}_3$  and  $\text{NaOCl}$ . These two compounds were used to synthesize ferrate(VI). Since ferrate(VI) used in this experiment was in-situ liquid ferrate(VI), liquid ferrate(VI) taken directly from the reactor contained  $\cdot\text{Cl}$  (chlorine radical) as the side product of the reaction.

#### 4. Conclusions

The efficiency of ferrate(VI) for the 2-bromophenol removal has been investigated. In the pH effect the neutral pH condition has been observed as the best condition with the removal efficiency 94.2% 2-BP (kapp value 1469.5  $\text{M}^{-1}\text{s}^{-1}$ ) compared to 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 of ferrate(VI) doses. The optimal removal efficiency (99.73%) was achieved at a ferrate(VI) dose 0.23 mM. In the molar ratio effect, the removal efficiency increased and then decreased when molar ratio ( $[\text{Fe(VI)}]/[\text{2-BP}]$ ) reached 42.7 : 1. In the observation of temperature effect, 25°C was observed as the optimal temperature condition with the kapp value equal to 1175.7  $\text{M}^{-1}\text{s}^{-1}$  in acidic condition. The activation energy for the reaction was 17.815

KJ/mol. The degradation pathway was proposed based on intermediate products identified using GC/MS. The 2-bromophenol degradation occurred through an oxidative pathway which involves the formation of phenoxy radical.

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## 6. References

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