Effect of mass transport limitation and pyrite particulate on the continuous electro-Fenton process treatment of textile industrial dye

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1. Introduction

In the current era, overexploitation of natural resources caused by urbanization, industrialization, and rapid population growth has endangered the naturally balanced ecological system [1]. It has exacerbated many environmental problems, among which environmental pollution and depletion of potable water are very serious. Industrialization has caused an enormous increase in global water demand. The incapability of water substitution for huge industrial applications has resulted in a water crisis. The UN-World Water Development reported that around 3.5 to 4.5 billion
people might face severe water problems in the coming three decades if the water crisis is sustained. Worldwide water stress in terms of quality has also emerged as a result of a failure to adopt strict rules for industrial water treatment and a lack of effective technologies. The textile industry uses huge quantities of water and chemicals for the wet processing of materials and releases an enormous quantity of polluted effluent into the environment [2]. This adversely affects human health and aquatic life [3]. The aromatic amine group of dyes effluent inflicts significant damage because of its poisonous nature and biological degradation resistivity [4]. A genotoxic study confirmed the carcinogenic nature of azo dyes, which is also responsible for allergic contact dermatitis and respiratory illness [5,6]. The textile industry has often employed these dyes for coloring purposes because of their lower price and excellent chromophore characteristics. In the last few decades, an extensive number of industrial effluent treatment technologies, including physical [7], chemical [8], biological [9], and advanced oxidation processes [10], have been widely tested and documented in the literature. Despite several research publications on textile dye decolorization, the vast majority of laboratory-developed decolorization failed when they were scaled up or tested with real industrial wastewater. The possible reasons could be (i) the complexity of the industrial mixture that comprised of different classes of dyes, including mono-azo, di-azo, poly-azo, reactive, acid, basic, etc.; (ii) alkalinity of the industrial effluent; (iii) high quantity of salt; and (iv) high treatment capacity requirement, i.e., the huge volume of wastewater treatment in a shorter period of time. Due to these reasons, developing an efficient, cost-effective, and practically applicable technology continues to be challenging. Adopting a streamlined strategy for treating dye effluent with chemical engineering technology tools and methods throughout the process development is needed. Electrochemical methods have attracted the interest of environmental researchers to treat the different micro and macro pollutants from various industrial sectors, particularly from the textile industry [11]. The EF process is more commonly used than other electrochemical processes because of its high mineralization efficiency, absence of harmful chemical additions, and environmental compatibility. In this process, hydrogen peroxide (H₂O₂) is produced in situ by reducing oxygen (O₂) on the cathode (Eq. 1), and the Fenton reaction occurs in the bulk solution under ferrous ions (Fe²⁺) presentation (Eq. 2) [12–14]:

\[ 2O_2 + 4H^+ + 4e^- \rightarrow 2H_2O_2 \]  \hspace{1cm} (1)

\[ 2Fe^{2+} + 2H_2O_2 \rightarrow 2Fe^{3+} + 2 \cdot OH + 2OH^- \] \hspace{1cm} (2)

This technology proved to be more efficient and powerful because of the controlled and in situ H₂O₂ production, continuous hydroxyl radicals (•OH) generation, and electro-regeneration of the Fe²⁺ through the cathodic reduction of Fe³⁺ (Eq. 3), which also reduced the production of iron sludge.

\[ 2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+} \] \hspace{1cm} (3)

The two main categories of electrochemical oxidation are (i) direct and (ii) indirect. In the direct method of electrolysis, direct electron exchange with pollutants occurs at the anodic surface, destabilizing or degrading the pollutants, whereas, in the indirect electrolysis method, electron exchange with pollutants is mediated by active species. In both types of electrolysis, the redox catalysis chain connects anodic surfaces to contaminants via a series of reversibly or irreversibly generated electroactive compounds [15]. Physically absorbed hydroxyl radicals (•OH) generated through non-active anodes also enhance the process efficiency by indirectly oxidizing the majority of organic molecules [16].

