

# Degradation of Reactive Black 5 by potassium ferrate(VI)

페레이트를 활용한 아조 염료 Reactive Black 5 분해 연구

Minh Hoang Nguyen · II-kyu Kim<sup>\*</sup> Minh Hoang Nguyen · 김일규<sup>\*</sup>

Division of Earth Environmental System Science, Pukyong National University 부경대학교 지구환경시스템과학부(환경공학 전공)

#### ABSTRACT

This paper aims to study the degradation process for refractory azo dye namely Reactive Black 5(RB5) by potassium ferrate(VI) synthesized using the wet oxidation method. The process of degradation of azo dyes by Ferrate was studied with several parameters such as pH, different Ferrate(VI) dosage, different azo dye initial concentration, and temperature. A second-order reaction was observed in all degradation processes for RB5 having the highest degradation efficiency. The highest  $k_{app}$  value of RB5 degradation was 190.49 M<sup>-1</sup>s<sup>-1</sup>. In the pH experiments, the neutral condition has been identified as the optimum condition for the degradation of RB5 with 63.2% of dye removal. The efficiency of degradation also depends on the amount of ferrate(VI) available in the reactor. Degradation efficiency increased with an increase in Potassium Ferrate(VI) dosage or a decrease of RB5 initial concentration. The temperature has been reported as one of the most important parameters. From the results, increasing the temperature(up to 45°C) will increase the degradation efficiency of azo dye by Ferrate(VI) and if the temperature exceeds 45°C, the degradation efficiency will be decreased.

#### 국문초록

본 논문은 회분식 반응기에서 습식 산화법으로 합성한 칼륨 페레이트(VI)에 의한 난분해성 아조 염료Reactive Black 5의 분해 과정을 연구하는 것을 목적으로 한다. 수용액에서 RB5의 분해는 pH, Ferrate (VI) 투입량, 초기 농도, 수용액 온도 등 다양한 변수의 조건에서 연구되었다. RB5 경우에는 최대 분해 효율은 pH 7.0에서 63.2%가 달성되었으며, 이 실험 조건에서 얻은 k<sub>app</sub> 값은 190.49 M<sup>-1</sup>s<sup>-1</sup> 으로 나타났다. 온도 또한 가장 중요한 매개 변수 중 하나로 연구되었으며, 그 결과로부터 온도(45°C까지)를 증가시키면 페레이트(VI)에 의한 아조 화합물 염료의 분해 효율이 증가하고, 온도가 45°C를 초과하면 분해 효율이 저하되는 것으로 나타났다.

Key words: Potassium Ferrate (VI), Reactive Black 5, Degradation, Azo dye

**주제어:** 칼륨 페레이트, 활성블랙5, 분해, 아조염료

\*Corresponding author: Il-kyu Kim (E-mail: kimilky523@gmail.com; Tel. 051-629-6528)

#### Minh Hoang Nguyen (Graduate Student) / Minh Hoang Nguyen (대학원생)

45, Yongso-ro, Nam-gu, Busan 48513, Republic of Korea 부산광역시 남구 용소로 45, 48513

#### Il-kyu Kim (Professor) / 김일규 (경교수)

45, Yongso-ro, Nam-gu, Busan 48513, Republic of Korea 부산광역시 남구 용소로 45, 48513

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# 1. Introduction

The textile industry is a source of significant dye effluents that contain highly toxic metal complex dyes. These dyes pose a challenge because materials can only absorb a fraction, ranging from 20% to 80%, of the dye from their mixtures. Consequently, about 10% to 15% of the dye is discharged into effluents due to the limited absorption capacity. As the use of synthetic chemical dves has been on the rise in recent years, a substantial quantity of industrial wastewater, laden with dyes, is released into aquatic and soil environments. Azo dyes, which feature one or more azo groups (-N=N-) in their chemical structure, represent a significant portion, ranging from 50% to 70%, of the synthetic dyes employed in textiles, paper, food, cosmetics, and pharmaceuticals. Traditional methods of treating water are widely employed and deemed suitable primarily because a significant portion of water contaminants, approximately two-thirds. consists of organic, biodegradable components. However, these biological treatment approaches become ineffective, particularly when dealing with persistent and hazardous biological pollutants such as textile dyes, phenols, and aniline. In contrast, non-biological approaches, including physical and chemical technologies, have garnered increasing global attention for the elimination of these hazardous contaminants from water and wastewater. Nonetheless, these non-invasive techniques essentially transfer organic matter from water to another phase, necessitating the further disposal of solid residues. On the other hand, more aggressive chemical methods have been designed to disintegrate contaminants through chemical oxidation or reduction, with the ultimate aim of entirely breaking down or transforming these pollutants into less harmful substances. Thus, chemical oxidation consistently holds a pivotal and foundational role in water and wastewater treatment, as other methodologies have shown their effectiveness to varying degrees. This article's primary rationale for selecting a potent oxidizing agent, such as Potassium Ferrate (VI) (K<sub>2</sub>FeO<sub>4</sub>), is to effectively eliminate azo dyes in water-based solutions. A number

