Reactive Black 5 Removal by Electrochemical Oxidation Using Titanium Dioxide Nanoparticle Electrodes

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Abstract:
Reactive Black 5 (RB5) is a commonly employed azo dye that is widely utilized in textile dyeing procedures due to its intense black color and simple application. Wastewater containing this dye may be released into the environment, consequently causing harm to the environment and the organisms therein. Hence, there is a need to treat wastewater containing pollutants such as RB5. Electrocatalysis is an effective method to degrade organic pollutants. Titanium dioxide (TiO2) nanoparticles are examples of electrocatalysts and have demonstrated superior efficacy in the degradation of a variety of organic compounds compared to other investigated electrocatalysts. However, there is a lack of comprehensive knowledge regarding the electrocatalytic degradation efficiency, and reaction kinetics of RB5 degradation using TiO2 nanoparticles. This work aimed to investigate the potential of TiO2 nanoparticle electrodes for electrocatalytic degradation of RB5 dye in wastewater. Electrolysis experiments and analytical measurements were conducted to determine optimal conditions of parameters such as voltage, electrolyte composition, and concentration, as well as pH. Different RB5 concentrations were used to determine the suitable environment for degradation. Optimization revealed that the ideal voltage for RB5 removal was 6 V. Sodium chloride (NaCl), and sodium sulfate (Na2SO4) were used as electrolytes, with NaCl outperforming Na2SO4 in RB5 removal efficiency. The ideal NaCl concentration and pH for RB5 removal were found to be 0.05 M and 7, respectively. The range of system adaptation which yielded the highest removal efficiency was found to be 100 mg/L of RB5. Under these optimized conditions, the apparent rate constant decreased over time, indicating effective degradation.

Keywords: Dyeing wastewater, Electrochemical oxidation, Nanoparticles, Reactive Black 5, Titanium dioxide.
Introduction

The textile industry is a significant contributor to global water pollution, accounting for approximately 20% of the total. This pollution primarily stems from dyeing and finishing processes, as well as the laundering of synthetic clothing, which releases pollutants into waterways (Patti et al., 2020). With an approximate use of 1.3 million tons of dyes, at an estimated cost of approximately $23 billion globally, the textile industry is known to use a lot of water, with the dyeing process consuming more than half of the total amount of water (Che & Yang, 2022; Pervez et al., 2021). Azo dyes account for more than 50% of all textile dyes used in the textile industry (Chung, 2016). Due to the widespread use of azo dyes in the textile industry, the likelihood of their presence in wastewater discharged into the environment is considerable. This contributes to water pollution and ecological disturbance and poses potential health risks. Reactive Black 5 (RB5), synthetic in nature is a commonly used azo dye in the textile industry, posing a serious threat to water safety and biological health (Feng et al., 2022). RB5 has a complex chemical structure that affects its degradation efficiency in dyeing wastewater. The dye gets released into the environment and is likely to pose environmental and health risks such as discoloration of water and harm to aquatic life as well as skin irritation, eye irritation, and allergic reactions in humans (Khan & Malik, 2014; Semiz, 2020; Srivastava et al., 2022). This highlights the importance of removing RB5 from wastewater using advanced techniques such as electrochemical oxidation which has successfully proven to degrade the dye, demonstrating its potential for effective wastewater treatment (Jager et al., 2018).

The treatment of wastewater containing dyes, especially RB5, has received attention due to the ecotoxicity and health issues associated with textile dyes. Several methods, including, photocatalytic degradation, coagulation / flocculation, ozonation, membrane separation, aerobic and anaerobic biological treatment, ionizing radiation degradation, and electrochemical oxidation, have been employed to eliminate RB5 from dyeing wastewater. Electrochemical oxidation has been used and showed promising removal of RB5 from wastewater, thereby contributing to water safety and ecological health (Feng et al., 2022). This method has been employed to effectively treat RB5 wastewater, achieving a remarkable removal efficiency of up to 91.6% (Feng et al., 2022). The use of medium pressure peracetic acid (MPPA)/UV to effectively remove RB5, has proven effective by achieving a removal efficiency of 75.0% within 5 minutes (Zhu et al., 2023). The removal efficiency significantly increased from 68.98% to 91.2% as the pH increased from 6 to 9. Researchers have made progress in using electrochemical methods to remove RB5 from wastewater, but there are some important limitations to consider. For instance, some researchers have not fully investigated different operating conditions, such as voltage, pH, different RB5 concentrations, or pH values (Droguett et al., 2020; Jager et al., 2018). In addition, some studies have had difficulties completely removing RB5 within a short period. Studies carried out by Naraghi et al. (2018) and Suryawan et al. (2018) revealed high removal efficiencies of 96% and 96.9%, but over longer time periods of 80 minutes and 5 hours, respectively. Currently, electrochemical methods, especially those using titanium dioxide nanoparticles, are being explored for their remedial potential (Al-Tohamy et al., 2022).

