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Using D-optimal experimental design to optimise remazol black B mineralisation by Fenton-like peroxidation

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The mineralisation of remazol black B (RBB) was studied at concentrations ranging from 20-1000 mgL$^{-1}$. The work was aimed at investigating the Fenton-like peroxidation of RBB at a concentration typically obtained in Batik cottage industries. Other response parameters were degradation and colour removal efficiencies. The parameters that were measured included total organic carbon (TOC), chemical oxygen demand (COD) as well as absorbance for mineralisation, degradation and colour. To optimise the process, the interaction effects of several controlling variables on the treatment process were examined using dispersion matrix-optimal design and response surface analysis. Four specific variables: initial dye concentration (Dye)$_i$, the molar ratio of oxidant to dye organic strength (H$_2$O$_2$):(COD); the mass ratio of the oxidant to the catalyst (H$_2$O$_2$):(Fe$^{3+}$) and reaction time ($t_r$), were observed. Three reduced empirical models, one for each response, were developed for describing the treatment process. For 20, 510 and 1000 mgL$^{-1}$, the optimum %TOC reduction and oxidation times were 44% for 95 min, 52% for 52.5 min and 68% for 10 min corresponding to 67, 81 and 75% COD reduction, respectively. The optimum COD reduction and oxidation times were 89% for 95 min, 91% for 10 min and 84% for 95 min for concentrations of 20, 510 and 1000 mg L$^{-1}$, respectively. For all concentrations, total colour removal was achieved. A comparison of the results obtained in this study with literature values for traditional Fenton, photo-Fenton and photo-Fenton-like oxidation indicated that the TOC reduction obtained using the Fenton-like process was satisfactory.

Keywords: Cottage Industries, Degradation (COD), Fenton-like, Mineralization, (TOC), Reactive Black B (RBB)

Introduction

Effluents from the textile industry are highly complex and their composition varies significantly due to the presence of several contaminants. These effluents generally contain synthetic dyes, surface-active agents and textile additive materials [1]. More than 10,000 dyes are currently in use, which are problematic components of this textile wastewater [1–3] with the largest group being the reactive dyes. These water-soluble dyes are characterised by an azo-based chromophore, which is usually combined with other groups, such as a vinyl sulfone. The azo group, identified by two nitrogen atoms (–N=N–), has great potential for binding to textile fibres covalently, therefore reducing energy consumption [4]. Their mutagenic effects are well established. Aesthetically, they impart strong colouring to the effluent, and adversely affect aquatic life [2].

Malik et al. [5] have detailed the drawbacks of most dye treatment technologies. However, oxidative processes utilising hydroxyl radicals (termed advanced oxidation processes (AOPs)), have demonstrated their effectiveness for treating recalcitrant and non-biodegradable products [6]. In this respect, Fenton and Fenton-like oxidation, the simplest and most cost effective AOP, has been widely used in the treatment of dye-containing wastewaters [6–11].

In the classical Fenton process, Fe$^{2+}$ is used as the catalyst whereas Fenton-like oxidation uses Fe$^{3+}$. As the cost of Fe$^{3+}$ is lower than Fe$^{2+}$, we elected to investigate Fenton-like oxidation in this study [12]. Fenton-like oxidation utilises in situ-generated hydroxyl radicals (•OH) [13] formed from the reaction between ferric ions (Fe$^{3+}$) or other transition metal ions and hydrogen peroxide (H$_2$O$_2$). The summary of the sequence of the hydroxyl radical (•OH) generation is: (i) the formation of a Fe$^{3+}$–H$_2$O$_2$ complex, followed by decomposition of the complex, in a uni-molecular way, to yield Fe$^{2+}$ ions and hydperoxide/superoxide radicals (H$_2$O•/O$_2$•). Thereafter, the yielded Fe$^{2+}$ ions catalyse the decomposition of H$_2$O$_2$ to yield •OH [14]. Equations (1)-(4) show the Fenton-like reaction scheme [12].

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe \cdots OOH^{2+} + H^+ \quad (1)$$

$$Fe \cdots OOH^{2+} \rightarrow HO_2^- + Fe^{2+} \quad (2)$$

$$H_2O_2 + Fe^{2+} \rightarrow •OH + OH^- + Fe^{3+} \quad (3)$$

$$•OH + RH \rightarrow R• + H_2O \quad (4)$$

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Sludge generation has been identified as the main setback for this process [5]. However, the consumption of the reagents at the end of the reaction has been shown to significantly decrease the amount of sludge produced [15]. Despite these advantages, applications of Fenton-like oxidation in dye treatment have been scarce [16]. Moreover, most reported Fenton and Fenton-like work on RBB treatment has focused on colour removal [2,10,17,18], assessed the treatment based on COD monitoring [1,19] or the process was not optimised [6]. The implication of the latter set of experimental designs is reporting an incorrect optimum, as the interaction effects of the controlling variables were not accounted for [20]. There have been other attempts to increase the efficiency by enhancing the •OH generation using UV-photolytic assistance [2,8,21]. However, the overall cost of the latter process is higher than that of the Fenton-like process.