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of years ago, a particular form of Iron (Fe) with an oxidation state of +6, known as Ferrate (VI), was identified. This unique compound possesses the potential for eco-friendly oxidation in the context of water and wastewater treatment (Ivanenko, 2020; Li et al., 2020). Its significant promise in water and wastewater treatment arises from the distinctive characteristic of Ferrate (VI) as an oxidizer in the initial stages of the reaction. Afterward, it transforms into a coagulating agent as Ferrate (VI) undergoes a change into Fe (III), resulting in an improvement in the effectiveness of the purification process (Zhang et al., 2020). This paper offers an examination of the properties of Ferrate (VI) and its application in removing azo dyes from both environmental and industrial settings. Ferrate (VI) is renowned for its stability and straightforward synthesis (Thompson et al., 1951). This compound is a black-purple substance that maintains its stability when exposed to air without moisture for an extended duration. In an aqueous solution, the Ferrate (VI) ion (FeO<sub>4</sub><sup>2-</sup>) exists as a monomer with a notable degree of four "covalent characters," featuring equivalent oxygen atoms (Goff H Murmann, 1971; Hoppe et al., 1982).

# 2. Materials and Methods

#### 2.1 Materials

Iron(III) Nitrate  $(Fe(NO_3)_3 \cdot 9H_2O)$  was from Katayama Chemical (Japan), sodium hypochlorite solution (NaOCl) and Potassium hydroxide (KOH) were all obtained from Junsei (Chuo-ku, Tokyo). RB5 was bought from Sigma – Aldrich (USA). Buffer solutions for pH adjustment (pH 4, 7, and 10) were all purchased from Samchun Chemicals Company (Seoul, Korea).

#### 2.2 Synthesis of Ferrate (VI)

The preparation procedure for Potassium Ferrate (VI) in this study utilized the wet method, which was detailed in a different publication (Thompson et al., 1951). To begin, 30 grams of KOH were added to 100 mL of

NaOCl. After the complete dissolution of KOH through stirring, the solution was cooled and passed through GF/C filter paper to eliminate NaCl from the water. This process was repeated 3 to 4 times, and the resulting filtrate was stored at a low temperature. Following this, 11.1 grams of Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O were introduced into the solution and stirred for about 40 minutes to synthesize  $\text{FeO}_4^{2-}$ . In order to solidify the substance, 16.7 grams of KOH were incorporated, and agitation continued for around 40 minutes. It was then placed in a refrigerator for approximately 30 minutes. After this cooling period, the solution was filtered using a G4 glass filter, and the filtrate was immediately mixed with a saturated KOH solution (11M) before undergoing another round of refrigeration. Finally, Ferrate (VI) crystals could be obtained by filtering the solution through GF/C filter paper. The relevant chemical reactions are outlined below. (Talaiekhozani et al., 2016):

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$$
 (1)

$$2Fe(OH)_3 + 3NaClO + 4NaOH \rightarrow$$
  
$$2Na_2FeO_4 + 3NaCl + 5H_2O$$
(2)

$$Na_2FeO_4 + 2KOH \rightarrow K_2FeO_4 + 2NaOH$$
 (3)

Ferrate (VI) crystals were initially dissolved in 3 M KOH and then combined with a saturated KOH solution. This mixture was refrigerated and subjected to filtration using GF/C filter paper to enhance purity. This filtration process was repeated two to three times. Subsequently, the Ferrate (VI) that remained on the filter paper was washed sequentially with 25 mL n-hexane, 10ml methanol, and 10 ml diethyl ether, and this washing process was repeated four times. The product was then dried under vacuum conditions and stored in a container. The purity of the final Ferrate (VI) product, which was determined using the ABTS measurement method (Li et al., 2005) with a DR 5000 UV-spectrometer (HACH), was found to be approximately 93%.

#### 2.3 Experimental Procedures

In line with the abstract's description, all batch experiments involving the degradation of azo dyes using Ferrate (VI) (K<sub>2</sub>FeO<sub>4</sub>) followed this prescribed protocol: Azo dyes were prepared in distilled water. The inquiry into azo dye degradation via Ferrate (VI) encompassed an examination of several variables, including pH levels (set at 4, 7, and 10), varying doses of Ferrate (VI), and temperature conditions. To maintain pH consistency, adjustments were made through the addition of acidic or alkaline solutions, or by employing a buffer solution. Temperature regulation was maintained using a temperature control bath. The degradation experiment was initiated by introducing a specified quantity of Ferrate (VI) into the reactor with concurrent stirring. At specific time intervals (1, 2, 5, 10 minutes), a sample was withdrawn using a water sampler and subsequently treated with 0.05 mM of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O to promptly arrest further reactions (utilizing any 1ml of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O for every 5ml of the sample). Following this, the levels of absorption within the sample were quantified using a DR 5000 UV-spectrometer (HACH), employing a wavelength of 486 nm for RB5.

#### 2.4 Analytical methods

In this research, the RB5 concentration was assessed by utilizing specific calibration curves tailored for each dye. After the absorption measurement of the dye in the sample was accomplished, the obtained absorption value was employed to refer to the relevant calibration curve for each dye, enabling the determination of the remaining concentration. The % degradation efficiency will be calculated using the following equation (4):

Degradation Efficiency (%) = 
$$\frac{C_O - C}{C_O} \times 100\%$$
 (4)

where  $C_o$  is the initial concentration and C is the final concentration.

