Ferrioxalate-induced solar photo-Fenton treatment of natural rubber latex wastewaters

Lekshmi Ashok, S. Adishkumar, J. Rajesh Banu and Ick Tae Yeom

ABSTRACT

This study evaluated a ferrioxalate-induced solar photo-Fenton process for natural rubber latex wastewater treatment. The reaction was carried out in a laboratory-scale solar photo-Fenton plug flow baffle reactor. An optimization study was performed using a central composite experimental design including the following variables: pH, initial concentrations of H₂O₂, Fe²⁺, and oxalic acid. The photocatalytic degradation efficiency was determined by the analysis of chemical oxygen demand (COD) removal. Under the optimum conditions of pH = 4, Fe²⁺ = 1.3 g/L, oxalic acid = 2.25 g/L, H₂O₂ = 82.5 g/L, and solar irradiation time of 6 hours, the COD removal efficiency was 99%. Treatment of latex wastewater by ferrioxalate-induced solar photo-Fenton process increased biodegradability ratio from 0.36 to 0.7 in 2 hours. The overall cost of ferrioxalate-induced solar photo-Fenton oxidation for the treatment of 5 m³ of latex wastewater per day was estimated to be US$85/m³.

Key words | central composite design (CCD), ferrioxalate, latex wastewater, solar photocatalytic reactor, solar photo Fenton

INTRODUCTION

The rubber industry is one of the fastest growing industrial sectors in India. The raw material for natural rubber production is a white fluid called ‘Latex’ which is obtained from Hevea brasiliensis trees. Rubber is mainly produced in three states of India, namely Kerala, Tamil Nadu, and Karnataka, among which Kerala accounts for 90% of the entire production of rubber in the country (Madhu et al. 1994). Rubber-processing industries generate wastewater in the range of 10–30 L/kg of raw material. This wastewater includes wash water, small amounts of uncoagulated latex, and serum with small quantities of protein, carbohydrates, lipids, carotenoids, and salts. The characteristics of generated wastewater depend on the configuration process with the variables as follows: pH = 4–5; total suspended solids (TSS) = 1962–14,142 mg/L; biochemical oxygen demand (BOD₅) = 3645–34,900 mg/L; and chemical oxygen demand (COD) = 5870–58,750 mg/L (Mohammadi et al. 2010). Without proper treatment, discharge of wastewater from rubber-processing industry can cause a significant threat to the environment due to toxicity, stability, poor biodegradability, and the ability to remain in the environment for a long period of time. Generally, the technologies of wastewater treatment of natural rubber processing in India are based on conventional biological processes, with the following examples: pond system, oxidation ditch, anaerobic digestion, and activated sludge. However, these systems are inefficient for the removal of recalcitrant organics and micro-pollutants in latex wastewater. In addition, these systems need long retention times and large treatment areas. Physical and chemical methods like coagulation–floculation, ultrasonic irradiation, ozonation, and electrochemical methods have been applied. Nevertheless, these methods have some operational problems like low efficiencies and reaction rates, sludge generation, phase change of pollutants, and high operative costs (Nguyen & Luong 2012). So far, there is no implementation of a full combination of the physical, chemical, and biological processes for the removal of the major pollutants in rubber-processing.
wastewater. Therefore, they are not able to properly treat the latex wastewater in order to meet the minimum national standards for discharge (MINAS 2009).

Advanced oxidation processes (AOPs) can be considered as an effective alternative and have become the most widely used treatment technologies for organic pollutants that are not treatable by conventional technologies, due to the high chemical stability and/or low biodegradability. AOPs involve in the generation of highly reactive radical species, mainly the hydroxyl radical (OH·) to oxidize the organic matter to the end products of water and carbon dioxide. Among AOPs, photo-Fenton and photo-ferrioxalate systems are considered as the two most important processes for the generation of hydroxyl radicals. The use of sunlight as the source of irradiation to perform AOPs reduces the processing costs and makes it more affordable for commercial use as a water treatment technology (Babuponnusami & Karuppan Muthu 2014; Hernandez-Rodriguez et al. 2014).