Due to this reason, several research papers suggest the application of the indirect oxidation approach for dye removal [11]. However, costly boron-doped diamond (BDD) electrode material has to be used for long-term practical applicability purposes in indirect oxidation [17]. It is also interesting that in the case of only using an active anode, i.e., without •OH radical availability for indirect oxidation, the occurrence of electrochemical degradation is still there because of a dissociation chemisorption reaction coupled with electron transfer [18]. The effectiveness of direct anodic oxidation is improved by the inclusion of many functional groups (e.g., azo linkages) on the dye molecules, making them electroactive for direct electron transfer [19]. Furthermore, the application of an active anode, e.g., stainless steel (or Fe electrode), proved to be...
a viable solution for textile dye treatment due to its cost-effectivity, eco-friendly nature, and production of less sludge [20]. Employing a low-cost iron-based sacrificial anode also favored the electrocoagulation process that proved to be supportive for dye treatment (Eqs. 4 and 5) [21]. Therefore, a synergy, by using an active anode that might serve as a sacrificial anode along with a source of direct electro-oxidation, could be fascinating for electrochemical process improvement [21]. Additionally, using sodium chloride (NaCl) as a supporting electrolyte favored the mediated oxidation phenomenon (Cl₂, HOCl) and electrocoagulation because of active chlorine generation and the availability of the iron-based anode (Eqs. 6 to 8) [22].

\[
\begin{align*}
4Cl^- & \rightarrow 2Cl_2 + 4e^- \quad (4) \\
2Cl_2 + 2H_2O & \rightarrow 2HClO + 2Cl^- + 2H^+ \quad (5) \\
2Fe^{2+} + 2HClO & \rightarrow 2Fe^{3+} + 2OH^- + Cl_2 \quad (6) \\
Fe(s) & \rightarrow Fe^{2+}(aq) + 2e^- \quad (7) \\
4Fe^{2+}(aq) + 10H_2O + O_2 & \rightarrow 4Fe(OH)_3(s) + 8H^+ \quad (8)
\end{align*}
\]

As dye effluents contain many chloride materials, this combined treatment (electrochemical cum electrocoagulation) will certainly favor the process [22]. The residual iron sludge formed at the stainless-steel anode during the electrocoagulation can be given as Eqs. 9 and 10 [21]:

\[
\begin{align*}
Fe(s) & \rightarrow Fe^{2+}(aq) + 2e^- \quad (9) \\
2Fe^{2+}(aq) + 5H_2O + \frac{1}{2}O_2 & \rightarrow 2Fe(OH)_3(s) + 4H^+ \quad (10)
\end{align*}
\]

Additionally, pyrite (FeS₂) crystal, a common iron ore, has successfully been tested as a substitute for the Fenton iron catalyst (Fe²⁺/Fe⁷⁺) [23]. The pyrite-added electro-Fenton process performed better than the classical electro-Fenton process as its presence regulated the iron ions in solution [24,25,26] (Eqs. 11 to 13). It also provided an acidic medium to the solution that was favourable for the process efficiency.

\[
\begin{align*}
FeS_2 + 3.5O_2 + 4H^+ & \rightarrow 2SO_4^{2-} + 2H_2O + 7Fe^{3+} \quad (11) \\
0.5FeS_2 + 7Fe^{3+} + 4H_2O & \rightarrow 7.5Fe^{2+} + SO_4^{2-} + 8H^+ \quad (12)
\end{align*}
\]

The current work focused on the charge and mass transport effect on the electro-Fenton process. The continuous electro-Fenton process was studied with a combined effect of electrocoagulation by using stainless steel and sodium chloride (NaCl) as the working electrodes and supporting electrolyte, respectively. Reactive orange 16, the most common reactive dye used in the textile industry, was taken as a model pollutant. The lab-scale developed process was evaluated for degradation rate, elimination capacity, current efficiency, and specific energy requirement. A universal dimensionless current density parameter was also formulated for the employed study cell to evaluate better the competitiveness of charge transfer and mass transport. The effect on the mineralization efficiency of current with the pyrite particulate addition was also studied for the contentious EF process.