## Results and discussion

#### 3.1 Effect of pH on the degradation of RB5

The experiments were carried out to determine the remaining concentration of RB5 (in mg/L) as it reacted with Ferrate (VI) over time, across different pH settings (4, 7, 10). To control pH levels, adjustments were made using either acidic or alkaline solutions, and a buffer solution was utilized to maintain pH stability. Samples were collected at specific time intervals: 30 seconds, 1, 2, 4, 6, 8, and 10 minutes. As depicted in Fig. 1, the natural conditions exhibited the highest degradation rate for the RB5 solution (63.2%), followed by pH 4 (45.35%), with the least efficient performance observed at pH 10 (21.37%).

The decomposition rate of Ferrate (VI) with water is far greater than the reaction rate with pollutants (Huang, 2021), whereas, at a high pH (>7), Ferrate (VI) is more chemically stable and lasts longer in the experimental reactor. Consequently, the experimental results demonstrated the highest EBT degradation was achieved in neutral conditions (pH 7). The result also confirmed that the initial pH had a great impact on Ferrate (VI)

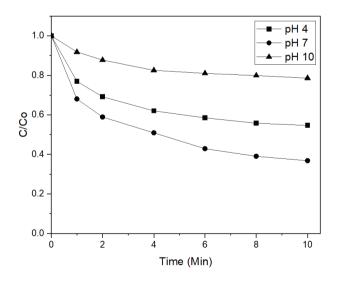


Fig. 1. Effect of different pH on the removal of  $C_0$  [RB5]=20mg/L by Ferrate (VI). (Experiment condition: Ferrate (VI) dosage=42 mg/L; Temperature = 20°C; reactor volume =100 ml)

oxidizing power because the decolorization rate at pH 7 was greater than at pH 10.

The research also included kinetic investigations of the degradation of RB5 by Ferrate (VI) under varying pH conditions. The kinetics of the reaction involving Ferrate (VI) and various other compounds have been explored, and they are well-described by second-order reaction rate laws (Sharma, 2013; Wang, 2019; Acosta et al., 2020; Yang et al., 2011; Liu, 2019).

In Fig. 2, the study displays the  $k_{app}$  value (with  $R^2 \sim 0.9$ ) for the degradation of RB5 by Ferrate (VI). The rate constant (k) values for the Ferrate (VI) reaction with RB5 under various conditions were established and computed through graphical methods. These k values were derived from the slopes of the graphs representing the exposure of Ferrate and the ratio of C/C<sub>o</sub>. The  $k_{app}$  value, in turn, provides insight into the reaction rates of each experiment conducted in the study.

For RB5, the rate constant (k) value was described in Fig. 2 and increased from 46.879  $M^{-1}s^{-1}$  to 56.047  $M^{-1}s^{-1}$  as the pH 10 and 4 respectively.  $K_{app}$  value reached its peak at pH 7 (190.49  $M^{-1}s^{-1}$ ) indicating that the highest k for RB5 removal was achieved at natural pH conditions.

# 3.2 Effect of dosages of Potassium Ferrate (VI) on the degradation of RB5

The study examined the degradation of RB5 by

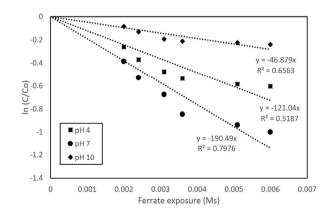


Fig. 2. Removal rate of Reactive black 5 by Ferrate at various pH levels.

Ferrate (VI) under various dosages of the oxidant to understand its impact. As depicted in Fig. 3, there was a noticeable trend where the removal of RB5 significantly increased with higher doses of Ferrate (VI). With increased dosages, nearly 88% of RB5 was efficiently eliminated within just 10 minutes, and the characteristic dark color of RB5 began to fade. This phenomenon can be attributed to the simultaneous self-degradation of Ferrate (VI), a phenomenon previously observed in prior research.

As Fig. 3 demonstrated, the top degradation rate was  $C_o[Ferrate (VI)] = 0.3 \text{ mmol/mL} (87.91\%)$ , next to that was  $C_o[Ferrate (VI)] = 0.212 \text{ mmol/L} (63.2\%)$  and  $C_o[Ferrate (VI)] = 0.0126 \text{ mmol/mL} (34.52\%)$  which these data molar ratio ( $C_o[RB5]$  :  $C_o[Ferrate (VI)]$ ) is 1:15, 1:10.6, and 1:6.3 respectively. These results, in line with earlier experiments involving azo dyes, strongly indicate that the higher the concentration of Ferrate (VI), the more effectively it can eliminate azo dyes. This is attributed to the by-products of Ferrate (VI) leading to the generation of Fe (III), which exhibits natural coagulation abilities in tackling pollutants (Zheng et al., 2020; Kovalakova, 2021).

