Utilization of Ferrate Ion (FeO$_4^{2-}$) as Oxidizing Agent for Reducing Color Intensity of Peat Water

Pemanfaatan Ion Ferrat (FeO$_4^{2-}$) sebagai Oksidator untuk Penurunan Intensitas Warna pada Air Gambut

Retno Agnestisia$^1$, Karelius$^{1*}$, Rendi Muhamad Iqbal$^1$, Dyah Ayu Pramoda Wardani$^1$, Midun Efendi Patar Sihombing$^1$, Sri Yulandari Simangunsong$^1$, Junita Dongoran$^1$

$^1$Department of Chemistry, Faculty of Mathematic and Natural Science, Universitas Palangka Raya, Kampus UPR Tunjung Nyaho, 73111, Indonesia

Email: karelius@chem.upr.ac.id

ABSTRACT

Peat water from Central Kalimantan is generally yellow to brownish-red in color. It causes peat water to not be used as a source of water for daily needs. Humic acid, fulvic acid, and humin are organic compounds that cause peat water to become colored. One alternative step that can be taken for reducing the color intensity of peat water is to degrade color-causing organic compounds by using an oxidizing agent. A hexavalent form of iron ion (Fe$^{6+}$), commonly called ferrate (FeO$_4^{2-}$) in potassium ferrate compound, is a powerful oxidizing agent used in the present study. Potassium ferrate (K$_2$FeO$_4$) was synthesized by a wet oxidation method and characterized using a UV-Vis spectrophotometer and an X-Ray Diffractometer (XRD). The ferrate solution is purplish-red in color with a maximum wavelength of 510 nm. The XRD pattern shows strong diffraction peaks at 2$\theta$ which are characteristic of K$_2$FeO$_4$. The ferrate solution was then used to degrade color-causing organic compounds in the peat water from Central Kalimantan. Determination of the optimum degradation conditions was monitored by the absorbance decrease of organic compounds in peat water at a wavelength of 370 nm. The results showed that ferrate solution with a concentration of 80 ppm was able to degrade organic compounds in peat water at pH 8, with a removal efficiency of 100%.

Keywords: oxidizing agent, ferrate ion (FeO$_4^{2-}$), peat water

ABSTRAK

Air gambut asal Kalimantan Tengah umumnya berwarna kuning hingga merah kecoklatan. Hal ini menyebabkan air gambut tidak dapat dijadikan sebagai sumber air untuk keperluan sehari-hari. Asam humat, asam fulvat, dan humin merupakan senyawa organik yang menyebabkan air gambut menjadi berwarna. Salah satu langkah alternatif yang dapat dilakukan untuk menurunkan intensitas warna pada air gambut adalah dengan mendegradasi senyawa organik penyebab warna menggunakan oksidator. Bentuk heksavalen ion besi (Fe$^{6+}$), biasa disebut ferrat (FeO$_4^{2-}$) dalam senyawa kalium ferrat, merupakan oksidator kuat yang digunakan dalam penelitian ini. Kalium ferrat (K$_2$FeO$_4$) disintesis dengan metode oksidasi basah dan dikarakterisasi menggunakan spetrotometre UV-Vis dan X-Ray Diffractometer (XRD). Larutan ferrat hasil sintesis berwarna merah keunguan dengan panjang gelombang maksimum sebesar 510 nm. Pola XRD menunjukkan puncak difraksi yang kuat pada 2$\theta$ yang karakteristis dengan K$_2$FeO$_4$. Larutan ferrat hasil sintesis selanjutnya digunakan untuk mendegradasi senyawa organik dalam air gambut asal Kalimantan Tengah. Penentuan kondisi optimum degradasi ditinjau dari penurunan absorbansi senyawa organik dalam air gambut pada panjang gelombang 370 nm. Hasil penelitian menunjukkan bahwa larutan ferrat dengan konsentrasi 80 ppm mampu mendegradasi senyawa organik dalam air gambut secara optimal pada pH 8 dengan efisiensi penyisihan sebesar 100%.

Kata kunci: oksidator, ion ferrat (FeO$_4^{2-}$), air gambut

Received: 24 November 2022; Accepted: 4 September 2023; Available online: 23 October 2023
1. INTRODUCTION

Central Kalimantan is one of the provinces in Indonesia where most of its area consists of peatlands, which cover around 3,012 million ha or 52.18% of the total peatland area on the island of Kalimantan (Soil Research Institute, 2011). Local people who have not received clean water services can use water sources from rivers or wells. This is considered more economical because of its abundant availability. However, in reality, river or well water in peatland areas does not meet the requirements for clean water set forth in Government Regulation No. 82 of 2001 concerning Water Quality Management and Water Pollution Control. This is because peat water has a low pH (3-5) with a high content of organic compounds, iron (Fe), and manganese (Mn) (Herlambang & Said, 2005). The high content of organic compounds causes the water to be yellow to brownish-red in color. These organic compounds are humic acid, fulvic acid, and humin (Sutrisno, 2006; Suherman & Sumawijaya, 2013). This characteristic causes peat water unfit for use as a water source for cooking, bathing, and washing purposes (Zahra et al., 2017; Sinambella et al., 2022).