2. Material and methods

2.1. Experimental and methods

For the experimental study, an undivided open cylindrical cell of borosilicate glass (500 mL volume) was used (Figure1).

![Experimental lab setup of continuous electro-Fenton process.](image)

The stainless steel (Kristeel brand) was used as the electrode plates for both the anode and cathode, with a total reactive submerged area of 20 cm² (5 cm x 4 cm). An inter-electrode spacing of 2 cm was kept between the electrodes for all the experiments. A DC power source (Alpha 10A-50 V DC power supply) with an average applied current density of 35 mA/cm² was used as the external energy source. A magnetic stirrer (Remi) at 350 rpm and an air pump (Sobo, Model: SB333A, China) were used for stirring the aqueous solution and surging the atmospheric oxygen (1.5 L/min of flow rate) from the bottom of the reactor basin, respectively. The simulated dye solution was made
by dissolving and diluting the RO16 dye in distilled water to the desired concentration. Sodium chloride (NaCl) was used as a supportive electrolyte because of the chloride presentation in higher concentrations in most of the dye effluents [22]. For generated iron sludge separation, 10 min centrifugation action was done at a rate of 6000 rpm. All the tests were conducted at room temperature.

2.2. Chemicals used

The model dye RO16 was purchased from Sigma-Aldrich, India, and its characteristics are listed in Table 1. Other chemicals, such as NaCl, HCl, and NaOH, were purchased from Hi-Media Laboratories, India. 1N NaOH and 1N HCl were used for the solution pH adjustment. All the chemicals were of analytical grade (AR) and utilized in the same condition as supplied without additional purification.

2.3. Characterization of pyrite crystals

The pyrite crystal (FeS₂) was arranged from Reiki Crystal Products (New Delhi, India) with a purity of 99.2%. First, it was milled and sieved for the particulate particles >80 nm. Then, to eliminate the surface impurities, the following process was adopted in a sequential manner:
5 min ultrasonication in 95% ethanol → 1.5 M Nitric Acid (HNO₃) wash → rinsing with deionized water → rinsing with 95% ethanol → final drying in a temperature controlled oven at 30°C. The scanning electron microscope (SEM) image of pyrite revealed its non-uniform nanoparticle shapes that ranged from 0.3 to 0.9 μm approximately (Figure 2a). In contrast, its X-ray diffraction (XRD) picture and the diffraction data files from the Joint Committee on Powder Diffraction Standards (JCPDS) (JADE 9, Materials Data Inc.) were in good agreement with each other (Figure 2b). In the aqueous solutions, the quantity of released Fe²⁺ ion from the pyrite dissolution was determined by spectrophotometry (UV-3000 LAB INDIA, Germany) using 1,10-phenantroline at a wavelength of 508 nm [27].

Table 1. Chemical structure and general characteristics of Reactive orange 16 dye.

<table>
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<tr>
<th>Parameters</th>
<th>Reactive orange dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₂₀H₁₇N₃Na₂O₁₁S₃</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>697 g/mol</td>
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<tr>
<td>Maximum wavelength (λmax)</td>
<td>493 nm</td>
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<td>Class of chromophore group</td>
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<td>Color index number</td>
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<td>Water solubility 19.85 °C (g/L)</td>
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<tr>
<td>Acute oral toxicity (mg/kg)</td>
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<tr>
<td>Fish toxicity (mg/l)</td>
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<tr>
<td>pH (10 g/L H₂O)</td>
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</tr>
<tr>
<td>COD (mg/g)</td>
<td>860</td>
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</table>
2.4. Analytical procedure