In the photo-Fenton process, the rate of OH· formation is increased by photoreactions of H2O2 and/or Fe3+ that produce OH· directly or regenerate Fe2+ (Babuponnusami & Karuppan Muthu 2014). The addition of oxalic acid to the photo-Fenton system promotes the formation of ferrioxalate complexes, which increases the oxidation efficiency of the solar photo-Fenton process, as ferrioxalate is a photosensitive complex which expands the useful range of the irradiation spectrum up to 450 nm. The photolysis of ferrioxalate generates more hydrogen peroxide, with which Fe2+ yields more hydroxyl radicals through the well-known Fenton reaction mechanism (Equations (1)–(6)), improving the degradation process (Monteagudo et al. 2009):

\[
\text{Fe(C}_2\text{O}_4\text{)}_3^{3-} + \text{hv} \rightarrow \text{Fe}^{2+} + 2\text{C}_2\text{O}_4^{2-} + \text{C}_2\text{O}_4^{*-} \quad (1)
\]

\[
\text{C}_2\text{O}_4^{*-} + \text{Fe(C}_2\text{O}_4\text{)}_3^{3-} \rightarrow \text{Fe}^{2+} + 3\text{C}_2\text{O}_4^{2-} + 2\text{CO}_2 \quad (2)
\]

\[
(\text{C}_2\text{O}_4)^{*-} + \text{O}_2 \rightarrow 2\text{CO}_2 + \text{O}_2^{*-} \quad (3)
\]

\[
\text{O}_2^{*-} + \text{H}^+ \rightarrow \text{HO}_2^* \quad (4)
\]

\[
\text{HO}_2^* + \text{HO}_2^* \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (5)
\]

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH} + \text{OH}^- \quad (6)
\]

The main goal of this work is to evaluate whether ferrioxalate-induced solar photo-Fenton technology is a suitable technology for the degradation of wastewaters from natural rubber latex industries and to find the proper operating conditions to achieve sufficient degradation and to produce enhanced biodegradability of the latex wastewater being discharged into a conventional activated sludge system.

**EXPERIMENTAL**

**Wastewater characteristics**

Latex wastewaters were obtained from a rubber industry located at Alapuzha district in Kerala, India. The tests were performed with primarily treated wastewater (collected at the outlet of the plain sedimentation tank). The sample was collected in plastic cans that were transported to the laboratory and were stored at 4 °C. The wastewater was characterized with a high organic load of COD and BOD5. The physicochemical characteristics of the wastewater were carried out as per *Standard Methods* (APHA 2005) and are listed in Table 1.

**Chemicals**

All reagents used in this experiment were of analytical grade, and they were used as received without further purification. The chemicals used in this study are ferrous sulfate heptahydrate (FeSO₄·7H₂O), hydrogen peroxide

### Table 1 | Typical characteristics of latex wastewater after primary clarification

<table>
<thead>
<tr>
<th>S.No</th>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>4.6</td>
</tr>
<tr>
<td>2</td>
<td>Colour</td>
<td>White</td>
</tr>
<tr>
<td>3</td>
<td>Total suspended solids (mg/L)</td>
<td>2132</td>
</tr>
<tr>
<td>4</td>
<td>Chemical oxygen demand (mg/L)</td>
<td>30,000</td>
</tr>
<tr>
<td>5</td>
<td>Biochemical oxygen demand (mg/L)</td>
<td>10,867</td>
</tr>
<tr>
<td>6</td>
<td>BOD₅/COD</td>
<td>0.36</td>
</tr>
</tbody>
</table>
(H₂O₂ 30% w/w), sodium thiosulphate (Na₂S₂O₃), sulphuric acid (H₂SO₄), potassium dichromate (Cr₂O₇²⁻), mercuric sulphate (HgSO₄), ferrous ammonium sulphate (Fe(NH₄)₂(SO₄)₂·6H₂O), sodium hydroxide (NaOH), and sodium sulphite (Na₂SO₃), which were purchased from Merck (India).