Titanium dioxide has garnered interest for its potential in wastewater treatment methods due to its excellent conductivity, affordability, ability to generate non-toxic products, and substantial surface area. Prior studies mainly focused on the use of TiO2 for the photocatalytic degradation of RB5 under UV or visible light. However, this approach is hampered by several drawbacks. The coagulation process during photocatalytic degradation impairs the catalytic activity of TiO2, especially due to the instability of the nanoscale particles, which hinders the penetration of light to the active sites and consequently reduces the efficiency (Dong et al., 2015). The techniques for modifying TiO2 in photocatalytic processes
often encounter difficulties due to the rapid recombination of photogenerated electrons and holes, which limits the effectiveness of the process (Jitan & Garlisi, 2020). Additionally, the lack of reactive sites on TiO$_2$ is likely to affect the overall efficiency of photocatalytic processes, which in turn affects the degradation of RB5 and other organic pollutants (Jitan & Garlisi, 2020). There is however a lack of comprehensive knowledge regarding the electrocatalytic degradation efficiency of RB5 using TiO$_2$ nanoparticles (Lucas et al., 2013). This emphasizes the requirement to fill this knowledge gap and investigate the potential of TiO$_2$ nanoparticles for RB5 electrocatalytic degradation. Given TiO$_2$’s demonstrated high effectiveness, low environmental impact, and unique qualities such as broad bandgap, and large surface area (Droguett et al., 2020; Lucas et al., 2013), more investigation is needed. Therefore, an exploration of electrochemical oxidation, especially using TiO$_2$ nanoparticles as electrodes, appears to be a viable solution for RB5 removal (Samsami et al., 2020), an approach that addresses the critical need for sustainable and effective dye removal technology. Although several researchers have investigated different parameters such as initial RB5 concentration, supporting electrolyte composition and concentration, electrode material, pH, and applied voltage, many did not work with these factors in integration. Therefore, more work is needed to optimize the process for different types of RB5 dyeing wastewater.

The study explored the efficiency of RB5 removal using TiO$_2$ nanoparticle electrodes in an electrochemical oxidation reactor. It optimized the voltage, electrolyte composition and concentration, pH, and initial RB5 concentration, providing insights into effective degradation under optimized conditions. This research aimed to develop sustainable wastewater treatment strategies using TiO$_2$ nanoparticles as electrocatalysts.

**Methods**

**Materials and Reagents**

All chemicals used in this study were of analytical grade and were used without further purification. Reactive Black 5 (RB5) solution ($C_{26}H_{21}N_5Na_4O_{19}S_6$), (MW 991.82 g mol$^{-1}$, R351226-100g, Lot # E2325905, dye content ≥ 50%, C.I.20505, CAS 17095-24-8), obtained from Shanghai Aladdin Biochemical Technology Co. Ltd, was used as wastewater. The molecular structure of RB5 is illustrated in Figure 1. The chemicals used for experiments and analysis were: sodium hydroxide (NaOH) Sinopharm Chemical Reagent Co. Ltd (96.0%), sulfuric acid (H$_2$SO$_4$) Shanghai Aladdin Biochemical Technology Co. Ltd (98.3%), sodium chloride (NaCl) Sinopharm Chemical Reagent Co. Ltd (99.5%), titanium dioxide (TiO$_2$) (CAS 13463-67-7, MW 79.87, 25 nm) Shanghai Aladdin Biochemical Technology Co. Ltd (99.8%), NafionD-521 (Cat: 042117. AC, Lot: R05H100, CAS: 31175-20-9) Thermo scientific, pure ethanol, and deionized water.

![Figure 1. Structural Formula of Reactive Black 5](source: Jager et al., 2018)

**Electrode Preparation**

A precursor solution was prepared by dissolving 10 uL Nafion (binding agent) in 90 uL ethanol.
While continuously agitating, a ground 5mg of P25 anatase TiO$_2$ powder was added to the precursor solution. The ratio of TiO$_2$ particles to solution depended on the intended electrode loading and thickness. 15 minutes of ultrasonication (using Sonicator model KQ2200DE) were applied to the mélange to promote the dispersion and homogeneity of the TiO$_2$ particles within the solution. This also assisted with the dissolution of any agglomerates present and enhanced the contact between the TiO$_2$ particles and the binding agent (Nafion) (Noman et al., 2019).

The thoroughly mixed solution was then dropped onto a 1.5 cm x 1 cm piece of carbon felt (the preferred substrate). To remove any residual solvent from the coated substrate (carbon felt), it was permitted to dry at ambient temperature. Following this, a thermal treatment was performed using a muffle furnace (model PRD-D9000), at 500 degrees Celsius for 2 hours. This was done to enhance the crystallization of the TiO$_2$ and increase the properties of the electrode (Mohapatra & Nayak, 2018).

**Electrode characterization**

Scanning Electron Microscopy (SEM) is often used to characterize nanomaterials (Stepanova et al., 2018) to determine the morphology and composition of the material (Akhtar et al., 2018; Mayeen et al., 2018). In this study, SEM was used to detect the surface morphology and composition of carbon felt as well as TiO$_2$ nanoparticle electrode samples before and after the electrochemical oxidation of RB5. SEM images, graphs, and Energy Dispersive Spectroscopy (EDS) spectra are provided in Figure 2 below.