A Cyber Scan pH 1500 pH-meter from Eu-Tech Instruments (Singapore) was used to determine the pH of the solution. The change in absorbance was used to track the RO16 dye decolorization by using a UV-vis spectrophotometer (UV-3000 LAB INDIA, Germany) at $\lambda_{\text{max}}$. The percentage change of decolorization was computed by the following Eq. (14):

\[
\text{Decolourization Rate (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \tag{14}
\]

where $C_0$ and $C_t$ represent the initial and time $t$ absorbance values, respectively. It should be emphasized that the concentration of $\cdot$OH cannot be measured directly using chemical probes such as coumarin, but rather the amount of $\cdot$OH produced or the cumulative concentration of products of the reaction with $\cdot$OH can be estimated [14]. The fluorescence method was employed to quantify $\cdot$OH, using the N, N-dimethyl-p-nitroso-aniline (RNO) that acts as a spin trapper of $\cdot$OH (Eq. 15). With the F97Pro fluorescence spectrophotometer (Shanghai, China), the bleaching of the yellow color (RNO) was determined at 440 nm [28].

\[
RNO + \cdot\text{OH} \rightarrow R - \text{NO} - \cdot\text{OH}(\text{Yellow color}) \tag{15}
\]

The quantity of $\cdot$OH measured can be inferred indirectly by calculating the concentration of RNO. It should be noted that chemical probes cannot be used to test the concentration of $\cdot$OH directly; instead, the volume of $\cdot$OH produced or the total volume of products of the reaction with $\cdot$OH can be estimated [29]. The mineralization efficiency (ME) of current I (A) in the electrolysis time period $t_e$ (hr) was calculated by the following Eq. (16) [30,31]:

\[
\text{ME (\%)} = \frac{100}{4.32 \times 10^7} \times \frac{n_e F V \Delta\text{TOC}}{m_c I t_e} \tag{16}
\]

where $F$ is the universal Faraday constant (96,487 C mol$^{-1}$); $V$ is the volume of the solution (L); $\Delta\text{TOC}$ is TOC decay of RO16 dye (mg/L); $4.32 \times 10^7$ is the factor of homogenized unit conversion; and $m_c$ and $n_e$ are the number of carbon atoms (20) and electrons (84) consumed per RO16 of the dye molecule, respectively (Eq. 17):

\[
\text{C}_{20}\text{H}_{17}\text{O}_{11}\text{N}_{3}\text{S}_{3} + 41\text{H}_{2}\text{O} \rightarrow 20\text{CO}_{2} + 3\text{NH}_{3} + 3\text{H}_{2}\text{SO}_{4} + 84\text{H}^{+} + 84\text{e}^{-} \tag{17}
\]

where $D$ is a minimum distance from the epicenter of the flame to the object being considered and $\tau$ is the fraction of radiation heat transmitted through the atmosphere.

2.5. Degradation of RO16 dye in the continuous electro-Fenton process

The degradation of the RO16 dye was monitored for the continuous electro-Fenton process. The flow rate (varying from 0.05 to 0.4 L/h) of the synthetic dye solution was maintained with the help of a peristaltic pump. For constant reactor cell volume (500 mL) maintenance, the inflow and outflow rates were kept the same. The experiments were conducted at varying concentrations of dye (75, 100, 150, 200, and 250) with a constant electrolyte concentration of 0.4 M NaCl and pH 3.5. The continuous process was evaluated for elimination capacity ($E_c$) at various intake loading rates ($Q$) by using Eqs. (18) and (19).

\[
E_c (\text{mg/Lh}) = \frac{(q_{\text{in}} - q_{\text{out}}) Q V}{V} \tag{18}
\]

\[
Q (\text{mg/Lh}) = \frac{q_{\text{in}} Q V}{V} \tag{19}
\]
where $q_{\text{in}}$ and $q_{\text{out}}$ are the inlet and outlet concentrations of dye; $Q_v$ is the volumetric flow rate (L/h), and $V$ is the constant volume of the reactor cell (L).