Oxidation is a chemical method that was considered to be used for removing various water contaminants by using an oxidizing agent. The oxidizing agents can come from chemical species containing atoms with high oxidation numbers (Dwiasi & Suyata, 2011). Many studies have mentioned that several oxidizing agents can oxidize contaminants in water into a form that is safer for the environment. Some well-known oxidizing species are MnO₄⁻, MnO₂, Cr₂O₇²⁻, H₂O₂, and O₃ (Rice & Gomez-Taylor, 1986; Sharma, 2004; Oturan & Aaron, 2014). However, they also produce a broad variety of by-products, some of which are considered environmentally unfriendly due to their toxic nature (Panagiota & Graham, 2002). A hexavalent form of iron ion (Fe⁶⁺), commonly called ferrate (FeO₄³⁻), was considered as an effective and safe oxidizing agent (Lee et al., 2004; Sharma, 2002; Sharma, 2004; Bartzatt, 2016; Talaiekhozani et al., 2016). The reduction potential of ferrate was reported to be relatively high, at 2.20 V under acidic and 0.70 V under alkaline conditions, respectively (Lee et al., 2004; Talaiekhozani et al., 2016). As an oxidizing agent in water, Fe⁶⁺ will be reduced to form non-toxic by-products of Fe³⁺ or insoluble final product (Fe(OH)₃) (Lee et al., 2004; Sharma, 2004). Unexpectedly, the final by-product of Fe³⁺ was also reported to be used as a coagulant to efficiently remove metals, non-metals, and organic compounds (Sharma, 2004; Lim & Kim, 2009; Graham, Khoi, & Jiang 2010).

Several researchers reported that ferrate was found to be effective in degrading organic dyes from textile waste at a rate greater than 85%. These organic dyes were Acid Orange 7 (Dwiasi & Suyata, 2011), Methylene blue (Karelius & Asi, 2016), Remazol Black B (Prasetya, 2020), Congo Red (Fatimah et al., 2021), and Lissamine Green B (Jargalsaikhan, 2021). In addition, Bartzatt et al. (1992) showed that ferrate was able to remove a range of metal cations (e.g. Mn²⁺, Cu²⁺, Pb²⁺, Cd²⁺, Hg²⁺, and Cr³⁺) and non-metal anions (e.g. SO₄²⁻, SO₃²⁻, Cl⁻, and PO₄³⁻) to a low level. As³⁺ and Sb⁵⁺ could also be removed from aqueous solution using ferrate with removal efficiency were 98.39% and 11.22%, respectively (Wang et al., 2020). Besides dyes, metals, and non-metals, ferrate was able to remove humic and fulvic acids which also present in peat water as color-causing organic compounds by oxidation and coagulation (Lim & Kim, 2009; Graham, Khoi, & Jiang 2010). Based on these facts, the consideration arose to degrade color-causing organic compounds in peat water from Central Kalimantan using a powerful oxidizing agent like as ferrate. The utilization of ferrate with a dual function in this study is expected to efficiently reduce the color intensity of peat water and generate no hazardous by-products during treatment.

There are three methods commonly used to synthesize ferrate, i.e., wet oxidation, dry oxidation, and electrolysis (Lee et al., 2004). Among these methods, the wet oxidation is a method of ferrate synthesis that is considered simple to do with relatively low operational cost. This method has been used to create a variety of ferrate salts, including K₂FeO₄, Na₂FeO₄, Ba₂FeO₄, and Ag₂FeO₄. However, due to its comparatively simple synthetic process and resilience toward spontaneous breakdown to ferric oxide, K₂FeO₄ has been the most commonly utilized as an oxidizing agent (Sharma, 1999; Lee et al., 2004). Ferric ion is oxidized by sodium hypochlorite (NaOCl) in a strong basic solution (NaOH) to form ferrate ion (FeO₄³⁻). The excess potassium hydroxide (KOH) is then added to the ferrate-containing solution to produce potassium ferrate (K₂FeO₄) (Lee et al., 2004; Wei et al., 2015). K₂FeO₄ can be obtained with a highly pure of 90%.
At optimal conditions, it was found that the ferrate ion yield was over 70% (Lee et al., 2004). Therefore, the aims of the present study are to synthesize ferrate ion in the form of potassium ferrate (K$_3$FeO$_4$) using wet oxidation and utilize it for reducing the color intensity of peat water from Central Kalimantan.