![Figure 2. SEM Images, Graphs, and EDS Spectra of a) Carbon Felt, b) Carbon Felt with TiO$_2$ Nanoparticles (Un-used Electrode), and c) Carbon Felt with TiO$_2$ Nanoparticles (Used electrode)](image-url)
Furthermore, X-ray diffractometry (XRD) is a rapid and non-destructive technique used to identify crystalline phases in materials (Bunaciu et al., 2015). It provides information on unit cell dimensions and crystal structure, allowing for a complete understanding of materials at the atomic level (Ali et al., 2022). XRD is particularly useful for characterizing electrode materials, providing insights into their structure, and contributing to the optimization of electrochemical performance. Electrodes utilized in this study were characterized using the XRD technique and XRD patterns/graphs are provided in Figure 3, below.

![Figure 3. XRD Pattern of (a) Carbon Felt, (b) Carbon Felt with TiO2 Nanoparticles (Un-used Electrode), and (c) Carbon Felt with TiO2 Nanoparticles (Used Electrode)](image)

**Experimental Setup**

The electrochemical experiments were performed in an undivided plexiglass cell with a 40 mL volume and a lid comprising three holes. The holes were fitted for access to the counter electrode (CE); and one for the working electrode (WE), as well as for the pipette used for the collection of samples. The electrochemical measurements were routinely done in an electrochemical set-up which comprises an anode (counter electrode), cathode (working electrode), electrolyte, and the solution (pollutant) as shown in Figure 4. The reaction under inquiry occurs at the working electrode. The material used as the working electrode was TiO2 nanoparticles. The efficacy of an electrochemical analysis is based on the surface area and shape of the working electrode. The counter electrode is normally a conductive substance that does not react with the solution, which in this investigation was a platinum sheet.
Figure 4. Schematic Diagram of an Electrochemical Cell

The electrodes were placed in the RB5 aqueous solution with the electrolyte, which guaranteed that the solution was conductive enough for the electrochemical process. When a potential was supplied, a flow of current from the working electrode to the counter electrode was predicted to occur.

Electrolysis Experiments and Analytical Measurements

The electrochemical cell contained 40 ml of the solution of RB5 for electrolysis in 60 min. Independent variables considered for the system were dye concentration, electrolyte concentration, pH, and voltage. Table 1 shows the independent variables with their levels. The dependent variable was dye removal efficiency. All experiments were performed under stirring and at room temperature for 1 hour.

<table>
<thead>
<tr>
<th>Table 1. Operating Variables for the RB5 Degradation Using Electrochemical Oxidation by TiO2 Nanoparticles</th>
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<tbody>
<tr>
<td>Variables</td>
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<tr>
<td>Voltage (V)</td>
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<tr>
<td>Electrolyte (NaCl) concentration (M)</td>
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<tr>
<td>pH</td>
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<td>RB5 initial concentration (mg/L)</td>
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</tbody>
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Before initiating the electrochemical process, a sample of the RB5-containing effluent was collected, and the initial RB5 absorbance was determined using a UV-Vis spectrophotometer (JINESA model UV765), at a wavelength of 598 nm. The obtained measurement served as a baseline for calculating the concentration (using the equation of the standard curve and taking into consideration the dilution factor) and removal efficiency.

At regular time intervals (i.e., 0, 2, 5, 10, 15, 20, 25, 30, 40, 50, and 60 min), 3 mL samples were collected from the electrochemical cell and the absorbance for each sample was evaluated using the UV-Vis spectrophotometer. The RB5 degradation efficiency was evaluated by comparing the absorbance of RB5 concentration at each time interval to the absorbance of its initial concentration (da Silva et al., 2022).

The removal efficiency was calculated using the following formula:

\[
\text{Removal efficiency (\%)} = \left[\frac{(C_0 - C_t)}{C_0}\right] \times 100, \quad (1)
\]

where \(C_0\) is the initial concentration of RB5 and \(C_t\) is the concentration of RB5 at a specific time interval (Niazi et al., 2021). Graphs of results for the different independent variables were plotted to determine their effects on the removal efficiency of RB5 and the effectiveness of the nano TiO2 in degrading RB5. The experiment was repeated three times, and an average was calculated to ensure that the removal efficiency was accurate.

Data Evaluation

Kinetics of the RB5 electrochemical process were calculated based on a pseudo-first-order kinetic model, as described in Eq. (2) (He et al., 2022):
where $C_t$ (mg/L) is the RB5 concentration at time $t$ (min), $C_0$ (mg/L) is the initial RB5 concentration, and $k_{app}$ (min$^{-1}$) is the pseudo-first-order rate constant.

Results and Discussion

SEM and XRD

According to Figure 2, carbon felt appears to be made up of long smooth cylinder-like fibers, with additional materials or coatings present on the surface. The results also reveal an accumulation of TiO$_2$ nanoparticles with a spherical morphology and a relatively uniform size distribution. The nanoparticles appear to be irregularly dispersed and not or only partially agglomerated, indicating adequate particle-to-particle separation. The typical particle size is about 25 nanometers. The surface of the nanoparticles appears to be slightly rough and free of substantial defects or irregularities. There are however observable differences before and after the use of electrodes, with the TiO$_2$ nanoparticles appearing white and slightly darker, respectively. Additionally, the fibers of the carbon felt appear to have been degraded/deteriorated with TiO$_2$ nanoparticles still intact although a color change has been observed. The EDS diagrams (Figure 2) on the other hand confirm the presence of carbon, titanium, and oxygen in the sample, which is consistent with the expected composition of TiO$_2$. The carbon peak was dominant, indicating a high concentration of carbon due to the TiO$_2$ nanoparticles, which are sparsely distributed, leaving some parts of carbon felt uncovered. The dominance of the carbon peak is attributed to both the composition of the substrate used (carbon felt) and the presence of sparsely distributed TiO$_2$ nanoparticles, which result in certain areas of the carbon felt remaining uncovered. The titanium peak is the second strongest after carbon and indicates a high concentration of TiO$_2$ nanoparticles. The oxygen peak is also relatively prominent, indicating a stoichiometric TiO$_2$ composition. No other elements were detected above the detection limit of the EDS system.