For this study, the area of interest is Kota Bharu, Malaysia. This is an area with the highest concentration of Batik cottage industries. From a preliminary assessment of the treatment process, it could be concluded that the most common dye consumed is RBB. This observation is similar to other local dyeing industries [22]. This study was conducted to optimise the Fenton-like oxidation of RBB aqueous solution in terms of TOC, COD and colour removal at concentrations typically found in the Malaysian Batik cottage industries.

Materials and Method

Chemicals and preparation

The RBB dye was obtained from the Department of Environment (DOE), Kelantan, Malaysia (characteristics and structure shown in Table 1). Analytical grade reagents were used without any further purification. The catalyst source was ferrous sulfate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and sodium hydroxide (NaOH, 50% w/w), which were purchased from Fisher Scientific Sdn Bhd (Malaysia). The hydrogen peroxide (30%, w/w), its semi-quantitative measuring strips and sulfuric acid ($\text{H}_2\text{SO}_4$, 98%) for pH adjustment were sourced from Merck.

Three different working solutions at concentrations of 20, 510 and 1000 mg L$^{-1}$ were made by appropriate dilution of a freshly prepared 1 g L$^{-1}$ stock solution of RBB using water distilled from a Favorit W4L water distillation system (Nottingham, UK).

Experimental Procedure

The Fenton-like peroxidation batch experimental runs were conducted in a 250 mL Erlenmeyer flask using a constant reaction mixture volume of 100 mL of the appropriate dye solution (20, 510 or 1000 mg L$^{-1}$). The operating conditions were a temperature of 20°C, atmospheric pressure and a pH of 3. The initial dye solution COD was used as the basis for computing the required amounts of the oxidant ($\text{H}_2\text{O}_2$) and catalyst ($\text{Fe}^{3+}$) in the form of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The reagents were then added to the reaction mixtures to ensure the ratios in the experimental design matrix were consistent.

In light of the literature analysis on Fenton oxidative treatment of RBB, it becomes imperative to develop robust model equations that accurately predict the treatment process using Fenton-like oxidation.

Table 1. Characteristics and structure of remazol black B dye.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour index number</td>
<td>17095-24-8</td>
</tr>
<tr>
<td>Structure</td>
<td></td>
</tr>
<tr>
<td>Molecular weight, (g mol$^{-1}$)</td>
<td>991.82</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>$\text{C}<em>{26}\text{H}</em>{22}\text{N}<em>2\text{O}</em>{19}\text{S}_6$</td>
</tr>
<tr>
<td>Chromophore</td>
<td>Azo</td>
</tr>
<tr>
<td>Anchor</td>
<td>Vinylsulfone</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>597</td>
</tr>
</tbody>
</table>

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H$_2$O, thus decreasing the production of •OH. The addition of the catalyst, Fe$^{3+}$, in the form of FeCl$_3$·6H$_2$O was done and the oxidation reaction was initiated by transferring H$_2$O$_2$ to the reaction mixture under constant stirring using a Barnstead magnetic stirrer (Cimarec—SP46920-26, Iowa, USA). NaOH solution (50%, 3 M) was added to terminate the oxidation reaction. The pH adjustment (pH = 8) resulted in the immediate precipitation of the oxidised catalyst as Fe(OH)$_3$.

A solid settling time of 1 h was allowed and proceeded under quiescent conditions. The treated effluent was then decanted and Fe(OH)$_3$ was removed from the supernatant by filtering with a 0.45 μm Millipore membrane filter before subjecting the effluent to analysis.

**Analytical measurements**

Quantification of the residual H$_2$O$_2$ in the solution was carried out using H$_2$O$_2$ strips (Merckoquant, Merck). The determined residual H$_2$O$_2$ was within the range of 20-1000 mg L$^{-1}$, which allowed for adopting the theoretical correlation, shown in Equation (5), proposed by Talini and Anderson [26] to account for the positive interference of COD measurements:

\[
\text{COD} = \text{COD}_S - (R_{H_2O_2} \times 0.25)
\]  

(5)

where, COD = actual wastewater COD; COD$_S$ = measured COD in the treated effluent; and $R_{H_2O_2}$ = residual hydrogen peroxide value.

