Comparison of 2D and 3D electrochemical oxidation systems for removal of reactive dyes in water

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**Abstract**

In this study, the integration of granular activated carbon (GAC) in a traditional electrochemical oxidation (EO) system enhanced the removal efficiency of reactive dyes in wastewater. A two-dimensional (2D) EO model using a 20V-5A DC power supply and a mixed metal oxide (MMO) electrode was employed for the oxidation of SRH-Red and SBH-Blue reactive dyes in water. This 2D EO system was then upgraded to a three-dimensional (3D) EO system by adding a GAC column, which acts as a particle electrode. The effect of environmental factors (e.g., pH, electrolyte, electrolysis time, and GAC) on the dye removal efficiency was investigated for both 2D and 3D EO systems. Results showed that 3D EO was more efficient than 2D EO for removing reactive dyes in terms of removal efficiency, electric energy consumption, and reaction rate constant. The appropriate EO condition for 3D EO system was found at electrolyte concentration of 3 g/L of NaCl and 16 g/L of GAC, where the removal efficiency reached 93.13% at pH = 3 for SRH-Red (100 mg/L) and 94.04% at pH = 4 for SBH-Blue (200 mg/L) after 20 min of reaction. The Fourier-transform infrared spectroscopy results before and after treatment confirmed the functional groups and cyclic structures of the reactive dyes were decomposed and converted into simpler structures. Therefore, 3D EO is an innovative alternative with excellent efficiency of removing reactive dyes from the water matrix.

**Keywords:** Electrochemical oxidation; 3-dimension; Reactive dyes; Wastewater treatment

1. Introduction

The textile industry is one of the economic sectors occupying a significant position, contributing to economic growth while creating job opportunities for many workers in developing countries. However, it is also the cause of major environmental pollution problems, which is characterized by releasing many undesirable types of pollutants. Most of the dyes are persistent and relatively toxic pollutants, which would change after the dyeing process and become other compounds that are even more difficult to decompose. The textile industry causes challenges to the global environment by causing problems with soil, sediment, and surface water pollution [1]. In general, textile
wastewater is characterized by main pollution parameters such as pH, color, suspended solids, dissolved solids, chemical oxygen demand (COD), BOD, chlorides, sodium, some metals, salts, and temperature with high and varying levels due to the different production methods and processes of the factories [2–6]. Due to the highly polluted nature of textile wastewater, it causes many environmental problems if not going through the wastewater treatment processes and strict discharge regulations. High color prevents light scattering and transmittance in water, making it hard to live in and even kill aquatic plants and animals. Also, textile wastewater could cause death or endanger the survival of many aquatics because they contain some metals and chlorine [7]. Furthermore, the pollutants in textile wastewater can also be transformed into more toxic compounds, deposit in sediments, penetrate to food chains, and cause an imbalance in the ecosystem. It also has a direct impact on human health if not treated thoroughly. With the development of the textile industry, textile wastewater treatment technologies have also been developed, including primary and advanced treatment methods such as traditional physico-chemical methods (e.g., coagulation-flocculation, adsorption, and membrane filtration), advanced oxidation processes (e.g., photocatalysis, Fenton reactions, oxidation using \( \text{O}_3 \) and \( \text{H}_2\text{O}_2 \), UV treatment, electrochemical processes (e.g., photocatalysis, Fenton reactions, oxidation, and adsorption), and membrane filtration), advanced oxidation processes (e.g., photocatalysis, Fenton reactions, oxidation using \( \text{O}_3 \) and \( \text{H}_2\text{O}_2 \), UV treatment, electrochemical treatment), biological methods (e.g., aerobic and anaerobic treatment), and hybrid methods, to increase the treatment efficiency and meet the demand for water reuse and sustainable development in the future [8–10].