3. Results and discussion

3.1. Change in absorption spectra for RO16 dye characterization

In the preliminary study, the spectrophotometric approach was used to characterize and analyze the adequacy of the dye decolorization kinetics. A synthetic solution of 150 mg/L for RO16 dye was taken and treated electrochemically using the batch scale EF process. The change in the absorption spectra of RO16 dye is given in Figure 3 before (0th min) and after the 30th, 45th, and 60th min treatments. In the UV-Visible spectrophotometry analysis, the initial untreated RO16 dye displayed two strong peaks in the visible range at 493 nm and 398 nm and two peaks in the ultraviolet (UV) range at 256 nm and 299 nm. The peaks in visible ranges confirmed the aromatic structure of the dye, whereas the UV range peaks confirmed the conjugated structure of the azo bond (extended chromophores) [32]. The synthetic solution of dye that was subjected to the electrochemical treatment lost its color, as demonstrated by the disappearance of prominent peaks after 60 min of treatment without the emergence of any interference peaks that might be caused by the matrix and intermediates created during the electrolysis process. This showed the reliability of the method for the continuous mode processes study because the absorbance measured at $\lambda_{\text{max}}$ gives the maximum absorbance of the dye that was only linked with RO16 dye concentration, and this wavelength was not absorbed by any other species. Moreover, the loss of visible and UV range peaks confirmed the oxidation decomposition of the aromatic rings and its fragment breakdown in the dye molecule and intermediately generated products [33].

3.2. Continuous electro-Fenton process: Charge and mass transfer study

The performance of the continuous electro-Fenton process for RO16 dye treatment was studied at various concentrations (75-250 mg/L) and flow rates (0.05-0.4 L/h) (Table 2). The results for the decolorization efficiency and capacity of elimination are shown in Figure 4. The inlet loading rate ($Q$) was used to compute the reactor efficiency. For the dye concentrations 75 to 150 mg/L, the degradation rate showed a positive trend with the increment in $Q$. The degradation rate obtained for 150 mg/L of the synthetic dye solution with $Q$ as 120 mg/(L h) was 76 mg/(L h) (~63 percent of removal efficiency for inlet $Q$) for a 30 min residence time. This was the maximum capacity of elimination for the RO16 dye.

![Absorption spectrum of the RO16 for the electro-Fenton process treatment](image-url)

*Fig. 3. Absorption spectrum of the RO16 for the electro-Fenton process treatment ([RO16]$_{\text{initial}}$=150 mg/L, pH=3.5, [NaCl]=0.4 M, V=13 Volt).*
Table 2. Input data and corresponding results for the continuous electro-Fenton treatment of RO16 dye.

<table>
<thead>
<tr>
<th>RO16 conc. (mg/L)</th>
<th>Flow rate (Q) (L/h)</th>
<th>Rate of inlet loading (mg/L h)</th>
<th>Removal efficiency (%)</th>
<th>Elimination capacity (mg/L h) (%)</th>
<th>Current Efficiency (kWh g-dye(^{-1}))</th>
<th>Specific Energy (kWh g-dye(^{-1}))</th>
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Fig. 4. Study of inlet concentration and flow rate effect on RO16 dye the removal efficiency.