**Solar photo-reactor configuration**

All experiments were carried out in a laboratory-scale solar photo-Fenton plug flow baffle reactor with a working volume of 5 L capacity, as shown in Figure 1. The solar photo-Fenton plug flow baffle reactor is made of acrylic of size 0.45 × 0.21 × 0.08 m in the form of a pond divided by baffle plates at a spacing of 0.07 m. The irradiated surface area for solar Fenton plug flow baffle reactor is 0.09 m². The set-up consists of a flow-through reactor placed on a platform under solar irradiation. The wastewater was continuously recycled at a rate of 200 mL/min with the help of a circulating pump. Air was supplied into the wastewater using aerators.

**Experimental methods**

All photocatalytic experiments were carried out under solar illumination (UV intensity 32 ± 2 W/m²) on the sunny days of January to April 2014, between 10 a.m. and 4 p.m. at the Regional Centre of Anna University Campus, Tirunelveli, India (8° 44′ N, 77° 44′ E). Hydrogen peroxide was added to the reactor after the addition of Fe²⁺ and oxalic acid, and pH adjustment was made. The pH was previously adjusted (between 2 and 4) by using 0.1 N H₂SO₄. The time of hydrogen peroxide addition to the wastewater marked the beginning of the experiment. Before the analysis, all of the samples were withdrawn from the reactor and were immediately treated with 0.5 mL of sodium sulphite solution per 10 mL of wastewater sample to quench the oxidation reaction for hydrogen peroxide decomposition; and the pH was raised to 7 by adding 0.1 N NaOH solution for the iron salt precipitation. The COD and BOD analyses of the samples were carried out as per *Standard Methods* (APHA 2005).

**Experimental design and mathematical modeling**

Response surface methodology (RSM) was used for the experimental design and optimization of the process with minimum runs of experiment. This could remove the time-consuming phase which could not be achieved using conventional methods (one-factor-at-a-time approach). Besides, the central composite design (CCD) is well suited for fitting a quadratic surface, which usually works well for the process optimization. A central composite experimental design was set up to analyse the effects of four variables (pH, initial concentrations of Fe²⁺, oxalic acid, and H₂O₂) on the chosen response value (COD removal %) in the ferrioxalate-induced solar photo-Fenton treatment of natural rubber latex wastewaters. Incident solar power was not controlled during the experiment, but they were measured during the treatment, and their average values were included in the data analysis. Based on the preliminary studies conducted, the ranges of the operating parameter were fixed. The pH was varied between 2 and 4; the Fe²⁺ concentration was varied between 0 and 5 g/L; the oxalic acid concentration was varied between 0 and 3 g/L; and the H₂O₂ concentration was varied between 0 and 110 g/L. A total of 30 experiments were employed in this analysis by using Design Expert Version 9.0.2 software (Stat-Ease, Inc., Minneapolis, USA). To simplify the recording of the conditions of each experiment and the processing of the experimental data, the factor levels were selected by taking the higher level as +1.5 and the lower level as −1.5. After conducting the experiments, the polynomial model coefficients were
calculated using the following equation:

\[ Y = \beta_0 + \sum \beta_i X_i + \beta_{ii} X_i^2 + \beta_{ij} X_i X_j + \cdots \]  

(7)

where \( i \) and \( j \) are the linear and quadratic coefficients, respectively, and \( \beta \) is the regression coefficient. Predicted values were solved from the derived equation for each response. These predicted values were plotted to obtain the contour plots that were used for the optimization process. Analysis of variance (ANOVA) was used for graphical analysis of data to obtain the interaction between operating variables and response. The quality of fit of the polynomial model was expressed by the coefficient of determination \( R^2 \), and its statistical significance was checked by Fisher’s \( F \)-test. The model terms were evaluated by the \( P \)-value (probability value) with 95% confidence level. Three-dimensional plots were obtained for COD removal based on the effects of the four variables, namely initial pH, concentration of ferrous ion, oxalic acid, and hydrogen peroxide. Furthermore, the optimum region was identified based on the main parameters in the desirability plot.