Electrochemical treatment is a process of mineralizing pollutants in two ways of direct anodic oxidation and/ or indirect oxidation through reactive oxidation species in the solution and reduction reaction at the cathode [11]. The electrochemical method has been studied as an alternative for many basic treatment systems to deal with persistent organic pollutants, including textile wastewater, due to its high efficiency for many pollutants, low cost, easy to automate, and greenness [12]. However, the applicability of the electrochemical process is limited because of the short electrode life, high energy consumption, and low current efficiency [13]. Three-dimensional electrochemical oxidation (3D EO) is based on the mechanism of basic two-dimensional electrochemical oxidation (2D EO), where the large difference is the introduction of a third electrode such as a particle layer electrode. In 3D EO, under the appropriate voltage conditions, electrically charged microelectrodes are formed in the particle electrode (or bed electrode). This increases the conductivity, enhances the oxidative reactions to form free radicals (e.g., hydroxyl and sulfate radicals and active chlorine), provides adsorption sites for pollutants, and reduces electrical energy consumption [14]. Among the materials used as a particle electrode, granular activated carbon (GAC) is one of the most popular ones due to its stability, high surface area, and low cost [15]. Studies on the application of 3D EO systems for treating textile and dyeing wastewater have been reported frequently in recent years, showing that the possibility of applying this option in the future is feasible and promising [16–20,15,21]. The addition of GAC to upgrade an existing 2D EO system into a 3D system is very simple but provides a higher dye removal as well as strong effective color removal with shorter reaction time. This impressive effect is even more evident when replacing decolorization with GAC-column adsorption by this technology under the same conditions of operating cost. However, there has not been any study focused on detailed comparisons of 2D and 3D EO systems for the treatment of reactive dyes.

This study evaluated and compared the removal efficiency of 2D and 3D EO systems for removing two types of soluble anionic reactive dyes in water. The factors affecting the dye removal such as pH, particle electrode concentration, initial dye concentration, and reaction time were investigated. These suitable reaction conditions were obtained and compared for the two EO systems in terms of dye removal efficiency, reaction time, and energy consumption.

2. Materials and methods

Anion soluble reactive dyes of Suncion Red HE7B (CAS No. 61931-52-0, \( \text{C}_{32}\text{H}_{52}\text{ClN}_{14}\text{Na}_{8}\text{O}_{26}\text{S}_{8} \), MW 1774.19 g/mol; chemical structure can be found in [22], denoted as SRH-Red) and Suncion Blue HEGN (CAS No. 124448-55-1, \( \text{C}_{32}\text{H}_{52}\text{ClN}_{14}\text{Na}_{8}\text{O}_{26}\text{S}_{8} \), MW 1682.60; chemical structure can be found in [23], denoted as SBH-Blue) were purchased from Ohyoung Inc. (Korea). Other chemicals such as NaCl, NaOH, and \( \text{H}_2\text{SO}_4 \) were analytical-grade bought from Merck. Granular activated carbon was supplied by MM Corporation (Ahmedabad, India) with physical properties of 1,213.016 m\(^2\)/g (surface area), 0.285 cm\(^3\)/g (pore volume), and 3.34 nm (pore size) [24]. The dye solutions were prepared by dissolving a certain amount of SRH-Red and SBH-Blue dyes into a volume of supply water. The pH of these dye solutions was adjusted to pH 11 using 1 M NaOH solution. The solutions were then heated at 100°C for 2 h for complete dissolution, then cooled to room temperature, and diluted to 100 mg/L for SRH-Red solution and 200 mg/L for SBH-Blue solution.

Fig. 1 illustrates the experimental setup for the 3D electrochemical oxidation system. The EO tank with a volume of 5 L was placed on a magnetic stirrer. Two MMO

![Image](image-url)
electrodes with an area of 100 cm² are connected to a DC power source (24 V–5 A) with an electrode distance of 14 cm. In the case of the 3D EO system, the granular activated carbon (GAC) column was placed in the EO tank between the two MMO electrodes and served as a third electrode. A preliminary adsorption test was also conducted for the dyes using GAC without electrode and electricity. The adsorption capacity was determined to be less than 0.51 mg/g, which is similar to the same type of dyes that were determined in the previous study [25], after an equilibrium adsorption time of 60 min. These amounts of adsorbed dyes are too low and can be considered as a negligible contribution to the dye degraded by the whole electrochemical process.

The factors influencing the electrochemical oxidation process were investigated in the pH range of 1–10 by using H₂SO₄ or NaOH solutions, NaCl electrolyte concentration of 1–6 g/L, initial dye concentrations of 50–400 mg/L for SRH-Red or 150–800 mg/L for SBH-Blue, GAC mass of 60–120 g, and reaction time of 0–40 min. The light absorptions of SRH-Red and SBH-Blue were measured using a UV-Visible spectrophotometer (U-2900, Hitachi, Japan) at 542 nm for SBH-Blue and 624 nm for SRH-Red, and the adsorptions were then converted to concentrations of the dyes. The dye degradation efficiency is assessed through the dye removal efficiency and the electrical energy consumption. The solutions before and after the electrochemical oxidation process were also dried at 50°C for 24 h to obtain a powder, which was then mixed with KBr, pressed into a pellet to record the IR absorption spectrum in the wavenumber range of 500–4,000 cm⁻¹ using a Fourier-transform infrared spectrophotometer (FTIR-8400S, Shimadzu, Japan).