Furthermore, with an increment of the inlet concentration, the treatment efficiency of the electrochemical process was also enhanced. Therefore, it could be concluded that the decay kinetics of the RO16 dye was affected by the inflow concentrations of the dye solution. Another intriguing observation is that regardless of inflow concentrations, the removal efficiency increased with flow rate, i.e., with a decrease in retention time. For further insight into the flow rate effect
on process efficiency, a comparison of the applied current density \( J_A \), i.e., 35 mA/cm\(^2\) to the initial limiting current density values \( J_L^0 \), i.e., the dimensionless current density \( \rho \), was calculated as per Eq. (20):
\[
\rho = \frac{J_A}{J_L^0} \quad (20)
\]
Furthermore, \( J_L^0 \) can also be written in terms of the Faraday constant (\( F \)), mass transfer coefficient (\( k_M \)), and influent COD (COD\textsubscript{inlet}) using Eq. (21) \[34\]:
\[
J_L^0 = 4Fk_M\text{COD}_{\text{inlet}} \quad (21)
\]
From Eqs. (20) and (21), a new Eq. (22) for \( \rho \) can be re-written as:
\[
\rho = \frac{J_A}{4Fk_M\text{COD}_{\text{inlet}}} \quad (22)
\]
From Eq. (22), it is clear that the value of \( k_M \) must be known in order to calculate \( \rho \). For this purpose, the dimensionless Sherwood (\( S_w \)) number, expressed in terms of \( k_M \), the equivalent dia. (\( d_{eq} \)), and the diffusivity (\( D_f \)), was used and is given by Eq. (23) \[35\]:
\[
S_w = \frac{k_Md_{eq}}{D_f} \quad (23)
\]
The Sherwood number \( S_w \) number further can be expressed as the function of dimensionless Reynolds (\( R_y \)) and Schmidt \( (S_m) \) numbers (Eq. 24) \[36\], whereas \( S_m \) is given by Eq. (25) \[24\] and \( R_y \) for a stirred cell can be calculated from Eq. (26) \[37\]:
\[
S_m = \frac{R_y}{\nu} \quad (24)
\]
\[
R_y = \frac{d^2N}{\nu} \quad (25)
\]
\[
S_w = \frac{d_{eq}^3}{R_y S_m} \quad (26)
\]
where \( \nu \), \( d \), and \( N \) are the kinematic viscosity of the fluid, stirrer dia., and rotation speed, respectively. From Eqs. (23) to (26), the new form of the equation for \( k_M \) expression can be written as Eq. (27):
\[
k_M = \frac{\rho}{d_{eq}^3}D_f^{-1+\gamma}\nu^{-x}(d^2N)^z \quad (27)
\]
Finally, from Eq. (22) and Eq. (27), the general dimensionless expression for current density \( \rho \) in a stirred cell can be proposed by following Eq. (28):
\[
\rho = \frac{J_A}{4Fk_M\text{COD}_{\text{inlet}}} \frac{d_{eq}^3}{A}D_f^{-1+\gamma}\nu^{-x}(d^2N)^z \quad (28)
\]
In this work, the constants \( d_{eq} \), \( d \), \( D_f \), \( N \), \( A \), \( B \), and \( C \) were taken as 10.5 cm, 2 cm, \( 10^{-9} \) m\(^2\)/s \[38\], 100 rpm, \( 8.917\times10^{-7} \) m\(^2\)/s at 25\(^\circ\)C (Engineering Toolbox, 2004), 0.228 \[39\], 0.66 \[39\], respectively. From the selected constants, the \( k_M \) value of 1.7 \times 10^{-6} \) m/s was calculated for the study, which falls within the range of values reported in other studies for the stirred cell operation (\( \approx 5.9 \times 10^{-6} \) m/s) \[40,41,42\]. By the values of COD\textsubscript{inlet} (Table 3), \( \rho \) as the function of the dye and its initial concentrations was calculated and is shown in Figure 5. In every case, its values ranged between 28 and 83 and were always greater than 1, i.e., \( J_A \) was always greater than \( J_L^0 \). Consequently, it can be inferred that for the treatment process, decay kinetics was primarily controlled by mass transport \[34,43\]. Therefore, increasing \( Q \), i.e., mass flow rate, increased \( k_M \), which ultimately improved the kinetics of the decay process (Figure 6). To further access the process efficiency, the CE for the continuous electrochemical process was estimated as per Eq. (29) \[44\]:
\[
CE(\%) = 100 \times \frac{n_eFXQ_v}{A_{sub}IA} \quad (29)
\]
where \( A_{sub} \) is the submerged surface area of the electrode (20 cm\(^2\)), \( X \) is the current conversion yield \( (q_{in} - q_{out})/q_{in} \), and \( n_e \) represents the electrons required (84) for the RO16 breakthrough in carbon dioxide via electrochemical combustion (Eq. 17). For the continuous mode operation, the specific energy \( (E_{sp}) \) requirement was also estimated by using Eq. (30) \[45\]:
\[
E_{sp} = \frac{E_{cell}}{C_{in}XQ_v} \quad (30)
\]
where \( E_{cell} \) represents the cell voltage (V). For both current the efficiency and specific energy, Fig. 6 was drawn as a function of \( Q \) and [RO16]\textsubscript{initial}. At optimum condition, the energy requirement for full decolorization was about 6.5 kWh m\(^{-3}\) compared to the aluminium anode electrode, which was around 11 kWh m\(^{-3}\), as previously reported \[21\]. Thus, for electrochemical treatment of RO16 dye stainless steel anode proved to be more preferable than the aluminium anode.