The chemical oxygen demand (COD) measurement was made using dichromate closed reflux and colorimetric methods according to standard methods [27]. The COD digester and colorimeter were a HACH DR/890, respectively. The TOC was measured by combustion/non-dispersive infrared gas analysis method (NDIR) in a Shimadzu TOC-VCM 5000 analyser (Shimadzu, Japan) equipped with an ASI-V auto-sampler and a Shimadzu TOC5050 analyser. The solution pH was determined with a pH LabMeter 827 (Metrohm) equipped with a pH combination electrode.

For the discoloration monitoring, a UV-vis spectrophotometer (UV Line 9400, SECOMAM) was used. Firstly, the UV-vis spectra of RBB were determined by preparation of a calibration curve at various concentration values of the dye and scanning at a wavelength range from 200–800 nm. A spectrometric quartz cell with a 1 cm path length was utilised. From the spectra, a wavelength of 597 nm was determined to be the maximum absorbance wavelength. We thus monitored the decrease in the absorbance peaks at 597 nm to be directly proportional to the reduction in dye concentration.

**Experimental design**

Optimising the process allows for adequate utilisation of the Fenton reagents, which determines the overall operation costs as well as efficacy. In line with this, the specific variables of the Fenton process were optimised to improve the process efficiency by obtaining the optimal reaction conditions [28]. In this study, an application of the empirical equation developed for the treatment of effluents from many cottage industries is the objective. Thus, the choice of response surface methodology (RSM) was based on the effectiveness and robustness of the design in using the most significant points from the generated point to sufficiently and adequately represent the design region. There are different experimental designs available for the analysis of generated results. However, D-optimal design (D = dispersion matrix) satisfactorily fits these criteria, as there is no specific pattern to the design points against the conventional central composite design (CCD) and Box-Behnken designs. Here, the design points are built algorithmically to provide the most accurate estimates of the model coefficients [29].

In maximising the response parameters (mineralisation, degradation and colour percent removal), several factors are known to affect the process efficiency. The pH of the solution is critical to the performance of the Fenton process. However, numerous researchers who have extensively investigated the effect of this parameter established a pH of 3 to be the optimum [1,30,31]. Other independent variables considered in the D-optimal design were the initial dye concentrations, (Dye)$_t$; the reaction time, $(t_r)$ and the molar ratio of oxidant:dye COD, (H$_2$O$_2$):(COD)$_t$.

Based on the latter parameter, the amounts required for complete oxidation were computed as a mass ratio of oxidant:catalyst—(H$_2$O$_2$):(Fe$^{3+}$).

The four parameters identified and used for the optimisation have been established in the literature as the factors leading to optimal efficiencies when their levels are adequately and properly varied. The choice of D-optimal design was also informed by the technique’s minimisation of volume of the joint confidence interval for the model parameters. The use of the design involves three basic steps, namely: (a) level defining (b) selecting the appropriate model and (c) selecting the design points from the set of candidate points generated depending on the selected model [32].

A total of three design variables were studied at two levels plus additional centre points. For determining the best subset of experiments from the candidate points, the D-optimal strategy was then applied. The experimental matrix which consisted of 23 experiments (Table 3) was arguably sufficient for studying the main effects, all two factor interactions, and all square effects, separately.

Responses that were of interest were represented by a reduced polynomial model, shown by Equation (6):

\[
\eta = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i<j=1}^{k} \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_i x_i^2
\]

(6)

where \(\eta\) is the response, \(x_i\) and \(x_j\) are control factors, \(\beta_0\) is the constant coefficient, and the independent variable
interaction coefficients are represented by $\beta_i$, $\beta_j$ and $\beta_{ij}$ of linear, quadratic and the second-order terms, respectively.

**Results and discussion**

The objective for obtaining the empirical model was to adequately describe the factors influencing the treatment at the concentration ranges investigated. The results of the experimental runs with various treatment combinations (Table 2) and at a constant pH of 3 are presented in Table 3.

In this study, the stoichiometric theoretical amounts of oxidant required to totally mineralise the effluent at different organic loads were computed based upon the correlation proposed by Eckenfelder [33]. The values were then used in determining the suitable starting ratio of ($\text{H}_2\text{O}_2$):(COD) and subsequently the ($\text{H}_2\text{O}_2$):($\text{Fe}^{3+}$) ratio. Varied amounts of oxidants were employed to account for the several unpredictable activities that occurred during the Fenton oxidation.