The dye removal efficiency was determined by the following equation:

\[ H\% = \frac{C_0 - C_t}{C_0} \times 100 \]  

(1)

Electrical energy consumption for electrochemical processes was determined by the following equation from Soni and Ruparelia [26]:

\[ EC \left( \frac{kWh}{kgDye} \right) = \frac{U \times I \times \Delta t}{3.6 \times (C_0 - C_t) \times V} \]  

(2)

where \( C_0 \) and \( C_t \) are the concentration of the dye at initial and after \( \Delta t \) time (mg/L). \( U \) and \( I \) are the voltage (V) and amperage (A) of the power source. \( \Delta t \) is the reaction time (s) and \( V \) is the volume of wastewater (L).

The kinetic model of the electrochemical oxidation is shown by the following equation [27]:

\[ C_i = C_0 \times e^{-kt} \]  

(3)

where \( k \) is the pseudo-first-order reaction rate constant (1/min).

3. Results and discussion

3.1. Preliminary results of 2D EO process

The effect of reaction conditions on the removal efficiencies of SRH-Red and SBH-Blue dyes using the 2D EO process is described in Fig. 2. Regarding pH, the acidic condition is more favorable for the EO process as compared to the neutral and alkaline condition (Fig. 2a), which is consistent with the report from Karivajjanavar et al. [28]. Therefore, solution pH was chosen at 3 for SRH-Red and 4 for SBH-Blue in terms of dye removal efficiency (i.e., 85.4% for SRH-Red and 92.5% for SBH-Blue) and energy and chemical consumption. As seen in Fig. 2b, the dye removal efficiencies significantly increased from 54.2% to 85.4% for SRH-Red and 69.7% to 92.5% for SBH-Blue with the increase of NaCl concentration from 1 to 3 g/L and slightly increased with a further increase of NaCl from 3 to 6 g/L. Therefore, the NaCl concentration of 3 g/L was chosen as a suitable electrolyte concentration for further experiments. During the EO process, the dye removal efficiencies increased rapidly during the first 20 min for SBH-Blue and 20 min for SRH-Red and then slowly approached the complete removal (Fig. 2c). Therefore, 20 and 30 min were chosen as the appropriate time of electrochemical oxidation for removal of SBH-Blue and SRH-Red, respectively. The initial dye concentration had a negative effect on the dye removal efficiency (Fig. 2d), which was higher than 80% with SRH-Red concentration ≤200 mg/L and SBH-Blue concentration ≤300 mg/L. The efficiencies then decreased to 64.73% with SRH-Red concentration of 400 mg/L and 54.65% with SBH-Blue concentration of 800 mg/L.

3.2. Results from 3D EO process

Similar to the 2D EO system, the initial solution pH is an important parameter in the 3D EO system because it affects both direct and indirect oxidation [13]. Fig. 3 describes the effect of solution pH on the removal of SRH-Red and SBH-Blue dyes. It is obvious that the dye removal efficiency decreased with the increase of pH because the electrode surface is more passive in the alkali than in the acid condition [29]. Moreover, pH affects the speciation of active chlorine species in water when using NaCl as electrolytes, which are HClO with a high redox potential of 1.49 V under acidic conditions and OCl⁻ with a low potential of 0.94 V under alkaline condition. Moreover, HClO and OCl⁻ are both oxidized into ClO₃⁻ and ClO₄⁻ [28]. The addition of GAC increased the electrical conductivity as well as a greater concentration of free radicals. Besides, energy consumption increased with the increase of pH, and that in treating SRH-Red was approximately two times higher than that in treating SBH-Blue. Therefore, when treating wastewater using electrochemical technology, the high concentration will be more economical. Similar to 2D EO system, pH 3 for SRH-Red and pH 4 for SBH-Blue were chosen for further studies.