<table>
<thead>
<tr>
<th>No.</th>
<th>RO16 dye concentration (mg/L)</th>
<th>COD\textsubscript{inlet} (milli-mol-O(_2)/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>75</td>
<td>2.74</td>
</tr>
<tr>
<td>2.</td>
<td>100</td>
<td>3.65</td>
</tr>
<tr>
<td>3.</td>
<td>150</td>
<td>5.48</td>
</tr>
<tr>
<td>4.</td>
<td>200</td>
<td>7.31</td>
</tr>
<tr>
<td>5.</td>
<td>250</td>
<td>9.14</td>
</tr>
</tbody>
</table>
energy requirement and (b) to remove RO16 dye. Furthermore, the increasing and decreasing values of CE and \( E_{sp} \) with inlet concentration and flow rate confirmed the kinetics dependency and mass transport control of the continuous process. Also, the quantity of higher iron sludge generation (about 4.8 g/h) supports the role of the electrocoagulation mechanism which is even lower than the aluminium sacrificial anode (about 2.8 times less) at optimum conditions [21].

![Fig. 5. Effect of inlet RO16 dye concentration (mg/L) on the dimensionless current density (\( \rho \)).](image)

![Fig. 6. Effect of flow rate and inlet concentration on the current efficiency: (a) the specific energy requirement and (b) to remove RO16 dye.](image)
3.3. Role of supporting electrolyte NaCl

The chloride ion of the used supporting electrolyte NaCl produced in-site hypochlorite that contributed to the oxidation process of the dye pollutants. For the confirmation of OCl\(^{-}\) role in the degradation kinetics of dye pollutants, the process was electrolyzed for 25 min with 0.25 M NaCl in the absence of the dye pollutant. The spectrum drawn through the UV-Vis Spectrophotometer showed peak absorption at 290 nm for OCl\(^{-}\) (Figure 7), which confirmed the presence of OCl\(^{-}\) in the electrochemical oxidation process. The following reactions are expected to occur in the process (Eqs. 31 to 34) [46]:

- **Anode: Main reaction:**
  \[ \text{Cl}^{-} \rightarrow \frac{1}{2}\text{Cl}_{2} + e^{-} \]  

- **Bulk solution:**
  \[ 2\text{Cl}_{2} + 2H_{2}O \rightarrow 2\text{HOCl} + 2H^{+} + 2\text{Cl}^{-} \]  

- **2HOCl \rightarrow 2H^{+} + 2\text{Cl}^{-} \]  