The XRD pattern of carbon felt, and carbon felt with TiO$_2$ (before and after use) are shown in Figure 3. Carbon felt possesses a slightly sharp crystallinity peak at about 25°. TiO$_2$ on the other hand possess sharp crystallinity peaks at 25°, 37°, 48°, 53°, 55° and 63° for both used and un-used electrodes, which according to Loryuenyong et al. (2014) are reflections of anatase, thus significantly confirming that TiO$_2$ used is in the anatase form. The XRD pattern obtained has therefore provided the crystal structure of TiO$_2$, thereby proving the success load of TiO$_2$ nanoparticles.

Effect of Voltage

Voltage drives the redox reactions in electrochemical oxidation and influences the transfer of electrons between reactants and products (Zhu et al., 2016). Hence, the optimal applied voltage was determined by beginning with a lower voltage and then increasing it as the RB5 degradation efficiency was monitored. The applied voltages tested were 4V, 5V, and 6V (Figure 5). The voltage regarded to be optimal was that which did not considerably improve degradation when further increased.

As the voltage increased, the RB5 removal efficiency also increased (Figure 5 (a)). This is because the applied voltage drives the electrochemical oxidation reaction and increases the generation of hydroxyl radicals (Asghar et al., 2015). The optimal voltage for the removal of RB5 is 6 V, which is seen to have a high apparent rate constant of 0.1299 min$^{-1}$ as shown in Figure 5 (c), suggesting a fast reaction. At this voltage, the RB5 removal efficiency reaches 100% within 25 minutes (Figure 5 (a)) and the energy consumption is also known to be relatively low. At higher voltages, the RB5 removal efficiency is known not to increase significantly, but the energy consumption increases (Feng et al., 2022). At lower voltages, RB5 removal efficiency decreases, at the same time, energy consumption is also likely to be reduced. Although this allowed time to observe the reaction, 91% and 94% RB5 removal efficiencies were achieved.
after 1 hour using both 4V and 5V, respectively. This is quite a long time compared to the 25 minutes with 6V to reach 100% effective removal. The apparent rate constants of 4V and 5V are 0.0386 min\(^{-1}\) and 0.0344 min\(^{-1}\) (Figure 5 (c)), respectively, suggesting slower reactions in comparison to that of 6V.

![Graph](image)

**Figure 5.** (a) Removal Efficiency of RB5 vs. Time, (b) Pseudo-First-Order Kinetic Fitting, and (c) Apparent Rate Constant (k\(_{\text{app}}\)) for Different Applied Voltages (4 V, 5 V, and 6 V)

At higher voltages, the RB5 removal efficiency is known not to increase significantly, but the energy consumption may increase (Feng et al., 2022). Higher voltage leads to a faster reaction rate, as more electrons are transferred per unit time. This is primarily because, at higher voltages, the electric field strength is higher, which results in more efficient removal of RB5 particles (Golokolenov et al., 2021). However, the increased voltage also leads to a higher energy consumption, as more power is required to maintain the electric field strength (Golokolenov et al., 2021). Consequently, there is a trade-off between the removal efficiency and energy consumption at higher voltages. Additionally, higher voltages can pose a risk of oxygen generation (“Surface engineering to prevent oxygen evolution of high-voltage cathodes,” 2023), which can reduce the efficiency of electrochemical oxidation. Furthermore, when the voltage is increased, the electric field strength also increases. This results in a stronger electrostatic attraction between the RB5 particles and the electrode surface, which enhances the capture and removal of these particles from the medium.

On the other hand, at lower voltages (i.e., 4V and 5V), the RB5 removal efficiency decreases, and energy consumption is also likely to be reduced. Although this allowed time to observe the reaction, RB5 removal efficiencies of 91% and
94% for 4V and 5V, respectively were reached only after 60 minutes, in comparison to 6V which enabled a removal efficiency of 100% within 25 minutes. This could be because the electric field strength is lower at lower voltages, leading to a less efficient removal of RB5 particles. However, the reduced voltage also results in lower energy consumption, as less power is required to maintain the electric field strength. In this case, the trade-off between removal efficiency and energy consumption favors lower voltages, as they offer a more energy-efficient solution at the expense of reduced removal efficiency (Ahmed et al., 2022).

Several factors contribute to changes in RB5 removal efficiency and energy consumption at different voltages (Feng et al., 2022). One key factor is the charge of the RB5 particles. As the charge of the particles increases, the electric field strength required to remove them efficiently also increases. Consequently, higher voltages are necessary to achieve the same removal efficiency with highly charged particles. Another factor that affects the relationship between voltage, RB5 removal efficiency, and energy consumption is the size and shape of the RB5 particles. Larger or irregularly shaped particles may require higher voltages to achieve the same removal efficiency as smaller, more uniformly shaped particles (Rashtbari et al., 2023). This is because the electric field strength required to overcome the particle’s surface forces is higher for larger or irregularly shaped particles (Rashtbari et al., 2023).