Choosing a suitable NaCl concentration is an important step in the EO process, which should minimize the NaCl and energy consumption while maximizing the removal efficiency. As shown in Fig. 4, dye removal efficiency significantly increased from 39.91 to 89.58% for SRH-Red and from 71.37% to 93.02% with the increase of NaCl concentration from 1 to 3 g/L. However, the efficiency increased only about 8% for SRH-Red and 3% for SBH-Blue when increasing the NaCl concentration from 3 to 6 g/L. Therefore, the NaCl concentration of 3 g/L was chosen.
Fig. 2. Effects of reaction conditions on dye removal of 2D EO system: (a) pH, (b) NaCl concentration, (c) reaction time, and (d) initial dye concentration.

Fig. 3. The effect of pH on the dye removal by 3D EO system.
for further tests to reduce the chemical use and limit the
formation of halogenated organic compounds (AOX).

Besides NaCl, choosing a suitable dosage of GAC for
working as a particle electrode is also an important step
of the 3D EO process. As demonstrated in Fig. 5, the GAC
dosage seems to have little effect on the dye removal effi-
ciency as well as the energy consumption. At a GAC dos-
age of 16 g/L, the removal efficiencies reached the highest
values of 96.40% for SRH-Red and 96.13% for SBH-Blue. Lower dosage at 12 g/L or higher dosages of 20–24 g/L both
decreased the dye removal efficiency. It can be explained
by a large amount of GAC somewhat hindered the direct
and indirect oxidation on the anode while favored the
adsorption on the carbon surface, leading to reduced
to the appropriate GAC dosage
removal efficiency. Therefore, the appropriate GAC dosage
of 16 g/L was chosen for further studies.

Determining the appropriate reaction time is also an
important step in an EO process, which needs to achieve
the targeted removal efficiency with the lowest energy con-
sumption. The dye removal efficiency during the reaction
time of 30 min is exhibited in Fig. 6. The removal efficiency
increased quite rapidly after the first 20 min, increased
more slowly, and tended to be stable after 20 min with a
removal efficiency of 93.13% for SRH-Red and 94.04% for
SBH-Blue. Obviously, the longer the electrochemical time,
the more electrical energy consumption. Therefore, to save

Fig. 4. The effect of NaCl concentration the dye removal by 3D EO system.

Fig. 5. The effect of GAC dosage on the dye removal by 3D EO system.
cost and consider the satisfactory treatment performance, the electrochemical time required was chosen at 20 min, which was shorter than the time for the 2D EO system, particularly in the case of SRH-Red removal (e.g., 30 min).

Theoretically, an increase in the initial concentration of dye in the water will result in a decrease of the removal efficiency but also reduce the energy consumption, which is confirmed in Fig. 7. When the dye concentration reaches a critical value, the oxidation and adsorption are both hindered. In this study, when the concentration of reactive dyes increased quite high, up to 400 mg/L for SRH-Red and 800 mg/L for SBH-Blue, the dye removal decreased significantly. Specifically, the removal efficiency of SRH-Red decreased from 93.67% to 56.6% and the energy consumption decreased from 118.19 to 35.88 kWh/kg Dye when the concentration increased from 50 to 400 mg/L (Fig. 7a). Similarly, the SBH-Blue removal efficiency also decreased from 95% to 57% and the energy consumption decreased from 55.92 to 17.62 kWh/kg dye when the concentration increased from 150 to 800 mg/L (Fig. 7b).

Fig. 8 presents the FTIR spectra of solid dye samples before and after electrochemical oxidation reaction. Diazo groups of SRH-Red and SBH-Blue reactive dyes were characterized by the peak at a wavenumber of 1,542 cm\(^{-1}\). The peak at 1,208 cm\(^{-1}\) is assigned to the vibration of the –C–N functional groups in the aromatic ring structure of SRH-Red and SBH-Blue dyes. The decrease in the intensity of these peaks after electrochemical treatment indicated the decomposition of the dyes during the electrochemical oxidation process. Peaks at 1,047 and 617 cm\(^{-1}\) correspond to the stretching vibration of –S=O bonding in the sulfonate group (SO\(_3^-\)), whose intensity decreased after the electrochemical oxidation process [30,31]. The FTIR spectra confirmed that the products produced after the electrochemical oxidation are new compounds with simpler structures. The reactive dye structure is broken while the diazo groups and some aromatic rings are decomposed.