- **3.4. Role of pyrite particulate electrodes**

The effect of the pyrite particulate electrode on the process was also carried out. For the unchanged experimental conditions (150 mL of RO16 dye solutions; 0.15 mM Fe\(^{2+}\) catalyst), both the traditional electro-Fenton process and the EF with pyrite particulate were tested. The results showed a higher mineralization rate for the pyrite particulate added electro-Fenton process. Total TOC abatement that was about 75% in the traditional electro-Fenton process increased up to 80% with the pyrite added EF process at the end of the treatment (Figure 8a). This higher mineralization is attributed to the higher amount of Fe\(^{2+}\) ions generated from the pyrite particulate (3.5 mM for 2.5 g/L pyrites) with a self-regulating advantage at its surface (Eq. 35 to 37). The additionally generated Fe\(^{2+}\) ions favored the •OH production and process efficiency by the Fenton reaction, as explained in Eq. 38 [47,48,49].

- **FeS\(_2\) + 3.5O\(_2\) + H\(_2\)O \rightarrow Fe^{2+} + 2SO\(_4^{2-}\) + 2H\(^{+}\) \]  

- **FeS\(_2\) + 7.5H\(_2\)O \rightarrow Fe^{3+} + 7H\(_2\)O + 2SO\(_4^{2-}\) + H\(^{+}\) \]  

- **\(\frac{3}{2}\)FeS\(_2\) + 7Fe\(^{3+}\) + 4H\(_2\)O \rightarrow 7.5Fe^{2+} + SO\(_4^{2-}\) + 8H\(^{+}\) \]  

The ME curve shown in Fig. 8b reveals that the pyrite particulate added electro-Fenton process resulted in greater process efficiency than the conventional electro-Fenton process (13.1 percent vs. 9.9 percent). These findings support pyrite as a potential particulate catalyst in the electrolysis treatment of persistent organic pollutants, such as azo dye, even when less active anodes such as stainless steel for the formation of M(•OH) were used (M stands for metal electrode). During electrolysis, the drop in the ME confirmed the generation of more resistant intermediates and fewer organic products that accelerated the parasitic reactions (Eqs. 39 to 41).

\[ M(\cdot OH) \rightarrow M + \frac{1}{2}O_{2} + H^{+} + e^{-} \]
\[
\begin{align*}
\cdot & \quad \text{OH} \rightarrow \frac{1}{2} \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + \cdot \text{OH} & \rightarrow \text{HO}_2^- + \text{H}_2\text{O}
\end{align*}
\] (40) (41)

The result provides an economic benefit over the costlier price of the BDD electrode [50], as in the case of indirect oxidation of the electrochemical process for long-term applicability suitability. Additionally, at the end of every electrolysis process, the used pyrite can be re-collected, filtered, and reused, which is a considerable improvement in the sustainability of the process.

4. Conclusions

In the current work, the continuous electro-Fenton process with stainless steel cost-effective electrodes and sodium chloride (NaCl) supporting electrolytes were used for the synthetic RO16 azo dye treatment. The result of the study shows that the decay kinetics of the RO16 dye was affected by the inflow concentrations of the dye solution and primely controlled by mass transport. Increasing the mass flow rate increased the mass transfer coefficient (\(k_m\)) and so improved the kinetics of the decay. Also, regardless of inflow concentrations, the removal efficiency increased with the flow rate, i.e., a decrease in retention time. It was found that for the electrochemical treatment of RO16 dye, the stainless-steel anode electrode was preferred over the aluminium anode due to lower energy requirements (6.5 kWh m\(^{-3}\) vs. 11 kWh m\(^{-3}\)) and less iron sludge production (almost 2.8 times lower) [18]. The UV-Vis spectrophotometer results of the NaCl electrolyte confirmed the presence of OCl\(^-\) ions in the electrochemical oxidation process. Additionally, the applicability of pyrite particulate showed good improvement (~5%) in efficiency while maintaining its sustainability for reuse. Thus, the result showed an efficient and economical benefit over the costlier BDD electrode used in the case of indirect oxidation of the electrochemical process for long-term applicability.

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References

followed by membrane separation. Advances in environmental technology, 7(3), 171-183.