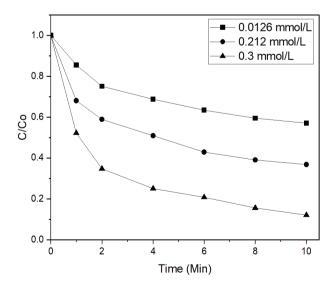


Fig. 3. Effect of different Ferrate (VI) dosages on the removal of RB5 after 10 minutes of reaction time. (Experiment condition: Temperature =  $20^{\circ}$ C; reactor volume =100 ml; C<sub>o</sub> [RB5]=20 mg/L).

In a manner similar to the pH factors, we conducted kinetic studies to analyze the degradation of RB5 when exposed to varying quantities of Ferrate (VI). The chemical reactions between Ferrate (VI) at doses of 25, 42, and 60 mg/L and RB5 with an initial concentration of 20 mg/L followed second-order reaction kinetics at a pH level of 7. The findings displayed in Fig. 4 indicated that the rate constant (k) exhibited an upward trend as the dosage of Ferrate increased. The order of k value followed as  $k_{60}$  (380.78  $M^{-1}s^{-1}$ ) >  $k_{42}$  (190.49  $M^{-1}s^{-1}$ ) >  $k_{25}$  (104.08  $M^{-1}s^{-1}$ ).

# 3.3 Effect of initial concentration of RB5 on the degradation

Given that the oxidation process is notably influenced by the initial concentration of the specific compound being targeted, the research included an assessment of how the degradation rate of RB5 varied concerning its initial concentrations when treated with Ferrate (VI). The experiments aimed to determine the residual concentration (in mg/L) of RB5 following its interaction with Ferrate (VI) at a constant Ferrate concentration ([Ferrate (VI)] = 42 mg/L) across different initial RB5 concentrations over time.

As predicted, it was observed that the degradation of RB5 by Ferrate (VI) became less efficient as the initial concentration of azo dyes increased. Consequently, the results confirmed that the most effective removal rate

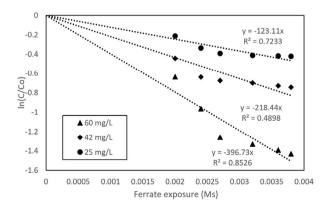


Fig. 4. Ferrate (VI) exposure and Ferrate (VI) doses plot in the determination of RB5  $k_{\text{app}}$  value.

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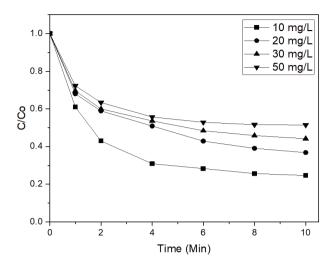


Fig. 5. Removal ratio of different  $C_o$  [RB5] after 10 minutes of removal by Ferrate (VI) 42 mg/L with pH 7, Experiment temperature = 20°C.

achieved by Ferrate (VI) occurred at the lowest initial RB5 concentration. For instance, after a 10-minute reaction with 42 mg/L of Ferrate (VI), the decolorization percentages for initial dye concentrations of 10, 20, 30, and 50 mg/L were determined to be 75.37%, 63.2%, 55.8%, and 48.5%, respectively.

# 3.4 Effect of temperature on the degradation of RB5

A parallel series of experiments was conducted employing a hotplate stirrer and water jackets to attain five distinct temperatures, aiming to investigate their impact on the degradation of azo dyes. It's important to mention that, in this particular experiment, the dosage of Ferrate (VI) was set at 50 mg/L.

As illustrated in Fig. 6, the degradation of RB5 displayed an increase in efficiency with rising temperatures. To be more precise, the removal rates for RB5 were recorded at 63.19%, 68.4%, 72.3%, and 55.01% at temperatures of  $25^{\circ}$ C,  $35^{\circ}$ C,  $45^{\circ}$ C, and  $50^{\circ}$ C, respectively. It's worth noting that the lowest removal percentage was observed at  $50^{\circ}$ C (55.01%), while the peak degradation rate occurred at  $45^{\circ}$ C (72.3%). In previous work, (Wagner et al., 1952) showed that Ferrate (VI) solution was much more stable at  $0.5^{\circ}$ C than at

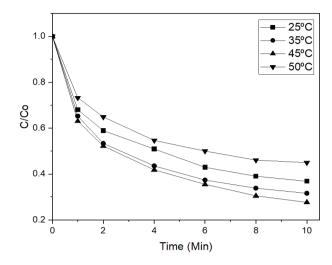


Fig. 6. The ratio of RB5 in different temperatures after 10 minutes of removal by Ferrate (VI) 50 mg/L, pH 4.

25°C. Due to the accelerated self-decay of Ferrate (VI), the high temperature was detrimental to the removal of RB5. At temperatures higher than 45°C (for example, 55°C or 60°C), Ferrate (VI) tends to be unstable. Other researchers have also confirmed these phenomena that the Ferrate (VI) concentration decreases with an increase in temperature above 50°C (Thomas et al., 2021). The process of RB5 removal by Ferrate (VI) in this study was confirmed to follow a second-order reaction. In Fig. 6, the  $k_{app}$  value for RB5 is depicted across a temperature range from 20°C to 60°C, with the highest  $k_{app}$  value noted at a temperature of 45°C (Hoang and Kim, 2021).