### RESULTS AND DISCUSSION

#### Model fitting and statistical analysis

The experimental data for COD removal by ferrioxalate-induced solar photo-Fenton process are given in Table 2. The relationship between the four variables (pH, initial concentrations of \( \text{Fe}^{2+} \), oxalic acid, and \( \text{H}_2\text{O}_2 \)) and COD removal efficiency was analysed using CCD. The predicted values were obtained from the model fitting technique, using the design expert version 9.0.2 software, and were seen to be sufficiently close to the observed values. The regression coefficients of the model describing the COD removal are summarized in Table 3. The significance of each coefficient was determined by \( F \)-value and \( P \)-value. Corresponding to the \( P \)-values, it was suggested that among the test variables used in this study, A, B, C, D, AB, AC, and AD are the significant model terms. Coefficients of the model terms are listed in Table 3. The values that are greater than 0.100 indicate that the model terms are not significant. The empirical regression equation for COD removal, in terms of coded factors, is given in the following equation:

\[ \text{COD removal (\%)} = +65.50 - 3.98A + 3.71B + 7.28C + 7.60D - 3.33AB + 3.97AC + 1.94AD \]  

(8)
ANOVA was applied in order to evaluate the significance of the fit of the developed model. $P < 0.05$ indicates that the model terms are significant at 95% of confidence level or higher. For the model predicted by Equation (8), $P$ was $< 0.0001$, indicating that it was significant for describing the COD removal efficiency. The lack of fit value 12 is not significant as the $P > 0.05$. For a model to be successfully used for prediction, the lack of fit should be insignificant and the response surfaces were sufficiently explained by the regression equation. A positive effect of a factor means that the response is improved as the factor level is increased, and a negative effect of the factor means that the response is not improved as the factor level is increased. The significant reaction parameters were as follows: $\text{H}_2\text{O}_2$ concentration $(7.60) > \text{oxalic acid concentration (7.28)} > \text{pH (−3.98)} > \text{interaction between pH and oxalic acid concentration (3.97)} > \text{Fe}^{2+} \text{concentration (3.71)} > \text{interaction between pH and Fe}^{2+} \text{concentration (−3.33)} > \text{interaction between pH and H}_2\text{O}_2 \text{concentration (1.94)}$. The high correlation between actual experimental data and the model for COD removal ($R^2 = 0.9746$) showed that 97.46% of the variability observed in data can be explained by the model built for COD removal efficiency, which only leaves 2.54% of variability owing to random error. Consequently, the model given by Equation (8) can be used to predict the COD removal efficiency, to create and explore the response surface, and to find the optimal conditions of the process.