These activities have a direct bearing on the amount of $\text{•OH}$ radicals available within the reaction system, thus limiting the use of the exact amounts of reagents theoretically computed. These reactions include: (i) self-scavenging reactions, in the case of $\text{•OH}$ (Equation (7)) and also through reactions with $\text{H}_2\text{O}_2$ (Equation (8)) thus leading to a loss of the radicals generated [34]. Although Equation (8) yields a product with oxidising potential [35], it possesses less of an oxidising potential relative to $\text{•OH}$.

\[\text{•OH} + \text{•OH} \rightarrow \text{H}_2\text{O}_2\]  
\[\text{HO}_2\text{•} + \text{•OH} \rightarrow \text{H}_2\text{O} + \text{O}_2\]  

(ii) Partial complexing of the iron catalyst by some organic components in the wastewater, thus limiting the available surface for the reaction with the oxidant [36], (iii) catalyst complexing results in an excess of unreacted $\text{H}_2\text{O}_2$ thereby inducing a scavenging reaction with $\text{•OH}$, (Equation (9)) [15,37].

\[\text{H}_2\text{O}_2 + \text{•OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2\text{•}\]  

(iv) Excess catalyst also consumes the available $\text{•OH}$, which clearly inhibits the process (Equation (10)) [37].

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

The experimental results were analysed and least-square estimates of the coefficients of the polynomial model

| Table 2. Experimental range and levels of the process variables studied. |
|--------------------------|--------------------------|--------------------------|
| Factor name             | Low actual value         | High actual value        |
| [Dye]₀ (mg L⁻¹)         | 20                      | 1000                     |
| [H₂O₂:dye]              | 2                      | 12                       |
| [H₂O₂:Fe³⁺]             | 5                      | 20                       |
| $t_r$ (min)             | 10                      | 180                      |

| Table 3. Experimental design matrix, experimental runs and predicted values on colour, COD and TOC removals (%) of the Fenton-like oxidation for RBB. |
|--------------------------|--------------------------|--------------------------|
| Run | [Dye]₀ (mg L⁻¹) | [H₂O₂]:[COD] | [H₂O₂]:[Fe³⁺] | $t_r$ (min) | Colour | COD | TOC | Colour | COD | TOC |
| 1   | 1000        | 2           | 5           | 180        | 95.1    | 78.4 | 44.3 | 95.5    | 77.7 | 42.3 |
| 2   | 20          | 12          | 5           | 180        | 99.6    | 35.0 | 19.1 | 96.6    | 76.7 | 24.0 |
| 3   | 20          | 7           | 5           | 10         | 99.3    | 85.0 | 19.1 | 96.6    | 76.7 | 24.0 |
| 4   | 20          | 2           | 20          | 10         | 26.2    | 11.6 | 8.6  | 21.4    | 11.3 | 9.4  |
| 5   | 20          | 7           | 12.5        | 95         | 97.3    | 67.4 | 43.6 | 100.0   | 62.1 | 37.4 |
| 6   | 20          | 2           | 5           | 95         | 58.4    | 15.0 | 27.4 | 60.0    | 23.1 | 22.7 |
| 7   | 510         | 7           | 12.5        | 95         | 98.6    | 80.9 | 52.5 | 98.6    | 89.3 | 59.4 |
| 8   | 510         | 2           | 12.5        | 95         | 97.3    | 72.8 | 32.3 | 97.3    | 67.8 | 33.9 |
| 9   | 1000        | 12          | 20          | 10         | 96.4    | 74.7 | 67.5 | 96.1    | 77.9 | 59.4 |
| 10  | 1000        | 2           | 20          | 95         | 96.4    | 73.7 | 45.0 | 94.5    | 74.9 | 45.0 |
| 11  | 20          | 2           | 20          | 10         | 17.2    | 11.6 | 8.8  | 21.4    | 11.3 | 9.4  |
| 12  | 510         | 7           | 12.5        | 180        | 97.1    | 91.6 | 44.9 | 97.1    | 93.1 | 47.4 |
| 13  | 20          | 12          | 12.5        | 10         | 93.3    | 74.4 | 16.9 | 94.8    | 78.8 | 15.0 |
| 14  | 1000        | 12          | 5           | 95         | 96.8    | 83.6 | 55.5 | 95.0    | 77.9 | 58.4 |
| 15  | 1000        | 7           | 12.5        | 95         | 96.9    | 83.5 | 50.0 | 97.0    | 84.4 | 48.4 |
| 16  | 20          | 12          | 20          | 95         | 99.8    | 88.9 | 17.8 | 99.9    | 92.1 | 28.0 |
| 17  | 1000        | 12          | 20          | 180        | 96.4    | 85.4 | 55.6 | 97.9    | 87.2 | 55.8 |
| 18  | 510         | 12          | 5           | 10         | 98.0    | 91.0 | 44.1 | 98.0    | 91.0 | 37.1 |
| 19  | 1000        | 2           | 5           | 10         | 95.9    | 75.1 | 44.0 | 96.7    | 76.7 | 46.0 |
| 20  | 1000        | 2           | 5           | 10         | 96.1    | 79.3 | 47.0 | 96.7    | 76.7 | 46.0 |
| 21  | 20          | 2           | 20          | 180        | 99.3    | 89.8 | 31.9 | 98.4    | 87.6 | 34.4 |
| 22  | 510         | 12          | 12.5        | 95         | 97.5    | 80.6 | 46.0 | 97.5    | 75.7 | 43.2 |
| 23  | 1000        | 12          | 20          | 10         | 95.4    | 84.6 | 50.0 | 96.1    | 77.9 | 59.4 |
derived were evaluated for each response function, see Equations (11–13).