In general, the Arrhenius equation was employed in this experiment to calculate the activation energy, and the resulting activation energy value was determined to be 92.2 kJ/mol for the degradation of RB5. Fig. 7 displays the Arrhenius plot for the breakdown of RB5 at various temperatures.

The graphs and the findings presented in Fig. 6 indicate that within the temperature range below the optimum point (45°C), the decolorization reaction involving Potassium Ferrate (VI) exhibits a high activation energy ( $E_a$ ), which subsequently starts decreasing beyond 50°C. Additionally, the plot of the



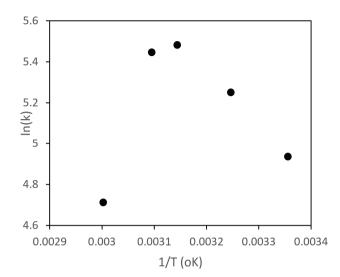


Fig. 7. Arrhenius plot for the decomposition of RB5 in different temperatures with pH 7,  $C_0$ [RB5]=20 mg/L.

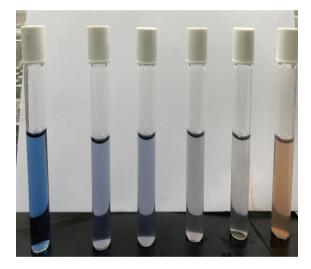


Fig. 8. Degradation process of Reactive Black 5 by Potassium Ferrate (VI)

(From left to right: 1 minute, 2 minutes, 4 minutes, 6 minutes, 8 minutes, 10 minutes of treatment with Potassium Ferrate (VI)).

natural logarithm of the rate constant (ln (k)) against time offers a useful means to visually assess the stability of the decolorization process.

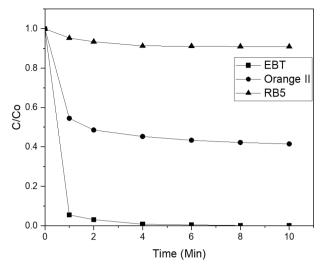


Fig. 9. Differences between the degradation efficiency by Ferrate (VI) with the optimal condition for each azo dye. (Experiment condition: Ferrate (VI) dosage= 10mg/L; Temperature = 45°C; reactor volume =120 ml; pH for EBT and RB5 is 7; pH for Orange II is 4; C<sub>o</sub> [Azo dyes] = 100 mg/L)

# 3.5 Differences between the degradation processes of azo dyes

### 3.5.1 Comparison between EBT, Orange II, and Reactive Black 5 degradation efficiency

As Fig. 9 shows, we can see how effective Potassium Ferrate (VI) can degrade mono azo dye (EBT, Orange II) with small doses of oxidants while most of the Reactive Black 5 remains in the solution. This difference in the degradation efficiency in this graph can be explained by the azo dye structure. Reactive Black 5 is a di azo dye that contains 2 azo bonds (the bond that is responsible for the color of the dye). Therefore, the amount of power required to decolorize the Reactive Black 5 is larger than that of Orange II and EBT. As a result, more Potassium Ferrate (VI) is needed to break 2 azo bonds in the Reactive Black 5 structure (Silva et al., 2006).

Another point worth mentioning here is that, for EBT and RB5, the optimal pH condition for degradation is in natural condition while the acid condition is the best pH condition for Orange II to be degraded by Potassium pp. 029–0

Ferrate (VI). The main reason is also due to the structure of azo dyes (Hoang and Kim, 2022).

The reaction temperature plays a crucial role in influencing the degradation process. According to the results, all experiments share a common optimal temperature for degradation, which is 45°C. This outcome aligns with the concept that reactions occur when reactants come into contact, and at higher temperatures, such as 45°C, molecules move more swiftly, leading to increased collision frequencies. This is unlike the reaction dynamics involving organic chemicals and traditional oxidants (e.g., persulfate, potassium permanganate), where elevated temperatures have a favorable impact on the efficient degradation of target compounds. In other research, (Wagner et al., 1952) it was demonstrated that the stability of Ferrate (VI) solution was significantly better at 0.5°C compared to 25°C. The elevated temperature, in this context, had an adverse impact on the removal of EBT due to the self-decomposition accelerated of Ferrate (VI). Temperatures exceeding 45°C, such as 55°C or 60°C, tended to render Ferrate (VI) unstable. Other scientific investigations have likewise validated these observations, indicating that Ferrate (VI) concentrations decrease with rising temperatures above 50°C (Thomas et al., 2021).

## 3.5.2 Comparison between Reactions of Reactive Black 5 (diazo dye), EBT, and Orange II (mono azo dye)

As mentioned before, from this thesis results, diazo dye is harder to degrade compared to azo dye. Some studies have also shown similar results and the major reason for this phenomenon is due to their more complex molecular structure (Silva et al., 2006).