**Table 3 | Estimated regression coefficients corresponding to ANOVA results from the data of central composite design**

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>df</th>
<th>Mean squares</th>
<th>$F$-value</th>
<th>$P$-value</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>3958.94</td>
<td>14</td>
<td>282.78</td>
<td>41.04</td>
<td>$&lt; 0.0001$</td>
<td>significant</td>
</tr>
<tr>
<td>A-pH</td>
<td>379.99</td>
<td>1</td>
<td>379.99</td>
<td>55.15</td>
<td>$&lt; 0.0001$</td>
<td>significant</td>
</tr>
<tr>
<td>B-Fe$^{2+}$</td>
<td>330.11</td>
<td>1</td>
<td>330.11</td>
<td>47.91</td>
<td>$&lt; 0.0001$</td>
<td>significant</td>
</tr>
<tr>
<td>C-oxalic acid</td>
<td>1271.66</td>
<td>1</td>
<td>1271.66</td>
<td>184.55</td>
<td>$&lt; 0.0001$</td>
<td>significant</td>
</tr>
<tr>
<td>D-$\text{H}_2\text{O}_2$</td>
<td>1384.67</td>
<td>1</td>
<td>1384.67</td>
<td>200.96</td>
<td>$&lt; 0.0001$</td>
<td>significant</td>
</tr>
<tr>
<td>AB</td>
<td>177.05</td>
<td>1</td>
<td>177.05</td>
<td>25.70</td>
<td>$&lt; 0.0001$</td>
<td>significant</td>
</tr>
<tr>
<td>AC</td>
<td>252.00</td>
<td>1</td>
<td>252.00</td>
<td>36.57</td>
<td>$&lt; 0.0001$</td>
<td>significant</td>
</tr>
<tr>
<td>AD</td>
<td>60.45</td>
<td>1</td>
<td>60.45</td>
<td>8.77</td>
<td>0.0097</td>
<td>significant</td>
</tr>
<tr>
<td>BC</td>
<td>3.26</td>
<td>1</td>
<td>3.26</td>
<td>0.47</td>
<td>0.5020</td>
<td></td>
</tr>
<tr>
<td>BD</td>
<td>9.32</td>
<td>1</td>
<td>9.32</td>
<td>1.35</td>
<td>0.2630</td>
<td></td>
</tr>
<tr>
<td>CD</td>
<td>3.33</td>
<td>1</td>
<td>3.33</td>
<td>0.48</td>
<td>0.4975</td>
<td></td>
</tr>
<tr>
<td>Residual</td>
<td>103.36</td>
<td>15</td>
<td>6.89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of fit</td>
<td>65.86</td>
<td>10</td>
<td>6.59</td>
<td>0.88</td>
<td>0.5990</td>
<td>not significant</td>
</tr>
<tr>
<td>Pure error</td>
<td>37.50</td>
<td>5</td>
<td>7.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor total</td>
<td>4062.29</td>
<td>29</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 2 | 3D response surface and contour diagram showing the effects of the mutual interactions between pH and $\text{H}_2\text{O}_2$ ($\text{Fe}^{2+} = 1.3 \text{ g/L}$, oxalic acid $= 2.25 \text{ g/L}$, irradiation time $= 6 \text{ hours}$).**
pH of 4, the decrease in COD was the greatest. When the pH is 4, the predominant Fe(III) species are \([Fe(C_2O_4)_2]^-\) and \([Fe(C_2O_4)_3]^{3-}\), which are highly photoactive; under solar light, they can effectively convert Fe$^{3+}$ into Fe$^{2+}$, and more \(^{•}\)OH radicals are produced by the reaction of the generated ferrous ions with hydrogen peroxide. The decrease in COD removal efficiency, when the initial pH was below 4, can be explained by the production rate of the highly reactive \(^{•}\)OH radicals, which were poorer than at pH 4, hindering the photo-oxidation process (Monteagudo et al. 2010a). However, when the pH value is increased above 4, (data not shown) the Fe(III)-oxalate species are mainly Fe(C$_2$O$_4$)$^{2+}$ and \([=Fe(C_2O_4)]^{+}\), which are less photoactive, resulting in a lower degradation rate. In addition, the degradation efficiency decreases above these pH values, since the Fe$^{3+}$ and Fe$^{2+}$ species are almost non-existent in the solution; and the predominant species of Fe is Fe(OH)$_3$ as a precipitate, which is barely photoactive and cannot be regenerated to the ferrous ion (Jeong & Jeyong 2005). Increasing the concentration of H$_2$O$_2$ correspondingly increased COD removal, up to a H$_2$O$_2$ concentration of 82.5 g/L. A further increase of hydrogen peroxide concentration has a negative effect on degradation, because an excess of hydrogen peroxide reduces catalytic activity, as it favours reactions (6) and (9), diminishing the amount of H$_2$O$_2$ and \(^{•}\)OH radicals. Although other radicals are generated (HO$_2$), their oxidation potential is much smaller than that of the hydroxyl radicals (Monteagudo et al. 2010b):

\[
H_2O_2 + ^{•}OH \rightarrow HO_2^- + H_2O
\]  

(9)