\[ \eta_{\text{colour}} = 32.39 + 0.03 \times (\text{Dye})_o + 18.36 \]
\[ \times (\text{H}_2\text{O}_2):(\text{COD}) - 2.18 \times (\text{H}_2\text{O}_2):(\text{Fe}^{3+}) - 1.36 \times (t_r) + 4.72 \times 10^{-5} \times (\text{Dye})_o^2 - 0.84 \]
\[ \times (\text{H}_2\text{O}_2):(\text{COD})^2 + 0.02 \times (t_r)^2 - 0.02 \]
\[ \times (\text{Dye}) \times (\text{H}_2\text{O}_2):(\text{COD}) + 0.02 \times (\text{Dye})_o \]
\[ \times (\text{H}_2\text{O}_2):(\text{Fe}^{3+}) - 1.31 \times (\text{Dye})_o \times (t_r) \]
\[ - 0.02 \times (\text{H}_2\text{O}_2):(\text{COD}) \times (t_r) + 0.01 \]
\[ \times (\text{H}_2\text{O}_2):(\text{Fe}^{3+}) \times (t_r) - 7.54 \times 10^{-5} \times (t_r)^3 \]
\[ + 8.57 \times (\text{Dye})_o^2 \times (\text{H}_2\text{O}_2):(\text{COD}) - 2.03 \]
\[ \times (\text{Dye})_o \times (\text{H}_2\text{O}_2):(\text{Fe}^{3+}) + 1.09 \times (\text{Dye})_o^2 \]
\[ \times (t_r) + 7.51 \times (\text{Dye}) \times (\text{H}_2\text{O}_2):(\text{COD})^2 \] (11)

\[ \eta_{\text{COD}} = 18.88 + 0.01 \times (\text{Dye})_o - 18.75 \]
\[ \times (\text{H}_2\text{O}_2):(\text{COD}) - 7.65 \times (\text{H}_2\text{O}_2):(\text{Fe}^{3+}) - 0.06 \times (t_r) + 5.78 \times 10^{-5} \times (\text{Dye})_o^2 \]
\[ - 0.75 \times ((\text{H}_2\text{O}_2):(\text{COD}))^2 + 0.25 \]
\[ \times (((\text{H}_2\text{O}_2):(\text{Fe}^{3+}))^2 - 0.01 \times (\text{Dye})_o \]
\[ \times (\text{H}_2\text{O}_2):(\text{Fe}^{3+}) - 0.03 \times (\text{H}_2\text{O}_2):(\text{COD}) \]
\[ \times (t_r) + 0.03 \times (\text{H}_2\text{O}_2):(\text{Fe}^{3+}) \times (t_r) \]
\[ + 7.20 \times 10^{-6} \times (\text{Dye})_o \times (\text{H}_2\text{O}_2):(\text{COD}) \]
\[ - 1.44 \times 10^{-5} \times (\text{Dye})_o^2 \times (\text{H}_2\text{O}_2):(\text{Fe}^{3+}) \] (12)

\[ \eta_{\text{TOC}} = -15.15 + 0.05 \times (\text{Dye})_o + 7.40 \]
\[ \times (\text{H}_2\text{O}_2):(\text{COD}) + 1.24 \times (t_r) - 0.49 \]
\[ \times ((\text{H}_2\text{O}_2):(\text{COD}))^2 - 7.90 \times 10^{-3} \]
\[ \times (\text{Dye})_o \times (\text{H}_2\text{O}_2):(\text{COD}) - 1.72 \times (\text{Dye})_o \]
\[ \times (t_r) + 5.40 \times 10^{-5} \times (t_r)^3 + 6.23 \times 10^{-4} \]
\[ \times (\text{Dye})_o \times ((\text{H}_2\text{O}_2):(\text{COD}))^2 \] (13)