2. MATERIALS AND METHODS

2.1. Materials

The peat water was taken from river at the Wisata Air Hitam Kereng Bangkirai, Palangka Raya city, Central Kalimantan, Indonesia in July 2022. NaOCl 5.25% was obtained from clothing bleach “Proclin” and purchased from the market in Palangka Raya city. Analytical grade FeCl$_3$, KOH, NaOH, and HCl were obtained from Merck, Tbk. All solutions were prepared using distilled water.

2.2. Methods

2.2.1 Synthesis of K$_3$FeO$_4$

The wet oxidation method was used to synthesize potassium ferrate (K$_3$FeO$_4$). The synthesis was carried out by dissolving NaOH in NaOCl 5.25%. The mixture was stirred until NaOH was completely dissolved. The solution was then added FeCl$_3$ 0.3 M and stirred until the solution turned purple. The ferrate solution was stored in a dark condition for a day. The ferrate solution that had been left for one day was filtered with glass wool. The supernatant was then added KOH 0.3 M. The solution was stored in a dark condition for 2 days. Then the mixture was centrifuged for 10 min at 2000 rpm. The residue was dried under an incandescent lamp to reduce the moisture content. The obtained black precipitate of K$_3$FeO$_4$ was then crushed to a powder. The ferrate solution was then characterized by a UV-Vis spectrophotometer (OPTIMA, Spectrophotometer SP-300) with a wavelength range of 400-700 nm and the obtained K$_3$FeO$_4$ powder was characterized by an X-Ray Diffractometer (XRD, X’Pert PRO, PANalytical).

2.2.2 Optimization of degradation condition

The 1 mL of 100 ppm ferrate solution was used to degrade organic compounds in 10 mL of peat water at various pH values of 6, 8, 10, and 12. Furthermore, 1 mL of ferrate solution with various concentration values of 10, 20, 40, 60, 80, and 100 ppm was used to degrade color-causing organic compounds in 10 mL of peat water at an optimum pH. The reactions were conducted using a shaker at room temperature for 1 hour. The solution was collected using filtration method. All procedures were conducted in triplicate. The reduction of color intensity in peat water was monitored by decreasing the absorbance of organic compounds using a UV-Vis spectrophotometer (OPTIMA, Spectrophotometer SP-300) at the maximum wavelength of peat water. Determination of removal efficiency (%) was calculated using the following formula:

\[
\text{% Removal efficiency} = \frac{A_o - A_t}{A_o} \times 100%
\]

where $A_o$ is the initial absorbance of peat water, while $A_t$ is the absorbance of peat water after treatment.

3. RESULTS AND DISCUSSION

The FeCl$_3$ and NaOCl were reacted under alkaline condition to produce ferrate ion (FeO$_4^{2-}$). The FeCl$_3$ was used as a source of Fe$^{3+}$ ion, while NaOCl was used to oxidize Fe$^{3+}$ to Fe$^{6+}$. In addition, alkaline condition was also selected as the optimum conditions for the synthesis of K$_3$FeO$_4$. This is because FeO$_4^{2-}$ ion is more stable under alkaline condition than acidic condition. The H$_2$FeO$_4^+$, H$_3$FeO$_4^-$, and HFeO$_4^-$ ions are the predominant species in acidic condition (Sharma, 2002; Lee et al., 2004). The ferrate solution has a blackish-purple color. This color indicates that the ferrate has been successfully synthesized. The ferrate solution was then added KOH to produce precipitated potassium ferrate (K$_3$FeO$_4$). The reaction of K$_3$FeO$_4$ synthesis is showed in the following equation:

\[
2\text{FeCl}_3(l) + 3\text{NaOCl}(l) + 10\text{NaOH} \rightarrow 2\text{Na}_2\text{FeO}_4(l) + 3\text{NaCl}(l) + 5\text{H}_2\text{O}(l) \\
\text{NaFeO}_4(l) + 2\text{KOH}(l) \rightarrow \text{K}_3\text{FeO}_4(s) \downarrow + 2\text{NaOH}(l)
\]
It has been explained above that ferrate solution has a blackish-purple color. Therefore, the solution can be characterized by a UV-Vis spectrophotometer with a wavelength range of 400-700 nm. The result of determining the ferrate solution's maximum wavelength ($\lambda_{max}$) is showed in Figure 1.

**Figure 1.** Absorbance curve of ferrate solution in visible region

**Figure 1** shows that $\lambda_{max}$ of ferrate solution was 510 nm with an absorbance of 0.992. This result is appropriate with the previous study results which showed that ferrate solution has $\lambda_{max}$ between 505-510 nm (Lee et al., 2004; Dwiasi and Suyata, 2011; Wei et al., 2015; Prasetya et al., 2020). The XRD was then used to investigated the material composition of the synthesized K$_2$FeO$_4$ powder. The result was obtained as shown in **Figure 2**.