Diazo dyes are identified by the existence of one or multiple diazo groups (-N=N-) within their chemical composition. These groups are created through the interaction of an aromatic primary amine with nitrous acid, leading to the formation of a diazonium salt (Said B et al., 2020). Subsequently, this diazonium salt can be combined with a coupling agent to generate the ultimate dye molecule. The diazo group is a highly reactive functional group that is relatively stable compared to other functional groups commonly found in organic molecules. This stability arises from the resonance stabilization of the diazo group, which involves the delocalization of the positive charge on the nitrogen atom onto the adjacent aromatic ring (M.C. Eliot., 2005). This delocalization helps to stabilize the diazo group and makes it more resistant to chemical and biological degradation. In contrast, mono-azo dyes have a single azo group (-N=N-) in their chemical structure, which is less complex than the diazo group. The azo group is less stable than the diazo group and can be more easily cleaved by various chemical and biological agents. This makes mono-azo dyes more amenable to degradation in the environment than diazo dves. Furthermore, the presence of other functional groups in diazo dyes can also make them more difficult to degrade (Yang Liu et al., 2020). For example, many diazo dyes contain aromatic rings, which are highly stable and resistant to degradation. In addition, some diazo dves contain sulfonic acid groups, which can further enhance the water solubility and stability of the dye molecule, making it more difficult to degrade.

The bonding patterns in di-azo dyes are also more complex than those in mono-azo dyes, which can create more difficult and varied reaction pathways for degradation enzymes or chemicals. Specifically, di-azo dyes contain multiple aromatic rings connected by nitrogen atoms, which can form different types of bonds and configurations depending on the specific structure of the dye (Jose et al., 2021). In di-azo dyes, the nitrogen atoms can form various types of bonds, such as double bonds, single bonds, or coordinate bonds, depending on the specific position and arrangement of the nitrogen atoms and aromatic rings. Additionally, the positions of substituent groups on the aromatic rings can affect the reactivity of the molecule, as well as the orientation of the nitrogen atoms and their bonding patterns. The presence of multiple types of bonds and configurations in di-azo dyes can create more complex and varied reaction pathways during degradation, as different

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enzymes or chemicals may be required to break down specific bonds or configurations in the molecule (Said B et al., 2020). This can make degradation processes slower less efficient and more difficult to predict or control. Moreover, the aromatic rings in di-azo dyes are typically large and have many electrons, which can form stable pi-bonds and make the molecule more resistant to oxidation or reduction reactions. This can further contribute to the difficulty of breaking down di-azo dyes.

The molecular weight of di-azo dyes is also affected the degradation process. To be more detailed. di-azo dyes are typically larger than mono-azo dyes, which makes them harder to transport and metabolize within microorganisms or other biological systems (Sheela et al., 2021). Overall, the chemical structure of azo dyes can have a significant impact on their degradability, with factors such as the presence of multiple azo groups, other functional groups, and electron-withdrawing or electron-donating groups affecting the stability and susceptibility of the dye to degradation.

# 4. Conclusion

The main objective of this paper was to demonstrate an efficient degradation method for RB5 by using an oxidant that is easy to manufacture, powerful over a wide pH range, and environmentally friendly for natural waters. For this purpose, Potassium Ferrate (VI) was chosen. For a starter, the preparation of Potassium Ferrate (VI) using the wet oxidation method has been experimented with and optimized to enhance the purity of the final product. Secondly, RB5 was selected for this paper to test the degradation efficiency of Potassium Ferrate (VI) through a variety of parameters. Significantly, the pH conditions, the initial dosage of the azo dye, the Potassium Ferrate (VI) dosages, and the temperature of the solution were investigated. The main results are the following:

1. Potassium Ferrate (VI) creation has been successfully experimented with and optimized. This research showed a step-by-step method to manufacture Potassium Ferrate (VI) using the wet method with very high purity ( $\sim 93\%$ ).

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2. The results of the experiment on the degradation process for azo dyes by Potassium Ferrate (VI) in different parameters and the investigation of degradation patterns prove that RB5 can be effectively degraded by Ferrate (VI) oxidation in a short amount of time (10 minutes of reaction time).

3. Different values of pH were tested to see their effect on the degradation of azo dye. It was found that the degradation efficiency was strongly dependent on pH value. As a result, the initial pH in the experiment solution is extremely important. To be more specific RB5 has its highest degradation efficiency at pH 7.

4. The initial dosage of the azo dye, the Potassium Ferrate (VI) dosages, and the temperature also have a big influence on the removal rate. It clearly shows that increasing the Ferrate (VI) dosages or decreasing the initial azo dye concentration can improve the degradation efficiency. Increasing temperature also increases the degradation rate, however, due to the Potassium Ferrate (VI) characteristic, the best temperature for all three experiments is 45°C.

5. Reactions between Ferrate (VI) and azo dyes followed second-order kinetics. Factors, including Ferrate (VI) dosages, the initial pH, and temperature, had significant effects on both the azo dye removal and the kinetic constants.

Overall, the results found in this paper also reaffirm the degradation power of Potassium Ferrate (VI) on diazo dye and provide a better knowledge of how azo dyes can be treated with a powerful oxidant. Further research based on these findings may lead to a more efficient and better understating of the complex nature of advanced oxidation and azo dyes treatment.