The process dependent variables were optimised using the commercial software Design-Expert software version 6.0.8 (Stat-Ease, Inc., USA). The statistical analysis of the experimental data is presented in the analysis of variance (ANOVA) table (Table 4). The ANOVA was performed to ascertain the validity of the proposed models and to establish their suitability. The analysis also ensures that the least square regression assumptions made are not violated [38]. The models were all found to be significant as seen from the observed \( F \)-values that ranged from 15.76–45.54, implying that there is only a 0.01% chance that models with \( F \)-values this large could occur due to noise. \( P \)-values less than 0.05 indicate that the model is significant, whereas \( P \)-values greater than 0.10 indicate the model is not significant. The corresponding \( P \)-values were all <0.001, suggesting a good fit. Furthermore, all the models also adequately explained the discrepancies between the predicted and the actual experimental data. This is evident from the satisfactory quadratic fit of the correlation coefficient (\( R^2 \)) values of 0.9936, 0.9750 and 0.9160 for colour, COD and TOC reduction, respectively. The ‘lack of fit’ \( F \)-values of 1.18, 2.57 and 0.53 implies that the ‘lack of fit’ was not significant relative to the pure error. An index of assessing the model’s signal-to-noise ratio is the adequate precision ratio. A minimum value of 4 must be attained and all the models exceeded the minimum value, signifying an adequate signal for TOC, COD and colour reduction percent.

### Decolourisation

Table 3 presents the results of the decolourisation. From the table it can be seen that the Fenton process was fast and efficient in the decolourisation of RBB with over 95% colour removal for almost all the samples treated. However, the destruction of the aromatic rings was difficult, which is evident from the low mineralisation of the organic component that is reflected in the TOC values.

This was to be expected, as most Fenton processes are known to be fast with respect to decolouration. The reason for the rapid colour removal is associated with the destruction of the long conjugated \( \pi \)-systems, which causes decolouration [39]. The azo groups are attacked first by the •OH radical. The \(-N=N-\) bonds are easily opened, leading to colour loss and accounting for the fast decolouration. However, for the aromatic ring, a longer oxidation time is required to destroy the adjacent ring structure. Dye molecules have different sizes, structural units as well as different types and number of functional groups, which results in the variation of mineralisation and degradation rates [39,40]. For RBB, apart from the \(-N=N-\) (representing azo linkages), other conjugates include a benzene ring and a naphthalene ring. The absorption of the chromophore containing the main conjugates was in the visible region for the azo linkage and in the ultraviolet region for the benzene and naphthalene rings [39]. Also, within the same absorption range, variations in the absorption wavelength occur as is the case with the benzene ring, which has a relatively lower absorption wavelength than the naphthalene ring [41]. This also leads to different responses to treatment.

For all the runs, almost complete/complete colour removal of the dye was obtained within the first 10 min of the reaction. Thus, it could be safely deduced that the kinetics were first order reaction kinetics with regard to dye concentration. Many authors have similarly shown RBB decolourisation kinetics to be first order [2,39]. In fact, for some kinetic studies, for example Bali et al. [8], sufficient...
Table 4. ANOVA results of the quadratic polynomial model for Fenton-like treatment of RBB solution.

<table>
<thead>
<tr>
<th>Response</th>
<th>Source</th>
<th>Sum of squares</th>
<th>Degrees of freedom</th>
<th>Mean square</th>
<th>F-ratio</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour Removal (%)</td>
<td>Model</td>
<td>11327.69</td>
<td>17</td>
<td>666.33</td>
<td>45.54</td>
<td>&lt;0.0002</td>
</tr>
<tr>
<td></td>
<td>Residual</td>
<td>73.16</td>
<td>5</td>
<td>14.63</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Lack of fit</td>
<td>32.14</td>
<td>2</td>
<td>16.07</td>
<td>1.18</td>
<td>0.4198</td>
</tr>
<tr>
<td></td>
<td>Pure error</td>
<td>41.02</td>
<td>3</td>
<td>13.67</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>11400.85</td>
<td>22</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>R^2 = 0.9936</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>R^2_adj = 0.9718</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Adq. Prec. Ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>23.2</td>
<td></td>
</tr>
<tr>
<td>S.D. = 3.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

