



# Comparison of 2,4,6-tribromophenol removal using in-situ liquid ferrate(VI) and stable ferrate(VI)

## 원위치 제조 액상 Ferrate(VI)와 안정화 Ferrate(VI)를 이용한 2,4,6-tribromophenol의 제거 비교연구

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### ABSTRACT

This paper provided the information related to the removal of 2,4,6-tribromophenol using in-situ and stable liquid ferrates(VI). This research's goal was to observe the differences of oxidation power between in-situ liquid ferrate(VI) and stable liquid ferrate(VI). The in-situ liquid ferrate(VI) ( $\text{FeO}_4^{2-}$ ) has been successfully produced with the concentration 42,000 ppm (Fe) after 11 minutes of reaction time. The stable liquid ferrate(VI) was also successfully produced following the modification method by Sharma with the produced concentrations 7,000 ppm. The stable liquid ferrate(VI) was stable for 44 days and slightly decreased afterwards. This research has been carried out using 2,4,6-tribromophenol as the representative compound. Both of ferrates(VI) have the highest oxidation capability at the neutral condition. Furthermore, the stable liquid ferrate(VI) has higher oxidation power than the in-situ liquid ferrate(VI).

**Key words:** Wet oxidation method, Liquid ferrate(VI), GC-ECD, GC-FID

**주제어:** 습식산화법, 액상 페레이트, GC-ECD, GC-FID

## 1. Introduction

Bromophenols have existed in the environment either from the substances of marine organism's metabolism product or waste products from the industrial sector. The mono-, di-, and tri- bromophenols in the environment were produced from the marine organisms such as algae (Pedersén et al., 1974), polychaetes (Fielman et al., 1999) and hemichordates (Ashworth and Cormier, 1967; Fielman et al., 1999). Those substances were used as the protection

agents against predators and biofouling (King, 1986). However, most of bromophenol contaminants were come from the industry with the production volume estimated to be 9,500 tons per year worldwide in 2001. 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 was 2,4,6-tribromophenol. Manufacturing industries produced significant amount of 2,4,6-TBP wastes. Some of it was discharged into the terrestrial, aquatic, and marine environments (King, 1988). In the environment, 2,4,6-tribromophenol generally is not able to be directly

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degraded by the organisms and exists for the long period of time. The 2,4,6-TBP has been detected at flue gas, river water, and estuarine sediments, where it were not common places for 2,4,6-TBP to exist (Gutiérrez et al., 2005). On the other hand, the 2,4,6-TBP can cause some dangerous effects toward the human health. The exposure of 2,4,6-TBP might led the dangerous impact toward thyroid hormone system (Meerts et al., 2000), reduction of cell growth and increasing of acetylcholinesterase activity (Rios et al., 2003). Several studies have been conducted (Li et al., 2015; Gao et al., 2013), but suitable alternatives for removal of 2,4,6-TBP are not presently available. The attempt such as pyrolysis of bromophenols can produce dangerous dioxin compounds (Evans and Dellinger, 2005). Therefore, the breakthrough solution for the 2,4,6-TBP removal was required. One of the promising 2,4,6-TBP removal agent is ferrate(VI). However, only few researchers have conducted the usage of ferrate(VI) for the removal of organic contaminants, especially 2,4,6-TBP. Ferrate(VI) is a hyper-valent species of iron ( $\text{Fe}^{6+}$ ) which has many functions. Ferrate(VI) can be used as the coagulant (Jiang, 2007), disinfectant (Jiang, 2014) and oxidant (Li et al., 2005) simultaneously. The oxidant based on iron is considered non-toxic unlike the other oxidants such as chromium and manganese. Therefore, ferrate(VI) is a suitable compound to remove contaminants in the water and wastewater. Even ferrate(VI) has many advantageous properties, challenges still exist for the implementation of ferrate(VI) technology for water and wastewater treatments. The problems of ferrate(VI) were caused by its instability property (Jiang, 2007). In order to solve this problem, research has been directed to the production and application of *in-situ* liquid ferrate(VI) (Jiang, 2014) and stable liquid ferrate(VI) (Sharma, 2015). Both of liquid ferrates(VI) were potential as the oxidant for removal of organic contaminants. *In-situ* liquid ferrate(VI) can be synthesized onsite with short period of time, so the instability property of ferrate(VI) did not become a problem. Otherwise, stable liquid ferrate(VI) was very stable. On its patent, it was mentioned that this ferrate(VI) can be last without decreasing of concentration at least 2 weeks. However, the research comparing the removal efficiency between *in-situ* liquid ferrate(VI) and stable liquid ferrate(VI) has never been investigated. In