The influence of the pH and oxalic acid concentration on COD removal efficiency is presented in Figure 3. The results revealed that varying the pH and the addition of oxalic acid could increase the reaction rate or cause inhibition effects, depending on the operating conditions. Thus, if the reaction was conducted at pH values below 4, the initial concentration of oxalic acid positively affected the photocatalytic reaction until an optimal concentration of 2.25 g/L is reached. This was due to the faster generation of Fe$^{2+}$ ion by photolysis of ferrioxalate and additional hydroxyl radicals produced at that optimal pH 4. Fe(II) may react according to Equations (6) and (10), by generating more \(^{•}\)OH radicals (Monteagudo et al. 2010c):

\[
Fe^{2+} + H_2O_2 + C_2O_4^{2-} \rightarrow Fe^{3+} [(C_2O_4)_3]^{3-} + OH^- + ^{•}OH
\]  

(10)

An excess of oxalic acid cannot complex with ferric ions in wastewater, and the light penetration through irradiated wastewater decreases. In addition, the excess of oxalate acts as an additional organic compound, so it competes the \(^{•}\)OH radicals with the organics present in the wastewater, thus reducing the degradation efficiency. On the other hand, the negative effect on the degradation with excess of oxalic acid can also be due to CO$_2$ produced according to Equation (3), which could be converted to CO$_2$ or HCO$_3^-$ at acidic pH; it may scavenge the hydroxyl radicals to decrease the degradation efficiency (Monteagudo et al. 2010b).

The influence of the pH and Fe$^{2+}$ concentration on COD removal efficiency is presented in Figure 4. An increase of Fe$^{2+}$ concentration to above 1.3 g/L negatively affected the degradation, because an inhibition effect was present possibly due to the excess Fe$^{2+}$ competing with organic molecules for various radicals (Monteagudo et al. 2010b, 2013) as shown in the following equations:

\[
Fe^{2+} + ^{•}OH \rightarrow Fe^{3+} + OH^-
\]  

(11)

\[
Fe^{2+} + HO_2^- \rightarrow Fe^{3+} (HO_2)^{2-}
\]  

(12)
It should be noted that the amount of Fe\textsuperscript{2+} ions used should be as low as possible for economic and environmental reasons, since high amounts of Fe\textsuperscript{2+} ions might produce a large quantity of Fe\textsuperscript{3+} sludge. The treatment of sludge containing Fe\textsuperscript{3+} is expensive and requires a large amount of chemicals and manpower (Monteagudo et al. 2015).

**PROCESS OPTIMIZATION AND VERIFICATION**

In numerical optimization, the desired goal for each factor and response is chosen from the menu. The available goals are as follows: maximize, minimize, target, within range, none (for response only), and set to an exact value (for factors only). The goals are combined into an overall desirability function. Desirability is an objective function that ranges from zero outside of the limits to one at the goal. Based on the solutions generated by the design software, the optimum conditions were predicted by response surface methodology for the maximum COD removal efficiency (91.6%) with a desirability value of 0.970, which was adopted for the verification experiment. In order to validate the optimum point generated by CCD, the experiment was carried out at pH of 4, Fe\textsuperscript{2+} = 1.3 g/L, oxalic acid = 2.25 g/L, H\textsubscript{2}O\textsubscript{2} = 82.5 g/L, and treatment time of 1 hour. In Table 4, experimental values (COD removal = 89.9%) were found to be in good agreement with the values predicted from CCD (COD removal = 91.6%).

### Study of the biodegradability and contact time

The main role of a chemical pre-treatment, such as AOPs, is partial oxidation of the biologically persistent part to produce biodegradable reaction intermediates. The percentage of degradation should be minimal during the pre-treatment stage in order to avoid unnecessary expenditure of chemicals and energy, thereby lowering the operating costs (Adishkumar & Kanmani 2010; De Torres-Socias et al. 2013). Therefore, biodegradability analysis must be performed with the aim of identifying the best possible combination point between the chemical and biological treatment steps. The initial biodegradability of the untreated latex wastewater (BOD\textsubscript{5}/COD = 0.36) suggests that it cannot be treated by conventional biological processes. In Figure 5, 2 hours of irradiation are enough to increase the BOD\textsubscript{5}/COD ratio to above 0.6 (biodegradability threshold). The treatment of latex wastewater by the solar/Fe\textsuperscript{2+}/oxalic acid/H\textsubscript{2}O\textsubscript{2} process increased biodegradability from 0.36 to 0.7 in 2 hours. Nearly all (99%) of COD was depleted at 6 hours (Figure 5). By increasing the contact time, the exposure of the reaction mixture to solar light allowed the utilization of more energy to produce more hydroxyl radicals from H\textsubscript{2}O\textsubscript{2} and Fe\textsuperscript{2+} (Adishkumar et al. 2012, 2014; Ginni et al. 2014). Table 5 shows the treated characteristics of the latex wastewater. The COD and BOD\textsubscript{5} of latex