Like other factors, it is important to optimize the applied voltage to achieve RB5’s high removal efficiency with relatively low power consumption. However, it is crucial to note that the ideal voltage might vary based on individual experimental circumstances, such as the composition and concentration of the electrolyte, the pH of the solution, and the initial concentration of RB5.

**Effect of Electrolyte Composition**

The optimization of the electrolyte composition is vital for the achievement of a high RB5 removal efficiency with relatively low energy consumption. Understanding the impact of different electrolytes on reaction rates makes it possible to tailor the composition to enhance efficiency while minimizing energy input. This optimization process involves experimental analysis and theoretical modeling to identify the most effective electrolyte composition for achieving the desired RB5 removal efficiency.

Two sets of 100 mg/L aqueous solutions of RB5 were prepared with different electrolytes in each, 1 set contained 0.05 M NaCl and the other set contained 0.05 M Na2SO4. Experiments were then carried out to determine the best electrolyte to be used for all the experiments in the study (Figure 6). During the experiments, the electrolyte type that achieved a balance between removal efficiency and practical factors was determined and considered to be the best. As a result, the RB5 removal efficiency is higher (100% within 25 minutes) in NaCl solution than in Na2SO4 solution which had a removal efficiency of 43% within 25 minutes and 80% after 60 minutes (Figure 6 (a)), thus, NaCl is the best electrolyte for the degradation of RB5. Figure 6 (b) illustrates the apparent rate constants of both electrolyte types. The apparent rate constant of 0.1299 min⁻¹ for NaCl suggests a quicker reaction rate than 0.0207 min⁻¹ for Na2SO4 which suggests a slow reaction rate (Figure 6(c)).

According to Baker et al. (2016), chloride ions can react with the hydroxyl radicals to form chlorine radicals which are known to be more reactive than the hydroxyl radicals and can oxidize RB5 more efficiently. In the case of the NaCl solution, the chloride ions have a higher affinity for the hydroxyl radicals, which results in a higher removal efficiency for RB5. On the other hand, sulfate ions in Na2SO4 solution have a lower reactivity with hydroxyl radicals, which leads to a lower removal efficiency for RB5 (Moore & Hahn). The difference in reaction between the two solutions was investigated and discussed by Wang and Wang (2020); how different ions with hydroxyl radicals can influence the removal efficiency.
Effect of Electrolyte Concentration

The electrolyte concentration affects the conductivity of the solution, which in turn affects the rate of the reaction. A higher electrolyte concentration leads to a higher conductivity, resulting in a faster reaction rate. Dissolved salts in the electrolyte serve as essential mediators for mineralization processes during electrochemical oxidation (Saha et al., 2022). Understanding the impact of NaCl concentration on RB5 removal efficiency is crucial for optimizing treatment processes in various industries such as wastewater treatment, textile manufacturing, and dyeing operations. Experiments with varied electrolyte concentrations of sodium chloride (NaCl) (i.e., 0.05 M, 0.1 M, and 0.2 M) were undertaken (Figure 7). During the experiment, the electrolyte concentration that achieved a balance between removal efficiency and practical factors was determined, considered the optimal electrolyte concentration, and utilized in all experiments of the study.

The results show that RB5 removal efficiency increases with increasing NaCl concentration (Figure 7 (a)).

According to Satapanajaru et al. (2011), increasing the NaCl concentration from 0.1 M to 1 M increases the kinetic removal rate of RB5, indicating a positive correlation between NaCl concentration and removal efficiency, meaning when the NaCl concentration is increased from 0.05 M to 0.1 M, there is an observed increase (i.e., 0.1299 min⁻¹ to 0.7157 min⁻¹, respectively) in the rate at which RB5 is removed. It is important to note that while increasing NaCl concentration may improve RB5 removal efficiency, there might be an upper limit beyond which further
increases may not yield significant improvements, which is the case when NaCl concentration was increased from 0.1 M to 0.2 M. The reaction rates decreased from 0.7157 min\(^{-1}\) to 0 min\(^{-1}\) for the mentioned concentrations, indicating that an upper limit has been reached. Hence, the optimal electrolyte concentration for the removal of RB5 is 0.05 M NaCl, for the reason of elongating the span for observational purposes of the reaction and supported by the apparent rate constant of 0.1299 min\(^{-1}\) which suggests a moderately fast reaction in comparison to 0.1 M and 0.2 M which have apparent rate constants of 0.7157 min\(^{-1}\) and 0 min\(^{-1}\), respectively (Figure 7 (c)). It is important to note that while increasing NaCl concentration may improve RB5 removal efficiency, there might be an upper limit beyond which further increases may not yield significant improvements. At the electrolyte concentration of 0.05 M, the RB5 removal efficiency is 100% within 25 minutes and the energy consumption is likely to be relatively low. At higher NaCl concentrations, the RB5 removal efficiency reached 100% within 10 minutes and 2 minutes for 0.1 M and 0.2 M, respectively, but the energy consumption is likely to increase (Iranpour et al., 2018). The rapid removal efficiency due to the high NaCl concentrations did not allow enough time to observe the reaction. However, the presence of NaCl improves various aspects of the RB5 removal process and further enhances its effectiveness under saline conditions.