this study, both of liquid ferrates(VI) were applied to investigate the influencing parameters for the 2,4,6-TBP 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 2,4,6-TBP removal. In particular, this paper evaluated the efficiency of *in-situ* liquid ferrate(VI) and stable liquid ferrate(VI) for the 2,4,6-TBP removal at the various pH conditions and ferrate(VI) doses.

## 2. Materials and Methods

### 2.1 Materials

The chemicals such as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , NaOCl and NaOH for the *in-situ* liquid ferrate(VI) production were purchased from Junsei Company (Ltd., Japan) with extra pure grade quality. The other chemicals such as  $\text{Fe}_2\text{O}_3$  and  $\text{Na}_2\text{O}_2$  which used as the core materials to synthesize stable liquid ferrate were also purchased from Junsei Company (Ltd., Japan) with extra pure grade quality. The 2,4,6-tribromophenol were purchased from Sigma-Aldrich with the purity 98%. All reagents were used without further purification. The  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  were used in the buffer solution for the determination of ferrate(VI) concentration. These reagents were purchased from Crown reagent (Ltd., Japan). Buffer 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 *in-situ* Liquid Ferrate(VI)

The preparation of the *in-situ* liquid ferrate(VI) was based on Thompson(1951) wet oxidation method. 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 NaOH into 60 mL of 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, 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) (Lee et al., 2004).

### 2.2.2 Synthesis of Stable Liquid Ferrate(VI)

The synthesis of stable liquid ferrate was produced by the Sharma's method (Sharma, 2015). The first step to synthesize this ferrate(VI) was heating 0.96 g  $\text{Fe}_2\text{O}_3$  and 2.36 g  $\text{Na}_2\text{O}_2$  at  $500^\circ\text{C}$  furnace for 30 minutes and the sample was cooled down. After that, 2 g of mixture was mixed and stirred with 60 mL NaOCl and 18 g NaOH added gradually to the reactor. The mixing process of all the reagents produced a purple solution, which indicated that the stable ferrate(VI) has been successfully produced. The solution was then filtered using 0.45  $\mu\text{m}$  filter paper to separate the solution from the solid contaminants. The concentration and stability of this ferrate(VI) were determined using spectrophotometer UV-Vis.

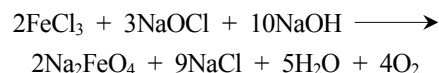
### 2.2.3 Degradation Experiments

The oxidation experiments were performed in a closed zero-head space glass reactor with port for sampling, pH probe, thermometer, and ferrate(VI) inlet. Ferrate(VI) solutions used in the experiments were *in-situ* liquid ferrate(VI) and stable liquid ferrate(VI) produced from the processes. After addition of ferrate(VI), the solution in the reactor was stirred and then 3 ml of samples were taken at the pre-selected time intervals. Afterward, the samples were extracted by n-hexane using liquid-liquid extraction method. Further, the 2,4,6-bromophenol concentrations were measured using gas chromatography equipped an flame ionization detector (FID). The temperatures of the injection port and the detector were  $250$  and  $280^\circ\text{C}$ , respectively. The temperature program began at  $100^\circ\text{C}$ , followed by a  $20^\circ\text{C}/\text{min}$  ramp until a final temperature of  $250^\circ\text{C}$  was reached. To stop further degradation reaction, quenching process using NaOH solution was conducted.

## 3. Results and Discussion

### 3.1 Synthesis of *in-situ* Liquid Ferrate and Stable Liquid Ferrate

In this experiment, the synthesis process employed NaOCl as the oxidizing agents to transform low oxidation state of iron (+3) into the highest oxidation state of iron (+6).  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was performed as the iron source. The NaOH with concentration 11.25 molars were used to optimize the synthesis condition (Sharma et al., 2001). The mixture between NaOCl and NaOH has strong oxidation power which converted yellow  $\text{FeCl}_3$  into the purplish solution of ferrate(VI). This method has successfully produced ferrate(VI) with the concentration of 42,000 ppm. The 86.1% of ferrate(VI) yield has been achieved in this experiment. The ferrate(VI) formation followed the reaction below.