\[
\text{Fe}^{2+} + \text{O}_2^{-} + \text{H}^+ \rightarrow \text{Fe}^{3+}(\text{HO}_2)^{2+} \quad (13)
\]

\[
\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{HO}_2^-
\]

\[
\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{HO}_2^-
\]

\[
\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{HO}_2^-
\]

\[
\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{HO}_2^-
\]

\[
\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{HO}_2^-
\]
wastewater after treatment were reduced to 200 and 85 mg/L, respectively.

**Reaction kinetics**

In order to achieve the proper design of a solar photo reactor, it is very important to determine the kinetic coefficients involved in a reaction. The reaction during ferrioxalate-induced solar photo-Fenton treatment of latex wastewater is very complex, in terms of many intermediates and ultimate products (Shahrezaei et al. 2014). A brief discussion on the kinetics study of COD removal will be given. The reactor was operated under optimum conditions, i.e. pH = 4, Fe$^{2+}$ = 1.3 g/L, oxalic acid = 2.25 g/L, H$_2$O$_2$ = 82.5 g/L, and irradiation time of 6 hours. The rate data were modelled by first-order kinetics as in the following equation, with the reactant concentration given as COD:

\[
d(COD)/dt = kCOD \tag{14}
\]

where \( t \) is reaction time and \( k \) is the rate constant. Integrating Equation (14) gives

\[
\ln(COD_0/COD) = kt \tag{15}
\]

where COD$_0$ is the initial COD value.

The correlation between ln(COD$_0$/COD) and the reaction time (\( t \)) was drawn based on Equation (15). The data fitted well with an \( R^2 > 0.995 \). The high values of determination coefficients \( (R^2) \) clearly indicate that first-order kinetics can be applied with a good degree of precision. Figure 6 shows the results of kinetic study on the treatment of latex wastewater under different systems. The order of rate constants was as follows: solar/Fe$^{2+}$/oxalic acid/H$_2$O$_2$ (0.702 hour$^{-1}$) > solar/Fe$^{2+}$/H$_2$O$_2$ (0.439 hour$^{-1}$) > Fe$^{2+}$/oxalic acid/H$_2$O$_2$ (0.163 hour$^{-1}$) > solar/oxalic acid/H$_2$O$_2$ (0.129 hour$^{-1}$) > solar/Fe$^{2+}$/oxalic acid (0.127 hour$^{-1}$).

**Design of the field-scale reactor**

The scaling up of the solar photo reactor is simple as there is no necessity for solar tracking system. The field-scale reactor was designed to treat the latex wastewater with a flow rate of 5 m$^3$/day. The reactor was designed for 99% COD removal. The average yearly solar UV light intensity for the location of study was calculated as $32 \pm 2$ W/m$^2$, and the average daily useful operating hours was found to be 6 hours. Sagawe et al. (2003) suggested the equation for the kinetic model, which accounts for the effect of pollutant concentration, volumetric flow rate, light intensity, and solar irradiation.

---

**Table 5 | Characteristics of ferrioxalate-induced solar photo-Fenton treated latex wastewater**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Parameters</th>
<th>Solar photo-Fenton treated wastewater</th>
<th>Minimal National Standards for disposal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>7.2</td>
<td>6.5–8.5</td>
</tr>
<tr>
<td>2</td>
<td>TSS (mg/L)</td>
<td>75</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>Colour</td>
<td>Colourless</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>COD (mg/L)</td>
<td>200</td>
<td>250</td>
</tr>
<tr>
<td>5</td>
<td>BOD$_3$ (mg/L)</td>
<td>85</td>
<td>100</td>
</tr>
</tbody>
</table>