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# References

- Acosta-Rangel, A., Sánchez-Polo, M., Rozalen, M., Rivera-Utrilla, J., Polo, A.M.S., Berber-Mendoza, M.S. and López-Ramón, M. V. (2020). Oxidation of Sulfonamides by Ferrate (VI): Reaction Kinetics, Transformation Byproducts, and Toxicity Assessment, J. Environ. Manag., 255.
- Benkhaya, S., M'rabet, S., and Harfi, A.E. (2020). Classifications, properties, recent synthesis and applications of azo dyes, Heliyon, 6(1), 32-71.
- Brandara. J., Mielczarski, J.A., and Kiwi. J. (1999). 1. Molecular Mechanism of Surface Recognition. Azo Dyes Degradation on Fe, Ti, and Al Oxides through Metal Sulfonate Complexes. Langmuir., 15, 7670-7679.
- Chung, K.T., Jr, S.E.S. (1993). Decolorization of azo dyes by environmental microorganisms and helminths, Environ. Toxicol. Chem., 12, 2121-2132.
- Ezzatahmadi, N., Teng, B., Liu, H., Millar, G.J., Ayoko, G.A., Zhu, J., Zhu, R., Liang, X., He, H., and Xi, Y. (2017). Catalytic degradation of Orange II in aqueous solution using diatomite-supported bimetallic Fe/Ni nanoparticles. RSC Advance, 14.
- Fan, J., Ding, Z., Zhao, Z., Liu, J. (2018). Degradation of p-Arsanilic Acid and Simultaneous in-Situ Removal of Arsenic Species with Ferrate(VI): Kinetics, Intermediate and Degradation Pathway, Chem. Eng. J., 350, 453-462.
- Guoting, L., Ninggai W., Bingtao, L., and Xiwang, Z., (2009). Decolorization of azo dye Orange II by ferrate(VI) – hypochlorite liquid mixture, potassium ferrate(VI) and potassium permanganate. Desalination, 249(3), 936-941.
- Hoang, N.M., and Kim, I.K. (2022). Degradation of Eriochrome Black T by Potassium Ferrate (VI), J. Water Sewerage, 36(3), 167-175.
- Huang, Z.S. (2021). Ferrate Self-Decomposition in Water Is Also a Self-Activation Process: Role of Fe(V) Species and Enhancement with Fe(III) in Methyl Phenyl Sulfoxide Oxidation by Excess Ferrate, Water Res., 197.
- Ivanenko, O. (2020). Application of Potassium Ferrate in Water Treatment Processes, J. Ecol. Eng., 21, 134-140.
- Jiang, J.Q. (2007). Research progress in the use of Ferrate (VI) for environmental remediation, J. Hazard. Mater., 146(3), 617-623.
- Jiang, J.Q., Wang, S., and Panagoulopoulos, A. (2005). The exploration of Potassium Ferrate (VI) as a disinfectant/ coagulant in water and wastewater treatment, Chemosphere, 63(2), 212-219.

- Jiang, J.Q., and Lloyd, B. (2005). Progress in developing and using Ferrate (VI) salt as an oxidant and coagulant for water and wastewater treatment, Water Res., 36(6), 1397-1408.
- Kovalakova P., Cizmas L., Feng M., McDonald T.J., Marsalek B., Sharma K.S. (2021). Oxidation of antibiotics by ferrate(VI) in water: Evaluation of their removal efficiency and toxicity changes, Chemosphere, 277, 130365.
- Li, X.Z., and Graham, N. (2005). A study of the preparation and reactivity of Potassium Ferrate, Chemosphere, 61(4), 537-543.
- Li Y., Jiang L., Wang R., Wu P., Liu J., Yang S., Liang J., Lu G., Zhu N. (2021). Kinetics and mechanisms of phenolic compounds by Ferrate(VI) assisted with density functional theory, J. Hazard. Mater., 415, 125563.
- LI Y., WU P., JIANG L., WU Y. (2020). Progress on Application of Ferrate(VI) for the Environmental Remediation. Materials Reports, 34(19): 19003-19009.
- Liang, X., and Fenglian, F. (2020). Se(IV) oxidation by ferrate(VI) and subsequent in-situ removal of selenium species with the reduction products of ferrate(VI): performance and mechanism, J. Environ. Sci. Health, 55, 528-536.
- Liu H., Pan X., Chen J., Qi Y., Qu R., Wang Z. (2019). Kinetics and mechanism of the oxidative degradation of parathion by Ferrate(VI), Chem. Eng. J., 365, 142-152.
- Liu, Y., Li, C., Bao, J., Wang, X., Yu, W., and Shao, L. (2020). Degradation of Azo Dyes with Different Functional Groups in Simulated Wastewater by Electrocoagulation, Water, 123.
- Machala, L., Zboril, R., Sharma, V.K., Filip, J., Jancil, D., and Homonnay, Z. (2009). Transformation of solid Potassium Ferrate (VI) (K<sub>2</sub>FeO<sub>4</sub>): Mechanism and kinetic effect of air humidity, Eur. J. Inorg. Chem., 8, 1060-1067.
- Maryam, M., Masoud, P., Kavoos, D., and Hamzeh, A.J. (2016). Optimizing Potassium Ferrate for textile wastewater treatment by RSM, Environ. Health Eng. Manag., 33, 137-142.
- Moore, S.B., and Ausley, L.W. (2002). Systems thinking and green chemistry in the textile industry: concepts, technologies and benefits, J. Clean. Prod., 12, 585-601.
- Ogugbue, C.J., and Sawidis, T. (2021). Bioremediation and Detoxification of Synthetic Wastewater Containing Triarylmethane Dyes by Aeromonas hydrophila Isolated from Industrial Effluent, Biotechnol. Res. Int., vol. 2011, Article ID 967925, 11.
- Ong, S.A., Eiichi, T., Hirata, M., and Hano, T. (2012).