The stable liquid ferrate(VI) has been successfully synthesized with the concentration 7,000 ppm. The stability of this ferrate was also tested on this experiment. On the patent (Sharma, 2015), the stability of liquid ferrate(VI) was at least 2 weeks. From the stability test conducted from this experiment, the liquid ferrate solution was stable for the 1.5 month (Fig. 1). With its high stability, this ferrate(VI) should be able to remove the organic contaminants

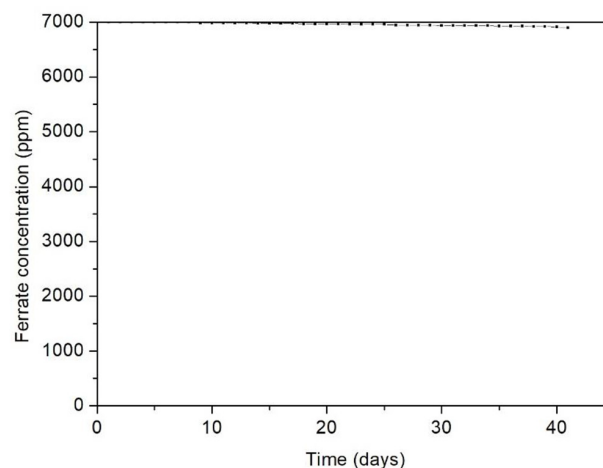
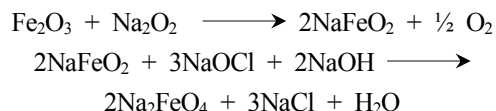


Fig. 1. Stability of ferrate(VI) synthesized with some modifications.

such as 2,4,6-TBP with high efficiency. The reaction in the synthesis process of ferrate(VI) was followed the equation below.



### 3.2 Effect of pH

In the previous study, the dependency of ferrate(VI) oxidation power on the pH condition has been investigated. From the research conducted by Graham et al. (2004), variations of pH condition on the ferrate(VI) efficiency for the removal of phenol and chlorinated phenol resulted in significant influence. The various pH conditions used in this experiment were acid (pH=4), neutral (pH=6.5), and base (pH=10). Even this experiment employ different kind of ferrate(VI), it showed the similar results with the research conducted by Graham et al. (2004). The neutral condition was optimal for the 2,4,6-TBP removal using both *in-situ* liquid ferrate(VI) and stable liquid ferrate(VI) (Fig. 2).

The degradation efficiency of *in-situ* liquid ferrate was 42.38% at neutral condition, while 33.12% and 20.76% at acidic and basic conditions, respectively. On the other hand, the degradation efficiency of stable liquid ferrate(VI) was 94.33% at neutral condition, while 77.89% and 58.65% at acidic and basic conditions, respectively. *In-situ* liquid ferrate(VI) and stable liquid ferrate(VI) showed the similar pattern where the highest removal efficiency observed at neutral condition and the lowest at the basic condition. As it is known, 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 (Rush et al., 1996). At basic condition, ferrate(VI) is very stable due to the oxygen ligand of ferrate(VI) which is very slow to be exchanged with water molecules (Sharma, 2002; 2010). Therefore, a reduction of degradation efficiency has been obtained at the basic condition (Laksono and Kim, 2017).

Further investigation to determine reaction rate of *in-situ* and stable liquid ferrate(VI) had been conducted. According previous research, the reaction of ferrate(VI) and organic