Figure 7. (a) Removal Efficiency of RB5 vs. Time, (b) Pseudo-First-Order Kinetic Fitting, and (c) Apparent Rate Constant (k\(_{app}\)) for Different NaCl Concentrations (0.05 M, 0.1 M, and 0.2 M).
Furthermore, NaCl enhances the adsorption capacity of the adsorbent material used for RB5 removal. The presence of salt ions in the solution increases the electrostatic interactions between the surface of the adsorbent and the RB5 dye molecules, leading to increased adsorption and subsequent removal of the dye from the solution (Lim et al., 2021). This is because the salt ions with their positive and negative charges can shield the negatively charged RB5 molecules from the adsorbent surface, reducing their electrostatic repulsion and facilitating their approach. Once the RB5 molecules are close to the adsorbent surface, the dye molecules are attracted to the surface by electrostatic attraction forces, mainly between the positively charged sites of the adsorbent and the negatively charged sulfonate groups of the dye. This adsorption process is further enhanced by the increased concentration of salt ions, which further shield the negative charges of the RB5 molecules and make them more susceptible to electrostatic attraction. Moreover, NaCl electrolytes can trigger electrochemical effects that contribute to improved RB5 removal. By creating an electrical double layer, electrolytes attract negatively charged RB5 molecules to the positively charged surface of the adsorbent, thereby enhancing adsorption. Electrolytes also facilitate redox reactions that break down RB5 molecules into less harmful components. These electrochemical processes improve adsorption efficiency and promote dye degradation, resulting in more effective removal of RB5.

**Effect of pH on RB5 Degradation**

The solution pH is a key factor influencing electrochemical reactions as it affects the availability of protons and the interaction between the adsorbate and the electric field (Govindarajan et al., 2022). Changes in pH can alter the concentration of proton donors or acceptors in the electrolyte, thereby influencing reaction pathways and kinetics (Govindarajan et al., 2022). In addition, pH changes can affect the adsorption behavior of species at the electrode surface, which alters the electric field near the interface and consequently affects the electrochemical results (Govindarajan et al., 2022). Therefore, understanding and controlling pH is essential for the optimization of electrochemical processes.

In this study, RB5 degradation was investigated at pH 3, 7, and 10 (Figure 8), allowing for an assessment of how the acidic, neutral, and alkaline conditions affected the degradation efficiency. RB5 removal efficiency notably increased with increasing pH (Figure 8(a)). The optimal pH for the removal of RB5 was 7, with the apparent rate constant being 0.1299 min⁻¹ as shown in Figure 8(c), suggesting a fast reaction. At this pH, the RB5 removal efficiency was high (100% within 25 minutes). The same findings were concluded in a familiar study on the use of TiO₂ to degrade Rose Bengal dye (Ahmed et al., 2018). This implies that under these conditions, the dye is effectively removed from the system, resulting in clean water or wastewater. At a lower pH value (pH 3), the RB5 removal efficiency decreased (71% within 25 minutes) and according to Figure 8(c) has a slow reaction demonstrated by an apparent rate constant of 0.0493 min⁻¹. The reaction is likely to be slow because the RB5 molecules tend to exist predominantly in their protonated form (RH⁺), which reduces their solubility and limits their interaction with adsorbents or other removal mechanisms at lower pH values (Jakubowski & Flatt; Marhalim et al., 2021). This also makes RB5 molecules less reactive with the hydroxyl radicals, which are known to be the primary oxidizing species in electrochemical oxidation (Jing & Chaplin, 2017). As a result, the removal efficiency may be lower at low pH levels. On the other hand, at high pH values (alkaline conditions), RB5 molecules tend to exist predominantly in their deprotonated form (R⁻), which increases their solubility but reduces their affinity towards adsorbents or other removal mechanisms.

At different pH levels, the chemical properties of both the dye and the degradation medium change to influence the efficiency of degradation processes (Reza et al., 2017). The higher pH values deprotonate the RB5 molecules, making
them more reactive with hydroxyl radicals that are generated on the surface of the TiO$_2$ nanoparticles and contributing to the enhanced electrochemical oxidation efficiency (Copete-Pertuz et al., 2018). This phenomenon is significant in understanding the mechanisms involved in electrochemical oxidation processes. At higher pH values, these molecules undergo deprotonation, a process that involves the removal of a proton from the molecule (da Cunha et al., 2014). This deprotonation results in the formation of negatively charged species, which can exhibit increased reactivity with other chemical species present in the environment (da Cunha et al., 2014).

Moreover, the optimal pH for RB5 degradation can be associated with the activity of specific enzymes or catalysts involved in the degradation process. Therefore, identifying and maintaining this optimal pH is crucial for achieving efficient RB5 degradation. The optimal pH for RB5 removal can be explained by considering the nature of the dye and its interaction with the environment.