| COD Removal (%)   | Model          | 13896.43       | 13                 | 1068.96     | 26.98   | <0.0001 |
|                   | Residual       | 356.58         | 9                  | 39.62       | –       | –       |
|                   | Lack of fit    | 298.42         | 6                  | 49.74       | 2.57    | 0.2351  |
|                   | Pure error     | 58.16          | 3                  | 19.39       | –       | –       |
|                   | Total          | 14253.00       | 22                 | –           | –       | –       |
| R^2 = 0.9750      |               |                |                    |             |         |         |
| R^2_adj = 0.9388  |               |                |                    |             |         |         |
| Adq. Prec. Ratio  |                |                |                    |             | 16.7    |         |
| S.D. = 6.29       |                |                |                    |             |         |         |

| TOC Removal (%)   | Model          | 5003.33        | 9                  | 555.93      | 15.76   | <0.0001 |
|                   | Residual       | 458.53         | 13                 | 35.27       | –       | –       |
|                   | Lack of fit    | 292.62         | 10                 | 29.26       | 0.53    | 0.8048  |
|                   | Pure error     | 165.91         | 3                  | 55.30       | –       | –       |
|                   | Total          | 5461.85        | 22                 | –           | –       | –       |
| R^2 = 0.9160      |               |                |                    |             |         |         |
| R^2_adj = 0.8579  |               |                |                    |             |         |         |
| Adq. Prec. Ratio  |                |                |                    |             | 12.773  |         |
| S.D. = 5.94       |                |                |                    |             |         |         |

data could not be obtained due to the very fast reaction rate of the process.

**Effect of initial dye concentration**

Initial concentrations of the RBB aqueous dye solution were varied and the effect of mineralisation and degradation by Fenton-like oxidation investigated. Figure 1 shows the influence of initial dye concentrations on the treatment. The figure shows that the extent of mineralisation increases with an increase in the initial RBB concentration. However, for different concentrations, the optimal mineralisation varied. When taking the optimum values, it could be seen that for the 20 mg L\(^{-1}\) concentration, a steady increase in TOC removal up to 100 min was observed, with the optimal reduction of 44% corresponding to ratios of 7 and 12.5 for (H\(_2\)O\(_2\)):(COD) and (H\(_2\)O\(_2\)):(Fe\(^{3+}\)), respectively. Thereafter, the removal rate stabilised with no apparent contribution to TOC removal. A slight decrease was observed at the end of the oxidation time signifying the initiation of the scavenging reactions.

For an initial concentration of 510 mg L\(^{-1}\), the optimal value was attained at 52.5 min corresponding to a 52% reduction in TOC at (H\(_2\)O\(_2\)):(COD) = 7 and (H\(_2\)O\(_2\)):(Fe\(^{3+}\)) = 12.5. A subsequent increase in the reaction time for all combinations of the parameters yielded lower TOC removals, confirming that the scavenging reactions had set in. However, the optimum COD reduction at this concentration (91%) was obtained within the first 10 min of the reaction. The corresponding TOC removal was 44%. This suggests that as the reaction progressed, the decreased COD removal was by driven by the increased...
reaction between Fe$^{3+}$ and HO$_2$ (hydroperoxy radicals) leading to increased Fe$^{2+}$ regeneration (Equation (14)) [1].

$$\text{Fe}^{3+} + \text{HO}_2^- \rightarrow \text{Fe}^{2+} + \text{HO}_2^-$$  \hspace{1cm} (14)

It has been reported that removal efficiencies decrease with an increase in dye concentration [2]. This was attributed to an increase in dye molecule concentration leading to a lesser amount of available •OH radicals. However, in this study, a different trend was observed. Figure 2 shows a steady increase with an increase in the dye concentration, which could be attributed to incorporating the initial concentration and the COD of the dye in determining the amount of reagents required for oxidation.

The highest TOC reduction (67%) was obtained at a concentration of 1000 mg L$^{-1}$, however, the corresponding COD reduction was not the highest. The optimum COD reduction (85%) was achieved at the same ratio of 12 and 20 for (H$_2$O$_2$):(COD) and (H$_2$O$_2$):(Fe$^{3+}$), respectively. However, the reaction time played a significant role, as an increase from 10 to 180 min resulted in a TOC decrease and COD increase of 10%. This implies an increase in collision probability of the oxidant and catalyst overtime, thus enhancing radical generation, favouring more interactions with the dye molecules and resulting in greater COD reduction. The increase in COD signified a higher degradation, which led to the generation of more intermediate by-products, probably carboxylic in nature that resisted mineralisation.