The degradation and mineralization of SRH-Red dyes was further confirmed by the continuous decreases in color and COD value of the water sample during the experiment (Fig. 9). Therefore, the toxicity of reactive dyes after the electrochemical oxidation process was significantly reduced and the wastewater could be suitable for further treatment by biological methods.

### 3.3. Comparison of 2D and 3D EO for removal of different reactive dyes

The reaction rate constant in the 2D and 3D EO system for SRH-Red and SBH-Blue reactive dyes was calculated and summarized in Table 1. Both 2D and 3D EO systems follow the pseudo-first-order kinetic model with \(R^2\) values of >95% for both reactive dyes. Based on the rate constant values, it is obvious that the reaction rate in the 3D EO system was faster than that in the 2D EO system. Besides, the rate constant increased with the increase of NaCl concentration and the rate constants of SRH-Red were higher than those of SRH-Blue.

Fig. 10 compares the removal efficiency and energy consumption of 2D and 3D systems for both SRH-Red and SBH-Blue reactive dyes. The SRH-Red removal was tested at a concentration of 100 mg/L, pH 3, and NaCl concentration of 3 g/L. The reaction time was 30 min for the 2D EO system and 20 min for the 3D EO system. The removal efficiency of SRH-Red by 3D EO was higher than that by 2D EO (e.g., up to 7.69%) despite its shorter reaction time. Therefore, the energy consumption of SRH-Red by 3D EO was higher than that by 2D EO (e.g., up to 7.69%) despite its shorter reaction time. Therefore, the energy consumption decreased from 140.22 kWh/kg dye in the 2D EO system to only 85.90 kWh/kg Dye in the 3D EO system with an energy consumption saving of 38.74%. Regarding SBH-Blue, the test was conducted at a concentration of 200 mg/L, pH 4, and 3 g/L of NaCl with a reaction time of 20 min for both 2D and 3D EO systems. As seen in Fig. 10, there was a slight increase in the SBH-Blue removal efficiency (from...
92.49 to 94.04%) and a slight reduction in energy consumption (from 43.82 to 42.59 kWh/kg dye) when applying the 3D EO system as compared to the 2D EO system. These results indicated that the improvement by 2D EO depends on the nature, structure, and composition of the dye. For dyes that have high removal efficiency by 2D EO process such as SBH-Blue in this study, the application of a 3D system is not needed. However, for dyes that are hard to be decomposed by a 2D EO process such as SRH-Red in this study, the use of a 3D EO system could significantly enhance the removal efficiency and reduce the reaction time, thus saving a lot of energy.

4. Conclusions

The application of electrochemical oxidation for the removal of reactive dyes in water was conducted to compare the effectiveness of 2D and 3D systems. 3D system

![Fig. 7. The effect of initial concentration of (a) SRH-Red and (b) SBH-Blue on the dye removal by 3D EO system.](image)

<table>
<thead>
<tr>
<th>Type of reactive dyes</th>
<th>NaCl concentration (g/L)</th>
<th>Rate constant $k'$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2D EO system</td>
</tr>
<tr>
<td>SRH-Red</td>
<td>3</td>
<td>0.0456</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.0744</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.0821</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.0320</td>
</tr>
<tr>
<td>SBH-Blue</td>
<td>4</td>
<td>0.0526</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.0732</td>
</tr>
</tbody>
</table>
Fig. 8. FTIR spectra of (a) SRH-Red and (b) SBH-Blue before and after electrochemical oxidation.

Fig. 9. Color and COD of the SRH-Red water sample during the reaction.
was found to be more efficient than the 2D system for removal of SRH-Red and SBH-Blue reactive dyes by electrochemical oxidation in terms of removal efficiency, reaction time, and energy consumption. For SRH-Red, the suitable condition was found at pH 3, NaCl concentration of 3 g/L, and initial dye concentration of ≤200 mg/L with a reaction time of 30 min for 2D and 20 min for 3D EO system. For SBH-Blue, the appropriate conditions were found at pH 4, NaCl concentration of 3 g/L, and initial dye concentration of ≤300 mg/L with a reaction time of 20 min for both 2D and 3D EO systems. Moreover, FTIR results confirmed the decomposition of reactive dyes into simpler compounds, which is safe for the environment and suitable for further treatment by the traditional biological method. Future works should be addressed on the degradation pathways, reaction mechanism, the adsorption and accumulation of the by-products, and optimization of the process for real wastewater treatment.

References