![Figure 8](image)

**Figure 8.** (a) RB5 Removal Efficiency vs. Time, (b) Pseudo-First-Order Kinetic Fitting, and (c) Apparent Rate Constant ($k_{app}$) for Different pH Values (3, 7, and 10)

**Effect of Initial RB5 Concentration**

The degree and pace of oxidation in electrochemical oxidation processes might vary based on the substrate's initial concentration (Mosur Nagarajan et al., 2023). Experiments were performed with different initial RB5 concentrations (i.e., 30 mg/L, 50 mg/L, 80 mg/L, 100 mg/L, 120 mg/L, and 150 mg/L) to determine the suitable RB5 concentration (Figure 9). During the experiments, the RB5 concentration that established a balance between removal efficiency and practical factors was determined to provide the best environment for the reaction.
Figure 9 presents the results of an optimization study to determine the environment that allows for effective RB5 removal using TiO$_2$ nanoparticle electrodes during electrochemical oxidation. The results show that the RB5 removal efficiency decreased as the initial RB5 concentration increased. This is because the RB5 molecules are adsorbed on the surface of the TiO$_2$ nanoparticles and compete for adsorption sites (Ghows & Entezari, 2011). At higher initial RB5 concentrations, more RB5 molecules compete for the adsorption sites, which decreases the overall removal efficiency. The results also show an increase in RB5 removal efficiency with time. This is because the RB5 molecules are oxidized to CO$_2$ and H$_2$O on the surface of the TiO$_2$ nanoparticles (Khan et al., 2021). The increase in RB5 removal efficiency with time can be attributed to the oxidation of RB5 molecules on the surface of the TiO$_2$ nanoparticles. The oxidation of RB5 is a first-order reaction, and the reaction rate in this study depends on all the parameters optimized. As the reaction progresses, the concentration of RB5 decreases, increasing the efficiency of removal.

The RB5 concentration that enabled the effective removal of the pollutant was 100 mg/L. At this concentration, the RB5 removal efficiency reached 100% within 25 minutes as shown in Figure 9 (a), and energy consumption is likely to be relatively low. In addition, the apparent rate constant of 0.1299 min$^{-1}$ (100 mg/L) as demonstrated by the linear fit (Figure 9 (b)) suggests a fast reaction. At a higher RB5 concentration (e.g., 150 mg/L), RB5 removal efficiency reached 100% within 30 minutes and the reaction rate was likely to be slow because of the apparent rate constant of 0.1163 min$^{-1}$ as illustrated in Figure 9 (c). The energy consumption of 150 mg/L is likely to have increased. This is simply because degradation of higher concentrations of dyes may take longer to achieve the desired level of degradation or removal. Therefore, long processing times can often lead to increased power consumption. At lower RB5 concentrations (e.g., 30 mg/L and 50 mg/L), RB5 removal efficiency is high (100% within the first 5 minutes for both concentrations), but energy consumption is also likely to have been relatively high. This rapid elimination indicated accelerated reaction rates, which may require higher energy input. Additionally, short processing times may require higher energy input to maintain the necessary reaction conditions during the short processing time.

The current findings are consistent with previous work on the same subject of RB5 degradation, where the increase in initial RB5 concentration decreased the removal efficiency. It is documented that as the initial concentration increases, the efficiency of removal decreases (Rápol & Tonk, 2021), emphasizing the importance of understanding this relationship to optimize treatment processes. In the initial stages of treatment, when the concentration of RB5 is low, the adsorption sites on the treatment medium are relatively empty, allowing for efficient removal of the dye. The high removal efficiency at lower RB5 concentrations could be an indication that the treatment process is effective in removing the dye from the solution and the high energy consumption could be a suggestion that there may be more efficient methods or conditions for achieving this level of removal efficiency without excessive energy usage, which could manifest by having to optimize process parameters. As the concentration increases, these sites become saturated, leading to a reduction in the removal efficiency (Heibati et al., 2014). Additionally, as the concentration of RB5 in the solution increases, the diffusion of the dye molecules through the treatment medium becomes more hindered (Giannakoudakis et al., 2016). This is due to the increased number of molecules present, which in turn reduces the available space for the dye to move and be removed. At higher initial RB5 concentrations, more RB5 molecules compete for the adsorption sites, consequently declining the removal efficiency. In many cases, a higher concentration of RB5 is expected to yield a higher reaction rate since there are more RB5 molecules available to react with the TiO$_2$ nanoparticles (Dharma et al., 2022). This is however not the case for this study as the reaction rate is 0.1299 and 0.1163 for 100 mg/L and 150 mg/L, respectively, illustrating
that a higher concentration has a lower reaction rate. This could be attributed to the saturation of the surface or a catalytic site by higher concentrations. Once these sites are saturated, further increases in concentration may not result in a corresponding increase in the reaction rate. This implies that a concentration higher than 50 mg/L may allow for an environment that potentially reduces the energy consumption associated with the treatment process. By identifying a good environment for the reaction, it may be possible to achieve a balance between efficient dye removal and reduced energy consumption, thereby leading to more sustainable and cost-effective treatment methods for RB5-contaminated water or wastewater.