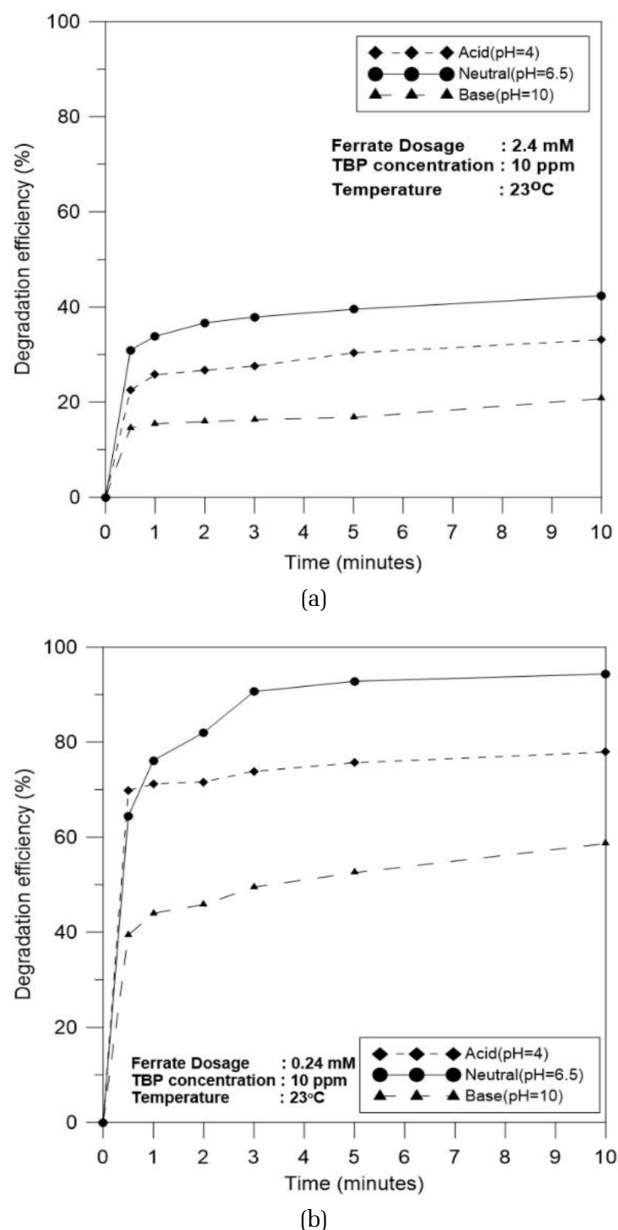


Fig. 2. The 2,4,6-TBP removal by a) *In-situ* liquid ferrate(VI) and b) Stable liquid ferrate(VI) in the various pH condition.

compound generally is a second order reaction rate (Yang et al., 2014). The second order reaction rate law can be described by Eq. (1).

$$-d[\text{TBP}]/dt = k_{\text{app}} [\text{FeO}_4^{2-}] [\text{TBP}] \quad (1)$$

Afterward, Eq. (1) was rearranged and  $d[\text{TBP}]/dt$  is integrated to become eq. (2).

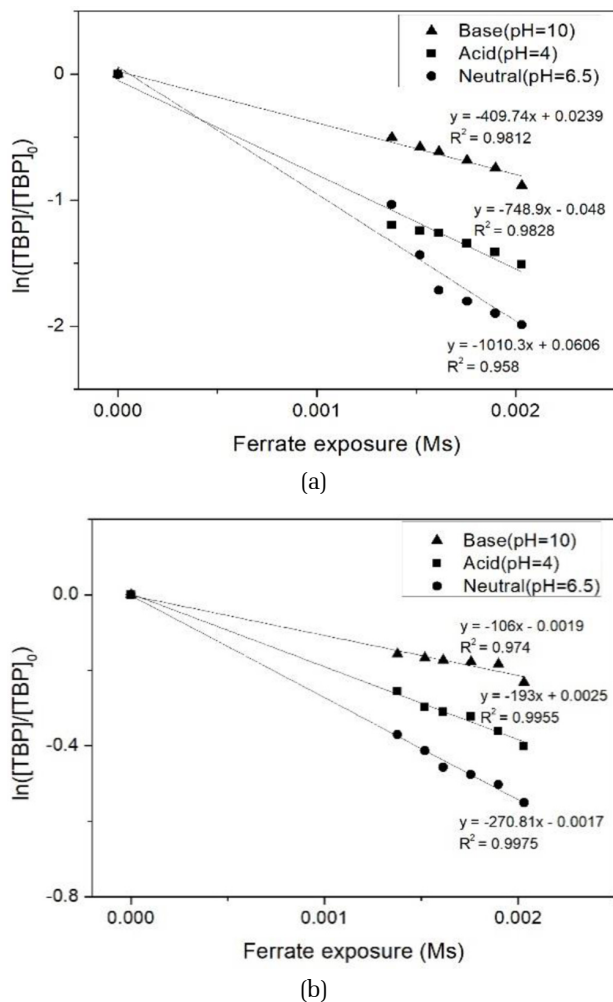


$$\ln(\text{TBP}) / [\text{TBP}]_0 = -k_{\text{app}} \int_0^t [\text{FeO}_4^{2-}] dt \quad (2)$$