**Figure 2.** The XRD pattern of the synthesized K$_2$FeO$_4$ powder (The JCPDS diffraction card serial numbers: No. 25-0652 for K$_2$FeO$_4$; No. 22-0346 for Fe(OH)$_3$, and No. 88-2300 for NaCl)

The strong diffraction peaks of K$_2$FeO$_4$ were found at 2$\theta$ of 25.9°, 28.4°, 29.3°, 30.3°, 31.2°, 40.6°, and 50.3° (JCPDS file no. 25-0652). However, the XRD pattern also implies the existence of impurities in the sample. These impurities are Fe(OH)$_3$ (58.7°; JCPDS file no. 22-0346) and NaCl (31.2° and 66.4°; JCPDS file no. 88-2300), which are by-products of K$_2$FeO$_4$ synthesis.

The $\lambda_{max}$ of of peat water was determined before investigating the optimum conditions for degradation of organic compounds in peat water by ferrate. It was carried out in the wavelength range between 350 nm to 500 nm. This analysis aims to determine the maximum wavelength at which the maximum absorbance of organic compounds in peat water is obtained. The $\lambda_{max}$ of a compound is characterized by its compound structure. The result shows that the $\lambda_{max}$ for organic compounds in peat water was 370 nm with an absorbance of 0.824 (**Figure 3**). This finding is
similar with Harfadli (2017) which mentioned that $\lambda_{\text{max}}$ of peat water from South Kalimantan was 370 nm.

![Figure 3](image1.png)

**Figure 3.** Absorbance curve of peat water in visible region

Optimization of the degradation condition was studied at various of pHs (6, 8, 10, and 12) and ferrate concentrations (10, 20, 40, 60, 80, and 100 ppm). The fruitfulness of the degradation is indicated by a decrease in the intensity of the color of the peat water, which could be measured by UV-Vis spectrophotometer based on the absorbance decrease of color-causing organic compounds. Lee et al. (2004) mentioned that pH has a significant impact on the reactivity of ferrate in aqueous solution. The optimum pH for degrading organic compounds was obtained at pH 8 with a removal efficiency value of 99.45% ± 0.77 (Figure 4). This is because ferrate as an oxidizing agent have better stability under alkaline condition (Sharma, 2002; Lee et al., 2004). However, the removal efficiency values decreased with increasing pH above 8. As well known, the concentration of OH$^-$ ions generally increases at pH > 8. This condition causes competition between OH$^-$ ions and organic compounds (e.g., humic and fulvic acids) to be coagulated by ferric ions, thereby reducing the efficiency of their removal in peat water. As previously described, ferrate ($\text{FeO}_4^{2-}$) has a dual function (Sharma, 2004; Lim & Kim, 2009; Graham, Khoi, & Jiang 2010). Basically, ferrate acts as an oxidizing agent to degrade organic compounds. However, ferrate will be reduced to a final by-product of ferric ion in the reaction, which can act as a coagulant to coagulate organic compounds that cause color in peat water.

![Figure 4](image2.png)

**Figure 4.** Effect of pH on % removal efficiency of color-causing organic compounds in peat water

Furthermore, Haneef et al. (2020) reported that the determination of the optimum value of ferrate concentration is also an important to conduct because it directly affects to the removal...
efficiency and operational cost. The effect of ferrate concentration on the removal efficiency of color-causing organic compounds is shown in Figure 5.

![Figure 5](image)

**Figure 5.** Effect of ferrate concentration on % removal efficiency of color-causing organic compounds in peat water

This figure shows that the value of removal efficiency increases with increasing the ferrate concentration and reached a maximum value at a concentration of 80 ppm, with a removal efficiency of 100%. In addition, the ferrate concentration more than 80 ppm do not seem to have a significant effect. It suggests that 80 ppm of ferrate is sufficient to obtain optimal removal efficiency. This study is necessary to determine the proper ferrate concentration for higher removal efficiency at lower operating costs.

4. CONCLUSIONS

The potassium ferrate (K₂FeO₄) was successfully synthesized by a wet oxidation method. The ferrate solution was then used to degrade color-causing organic compounds in the peat water from Central Kalimantan. The results showed that 80 ppm of ferrate solution was able to degrade organic compounds in peat water at pH 8, with a removal efficiency of 100%. This indicates that the synthesized ferrate which is believed to have dual functions can efficiently reduce the color intensity of peat water. Nevertheless, the optimum conditions for degradation that occur at alkaline pH must receive attention. Therefore, authors recommend to carry out further treatment of peat water in order to safe for use as a water source for cooking, bathing, and washing purposes.

ACKNOWLEDGMENT

Author wishes to thank the Faculty of Mathematics and Natural Sciences, Univeritas Palangka Raya for research grant in 2022 with contract number 705/UN.24.10/PL/2022.

LIST OF REFERENCES


*Abbreviated title ...*