Figure 9. (a) RB5 Removal Efficiency vs. Time, (b) Pseudo-First-Order Kinetic Fitting, and (c) Apparent Rate Constant (k_{app}) for Different Initial Concentrations (30 mg/L, 50 mg/L, 80 mg/L, 100 mg/L, 120 mg/L, and 150 mg/L)

Degradation and Removal Efficiency of RB5 Using Nano TiO₂ Electrocatalysts

The results show that the RB5 concentration decreased exponentially with time, and the RB5 removal efficiency increased exponentially with time (Figure 10). The RB5 removal efficiency was 100% after 25 minutes under optimal conditions, which is a very high removal efficiency, suggesting that TiO₂ nanoparticle electrodes are a very effective catalyst for the electrochemical oxidation of RB5. The RB5 removal rate was highest in the first 5 minutes of the reaction, with a removal efficiency above 41%. Furthermore, the RB5 removal rate slowed down as the reaction progressed. At 15 minutes, the removal efficiency was 90% and the RB5 concentration was 10 mg/L.

The linear fit of the data in Figure 11 shows that the ln(C₀/Cₜ) decreased linearly with time, indicating that the RB5 concentration decreased exponentially with time. The slope of the linear fit is 0.1299, which is the apparent first-order rate constant for the electrochemical oxidation of RB5 on TiO₂ nanoparticle electrodes. This rate constant was relatively high, indicating a quick reaction rate and that the TiO₂...
nanoparticle electrodes are effective catalysts for the oxidation of RB5. Moreover, Pearson’s correlation coefficient (r) for the linear fit was 0.998, which indicates a very strong linear correlation between ln(C₀/Cₜ) and time. The adjusted R-squared value for the linear fit is 0.996, which indicates that the linear fit explains 99% of the variation in ln(C₀/Cₜ). This is a very good fit, indicating that the linear model is a good representation of the experimental data strongly supporting the first-order reaction model.

Figure 10. RB5 Concentration and Removal Efficiency Curve at Different Time Intervals Using TiO₂ Nanoparticle Electrodes During Electrochemical Oxidation at 6V in 100 mg/L RB5 Solution with 0.05 M NaCl at pH 7

Figure 11. Pseudo-First-Order Kinetic Fitting of Initial to Final RB5 Concentration Versus Reaction Time Using TiO₂ Nanoparticle Electrodes During Electrochemical Oxidation at 6V in 100 mg/L RB5 Solution with 0.05 M NaCl at pH 7
Conclusions

The study revealed the importance of optimizing the following parameters for the electro-oxidation degradation of RB5 utilizing nano TiO2: (1) 6 V was the ideal voltage for removing RB5 since it uses comparatively little energy and offers a high apparent rate constant, quick reaction, and 100% removal efficiency in 25 minutes. (2) The effect of electrolyte composition showed that the NaCl solution had a better RB5 removal efficiency than the Na2SO4 solution. Overall, the presence of NaCl in the system positively influences the RB5 removal process by increasing reaction rates, improving adsorption capacity, enhancing mass transfer, and inducing electrochemical effects. Additionally, (3) As a function of electrolyte concentration, the findings demonstrate that RB5 removal efficiency improves with increasing NaCl concentration. Furthermore, (4) It was shown that the ideal pH for removing RB5 is 7. This pH showed a high removal effectiveness of 100% in just 25 minutes. Additionally, this was the faster reaction rate, indicating that in these conditions, RB5 can be successfully eliminated from water or wastewater systems. Finally, (5) The influence of the initial concentration of RB5 indicated that as the initial dye concentration increases, the removal efficiency of RB5 declines, and the reaction rate is likely to be sluggish. Additionally, the suitable RB5 concentration for removal was 100 mg/L with higher removal efficiency over a shorter period, and lower energy consumption. Furthermore, it was discovered that, when employing TiO2 nanoparticle electrodes during electrochemical oxidation at 6V in a 100 mg/L RB5 solution with 0.05 M NaCl at pH 7, the apparent rate constant of initial to final RB5 concentration (ln(C0/Ct)) decreased as a function of time. This suggests that because of the electrochemical oxidation process, the RB5 concentration gradually dropped.

The research on Reactive Black 5 dyeing wastewater treatment by electrochemical oxidation using titanium dioxide nanoparticles holds significant significance. It improves wastewater treatment effectiveness, solves environmental issues by offering a viable way to break down hazardous dyes, and may find use in industrial settings. The data show that the information is essential for industrial and environmental applications where wastewater containing RB5 needs to be treated efficiently. For instance, by identifying the ideal pH conditions for efficient degradation, it becomes possible to optimize treatment processes and minimize environmental impact, or optimizing the electrolyte composition would be essential for achieving high RB5 removal efficiency with relatively low energy consumption. In conclusion, the RB5 dyeing wastewater treatment using electrochemical oxidation with titanium dioxide nanoparticles is an effective and promising method for addressing the environmental concerns associated with textile dyeing wastewater. The use of TiO2 nanoparticles, in conjunction with electrochemical oxidation, enables the efficient degradation of RB5 dye, resulting in a significant reduction of toxicity and color removal from the wastewater.

Further research and development efforts should be focused on optimizing the process parameters, scaling up the treatment process for industrial applications, and investigating the potential of other nanomaterials or combined treatment methods for even more efficient removal of dye and contaminants from textile wastewaters. In addition, further research and investigation into these factors are necessary to develop efficient regeneration methods to enhance the reusability of TiO2 nanoparticle electrodes, for a better understanding of these relationships and to optimize system performance.

References


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