Where,  $\int_0^t [\text{FeO}_4^{2-}] dt$  defines the concentration of ferrate(VI) exposure, and the  $k_{\text{app}}$  is the apparent second order reaction rate constant (Sharma, 2013; Yang et al., 2011). The value of  $k_{\text{app}}$  was established by plotting the natural

**Table 1.**  $k_{\text{app}}$  value of 2,4,6-TBP removal in the variation of pH

Ferrate(VI) Type	Ferrate(VI) dose	Kapp ( $\text{M}^{-1}\text{s}^{-1}$ )		
		Acid	Neutral	Base
<i>In-situ</i>	2.4 mM	193.15	270.81	106
stable	0.24 mM	748.9	1010.3	409.47



**Fig. 3.** The 2,4,6-TBP removal by a) *In-situ* liquid ferrate(VI) and b) Stable liquid ferrate(VI) in the various pH conditions.

logarithm of target compound concentration ( $\ln C/C_0$ ) and the ferrate exposure. The calculation result of  $k_{\text{app}}$  values were shown in Table 1 and Fig. 3. In the previous research conducted by Lee et al. (2005),  $k_{\text{app}}$  value of solid ferrate(VI) ( $\text{K}_2\text{FeO}_4$ ) at pH 7 to remove 4-bromophenol was  $86 \text{ M}^{-1} \text{ s}^{-1}$  with the ferrate dose of 2 mg/L, while  $k_{\text{app}}$  value of *in-situ* and stable liquid ferrate(VI) at pH 6.8 to remove 4-bromophenol from this experiment was  $896.74 \text{ M}^{-1} \text{ s}^{-1}$  with the ferrate(VI) dose of 28 mg/L (Laksono and Kim, 2017). Even both of these experiments using different kind of ferrate(VI), the ratio of  $k_{\text{app}}$  value and ferrate(VI) doses ( $k_{\text{app}}/\text{ferrate(VI) dose}$ ) from both of experiments were only slightly different. The difference might be caused by the different of pH condition and ferrate(VI) dose. However, further investigation needed to be conducted to confirm this hypothesis.

### 3.3 Effect of Ferrate Dose

Ferrate(VI) dose is an important parameter which affected ferrate(VI) performance to remove organic contaminants (Sharma, 2013). The 2,4,6-TBP removal efficiency increased with an increase of ferrate(VI) dosage (Fig. 4). Fig. 5 showed the degradation results after 10 min. of reaction time. The results showed the effect of *in-situ* and stable liquid ferrate(VI) dosage for the 2,4,6-TBP removal. Both of ferrate(VI) successfully removed 2,4,6-TBP with certain dosages. Stable liquid ferrate(VI) has higher efficiency to remove 2,4,6-TBP than *in-situ* liquid ferrate(VI).

On the previous study, the removal efficiency increased proportionally with the increasing of ferrate(VI) dose. The removal of 2,4,6-TBP were strongly depended on the dosages of ferrate(VI) added in the reactor (Sharma and Bielski, 1991; Sharma et al., 2000; Yu et al., 2008). The similar increasing relationship between ferrate(VI) dose and removal efficiency had been observed in the experiments. The 0.24 mM of stable liquid ferrate(VI) dose was needed to degrade over 80% of 2,4,6-TBP while 7.2 mM of *in-situ* liquid ferrate(VI) needed to degrade over 70% of 2,4,6-TBP.