Decolorization of Orange II using an anaerobic sequencing batch reactor with and without co-substrates, J. Environ. Sci., 24(2) 291-296.

- Paixão, K., Abreu, E., Samanamud, G.R.L., França, A.B., Loures, C.C.A., Baston, E.P., Naves, L.L.R., Bosch, J.C., and Naves, F.L. (2019). Normal boundary intersection applied in the scale-up for the treatment process of Eriochrome Black T through the UV/TiO2/O3 system, J. Environ. Chem. Eng., 7, 102801.
- Robinson, T., McMullan, G., Marchant, R., and Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresour. Technol., 77(3), 247-255.
- Sharma, V.K. (2002). Potassium Ferrate (VI): an environmentally friendly oxidant, Adv. Environ. Res., 6(2), 143-156.
- Sharma, V.K., Yngard, R.A., Cabelli, D.E., and Clayton Baum J (2008). Ferrate (VI) and Ferrate (V) oxidation of cyanide, thiocyanate, and copper(I) cyanide, Radiat. Phys. Chem., 77(6), 761-767.
- Sharma, V.K. (2013). Ferrate (VI) and Ferrate (V) Oxidation of Organic Compounds: Kinetics and Mechanism, Coord. Chem. Rev., 257, 495-510.
- Sheela, T., Paul, O., Senthil, K. (2020). Microbial degradation of azo dyes by textile effluent adapted, Enterobacter hormaechei under microaerophilic condition, Microbiol. Res., 250.
- Talaiekhozani, A., Bagheri, M., Talaie khozani, M.R., and Jaafarzadeh, N. (2016). An Overview on Production and Applications of Ferrate (VI), Jundishapur J. Health Sci., 5, 1828-1842.
- Thomas, M., Drzewicz, P., Wieckol-Ryk, A., and Panneerselvam, B. (2021). Influence of Elevated Temperature and Pressure on Treatment of Landfill Leachate by Potassium Ferrate (VI), Water Air Soil Pollut., 232, 450.
- Thompson, J.E., Ockerman, L.T., and Schreyer, J.M. (1951).

Preparation and purification of Potassium Ferrate (VI), J. Am. Chem. Soc., 73, 1379-1381.

- Wagner, W.F., Gump, J.R., and Hart, E.N. (1952). Factors Affecting Stability of Aqueous Potassium Ferrate (VI) Solutions, Anal. Chem., 24, 1497-1498.
- Wang, J., Zheng, T., Cai, C., Zhang, Y., and Liu, H. (2019). Oxidation of Ethanethiol in Aqueous Alkaline Solution by Ferrate (VI): Kinetics, Stoichiometry and Mechanism, Chem. Eng. J., 361, 1557-1564.
- Wei, Y.L., Wang, Y.S., and Liu, C.H. (2015). Preparation of Potassium Ferrate from Spent Steel Pickling Liquid, Metals., 5(4), 1770-1787.
- Xu. G.R., Zhang. Y.P., and Li, G.B. (2009). Degradation of azo dye active brilliant red X-3B by composite ferrate solution, J. Hazard. Mater., 161(2-3), 30, 1299-1305.
- Yang, B., Ying, G.G., Zhang, L.J., Zhou, L.J., Liu, S., and Fang, Y.X. (2011). Kinetics Modeling and Reaction Mechanism of Ferrate (VI) Oxidation of Benzotriazoles, Water Res., 45, 2261-2269.
- Zhang, W. (2020). Effectiveness Analysis of Potassium Ferrate Pretreatment on the Disintegration of Waste Activated Sludge, Res. Environ. Sci., 33, 1045-1051.
- Zheng, L. (2020). Chemically Enhanced Primary Treatment of Municipal Wastewater with Ferrate (VI), Water Environ. Res., 93, 817-825.
- Zollinger, H. (1987). Synthesis, properties of Organic Dyes and Pigments, Color Chemistry, New York, USA: VCH Publishers, 92-102.
- Goff, H., and Murmann, R.K. (1971). Studies on the mechanism of isotopic oxygen exchange and reduction of ferrate (VI) ion  $(FeO_4^{-2})$ . J. Am. Chem. Soc., 93, 6058-6065.
- Hoppe, M.L., Schlemper, E.O., and Murmann, R.K. (1982). Structure of dipotassium ferrate(VI), Structural Science, Crystal Engineering and Materials, Acta Cryst., B38, 2237-2239.

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