Minimal National Standards (MINAS 2009).
area; these were used to arrive at a lump parameter \( K_3 \):

\[
K_3 = \ln\left(\frac{C_0}{C}\right) \times \frac{Q}{q_{UV} \times A} \tag{16}
\]

where \( K_3 \) = lump kinetic parameter representing the efficiency of the photocatalyst (m$^3$/W·min); \( C_0 \) = inlet concentration of COD (mg/L); \( C \) = outlet concentration of COD (mg/L); \( Q \) = volumetric flow rate (m$^3$/min); \( q_{UV} \) = time-averaged radiation density flux (W/m$^2$); and \( A \) = effective area of solar irradiation (m$^2$).

\[
K_3 = \ln\left(\frac{30,000}{200}\right) \times 1.527 \times 10^{-5}/(32 \times 0.0945) \\
= 2.53 \times 10^{-5} \text{m}^3/\text{W} \cdot \text{min}.
\]

The scaling up of the field-scale reactor can be given by the following equations:

\[
(K_3)_{\text{bench-scale reactor}} = (K_3)_{\text{field-scale reactor}} \tag{17}
\]

\[
\text{Area of field-scale reactor} = \ln\left(\frac{C_0}{C}\right) \times \frac{Q_{\text{field-scale reactor}}}{q_{UV}} \times (K_3)_{\text{bench-scale reactor}} \\
= 21.5 \text{m}^2 \tag{18}
\]

The depth of the reactor, based on detention time, included free board = 0.1 m.

**Economic analysis**

Cost is always a key topic when innovative technologies are considered, and standard commercial procedures indicate that any new technology should provide significant reductions in processing costs over competing technologies or significant new technical contributions for its successful marketing. In the case of ferrioxalate-induced solar photo-Fenton advanced oxidation process, CCD results confirmed that the H$_2$O$_2$ concentration, Fe$^{2+}$ concentration, and oxalic acid concentration positively affected COD removal.

Table 6 shows the estimated treatment cost of a ferrioxalate-induced solar photo-Fenton process. The overall cost of ferrioxalate-induced solar photo-Fenton oxidation for the treatment of 5 m$^3$ of latex wastewater per day was estimated to be US$85/m$^3$. This cost is higher than air stripping, adsorption or membrane technologies, but with the important advantage that solar photocatalysis is a real treatment process, while the others are only contaminant separation technologies (Benoit & Norvill 2014). In addition, the investment and operating costs of solar photocatalytic treatment are lower than for technologies such as incineration or wet oxidation, while other AOP technologies have similar investment and operating costs.

**CONCLUSIONS**

The degradation of natural rubber latex wastewater has been studied by means of the ferrioxalate-induced solar photo-Fenton advanced oxidation process. CCD results confirmed that the H$_2$O$_2$ concentration, Fe$^{2+}$ concentration, and oxalic acid concentration positively affected COD removal.
efficiency. Under the conditions selected in this work (pH of 4, Fe$^{2+}$ = 1.5 g/L, oxalic acid = 2.25 g/L, H$_2$O$_2$ = 82.5 g/L and treatment time of 1 hour), the COD removal efficiency was 99%. The kinetic study indicated that the degradation kinetics of latex wastewater followed the first-order kinetic. The order of rate constants was as follows: solar/Fe$^{2+}$/oxalic acid/H$_2$O$_2$ (0.702 hour$^{-1}$) > solar/Fe$^{2+}$/H$_2$O$_2$ (0.439 hour$^{-1}$) > Fe$^{2+}$/oxalic acid/H$_2$O$_2$ (0.163 hour$^{-1}$) > solar/oxalic acid/H$_2$O$_2$ (0.129 hour$^{-1}$) > solar/Fe$^{2+}$/oxalic acid (0.127 hour$^{-1}$). The ferrioxalate-induced solar photo-Fenton process-generated wastewater, which met the legal requirements for discharge into natural waters.

REFERENCES


First received 8 December 2014; accepted in revised form 19 May 2015. Available online 30 June 2015.