Producing processes of *in-situ* liquid ferrate(VI) and stable liquid ferrate(VI) were different. The main differences were the stable liquid ferrate(VI) the usage of  $\text{Na}_2\text{O}_2$  and the heating process on the furnace for 30 minutes to help

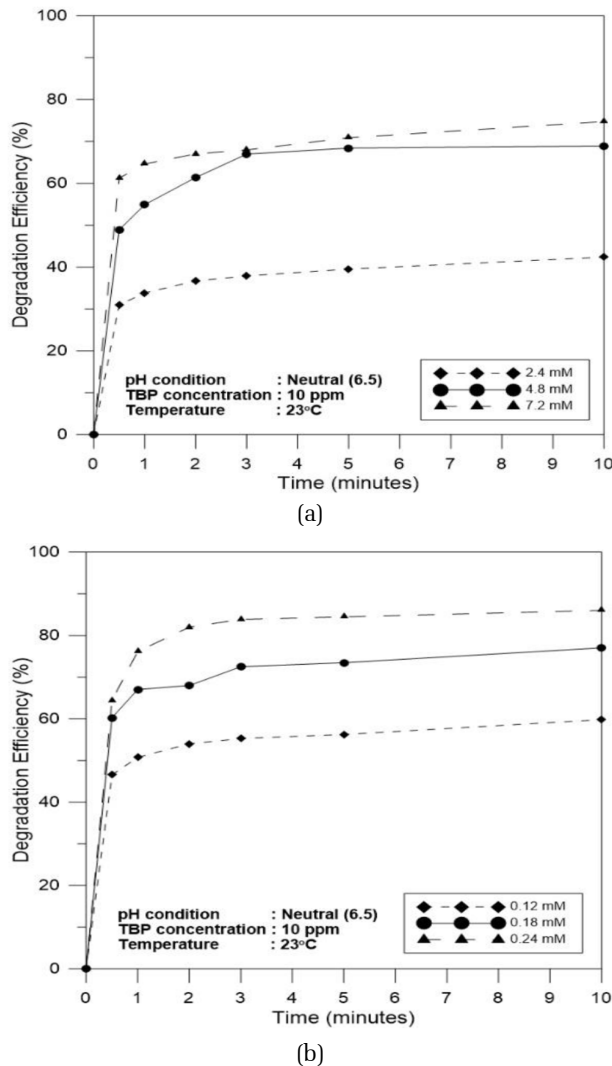


Fig. 4. The 2,4,6-TBP removal by a) *In-situ* liquid ferrate(VI) and b) Stable liquid ferrate(VI) in the various ferrate dosage.

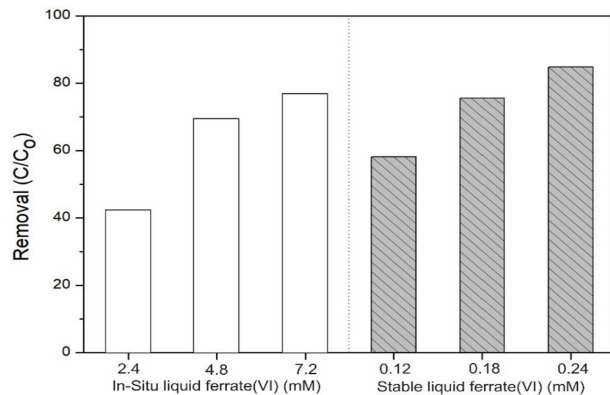


Fig. 5. Removal of 2,4,6-TBP by *In-situ* liquid ferrate(VI) and Stable liquid ferrate(VI).

ferrate(VI) for its stabilization. As the stable liquid ferrate(VI) is more stable, it will sustain longer in the reactor and keep removing the 2,4,6-TBP. Hence, the removal efficiency of stable liquid ferrate(VI) was higher.

#### 4. Conclusions

The oxidation power of *in-situ* liquid ferrate(VI) and stable liquid ferrate(VI) have been observed. The neutral condition had been the best condition for *in-situ* and stable liquid ferrate(VI) for the 2,4,6-TBP removal. The degradation efficiency of *in-situ* liquid ferrate was 42.38% at neutral condition, while 33.12% and 20.76% at acidic and basic conditions, respectively. On the other hand, the degradation efficiency of stable liquid ferrate(VI) was 94.33% at neutral condition, while 77.89% and 58.65% of removal were observed at acidic and basic conditions, respectively. Meanwhile, on the investigation of ferrate(VI) dosage effect, the 0.24 mM of stable liquid ferrate(VI) was needed to degrade over 80% of 2,4,6-TBP and 7.2 mM of *in-situ* liquid ferrate(VI) needed to degrade over 70% of 2,4,6-TBP. The stable liquid ferrate(VI) has higher oxidation power because its stable properties make it exist on the reactor for the longer period of time.

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