The ability of the Fenton oxidation to effectively mineralise effluent at higher concentrations without solution interference in the process is another attractive feature of the method. This is in contrast to the photo-Fenton process, where decreased •OH concentrations and lower efficiencies result from impeding the penetration of photons into the solution at high dye concentrations [2,8]. An example is the case of the photo-Fenton oxidation of RBB where increasing the dye concentration from $5.0 \times 10^{-5}$ mol L$^{-1}$ to $1.5 \times 10^{-4}$ mol L$^{-1}$ [2] resulted in a decolourisation decrease from 98% to 88%. In the same study, for the conventional Fenton process, the performance decreased from 96% to 83% in 7.5 min. The latter could well be associated with the scavenging reactions at higher dye concentrations.

The reaction time had a significant effect on the mineralisation and degradation processes. Generally, longer reaction times provide for enhanced interactions between the Fenton reagents and the reaction mixture, which subsequently leads to better efficiencies due to sufficient contact. For all the three different concentrations studied, a reaction time of 90 min was found to be adequate for the complete reaction. This is evident from the plot in Figure 1 and the results in Table 3 that show that the contribution to TOC and COD removal by extending the reaction time beyond 95 min was marginal. Also, since achieving this marginally higher removal efficiency required not only a further increase in reaction time but also a higher concentration of the oxidant.

Therefore, it may be reasonable and more cost effective to limit the mineralisation to 95 min for concentrations of 20 and 1000 mg L$^{-1}$ and to 10 min for 510 mg L$^{-1}$.

The mineralisation profile showed that reaction times above 10 min favour the treatment in the case of 20 mg L$^{-1}$; however, for 1000 mg L$^{-1}$, an increase in reaction time decreased the mineralisation. However, for 510 mg L$^{-1}$ RBB, an increase in the reaction time increased mineralisation up to 52.5 min, which then decreased with an increase in time until it stabilised after 95 min.

**Effect of the (H$_2$O$_2$):(COD) ratio**

For effective degradation of organic contaminants in the Fenton process, the concentration of the oxidant should be sufficient to generate substantial quantities of •OH in order to degrade the organic substances [30]. Owing to
the possibility of direct action of the hydrogen peroxide and loss of the oxidant, the H₂O₂ concentration was varied starting with the minimal amount required to oxidise and subsequently mineralise the pollutant. The minimum theoretical amount necessary for oxidation was computed based on the correlation proposed by Eckenfelder [33]. Thereafter, the molar ratio of (H₂O₂):(COD) was increased to a maximum value of 12. Several works have reported that optimal performance could be achieved at ratios ranging from 2.2–9 [15,42]. However, an excess concentration of the oxidant leads to a decrease in the system’s performance through radical scavenging.

The effects of this ratio are shown in the response surface graph (Figure 3). The observable trend of the interaction of this parameter with respect to the dye concentration was an increase in the COD removal with an increase in the ratio from 2 to 7, after which it began to decrease slightly above a ratio of 9.5. This clearly indicates the effect of •OH scavenging by excess H₂O₂ at ratios above 9.5. However, an increase in the ratio from 2 to 7 resulted in a significant increase in the reaction of the pollutants, with more •OH generated from the higher amount of the H₂O₂ being made available in the system.

In summary, optimum COD removal efficiencies, as seen in Figure 3, were found to lie within a ratio range of 6.5–7.5. The optimum COD removal observed at these mass ratios was in close agreement with the results reported by dos Santos and Masini [43].

**Effect of the (H₂O₂):(Fe⁴⁺) ratio**

Many researchers have agreed that this ratio is vital to oxidation and the performance of the process. However, the value at which the best results are achieved has not been agreed upon [44]. Examples of wide variation in this ratio have been reported as the optimum, ranging from 0.6–10 [15,43,44]. In fact, values up to 150 can be found in the literature [38].

Optimising the mass ratio of (H₂O₂):(Fe⁴⁺) is significant as higher concentrations of the Fe⁴⁺ catalyst result in kinetically faster oxidation rates [30]. This could be better understood from the scheme of reactions of radical generation and Fe³⁺–Fe²⁺ formation. Dosing with sufficiently low levels of Fe³⁺ results in a low concentration of Fe³⁺–H₂O₂ complex formation, reported by Jiang et al. [14] and shown in Equations (15) and (16), which have small equilibrium constants $(3.1 \times 10^{-3})$. This stage is proceeded by Equations (17) and (18) where uni-molecular decomposition of the Fe³⁺–H₂O₂ complex generates a low amount of Fe²⁺ with a subsequent increase in the Fe³⁺ concentration enhancing the Fe³⁺–H₂O₂ complex formation and catalysing the formation of Fe²⁺ and •OH, which leads to higher oxidative efficiencies.

\[
\begin{align*}
\text{Fe}^3+ + \text{H}_2\text{O}_2 &\leftrightarrow \text{Fe}^{II}(\text{HO}_2)^{2+} + \text{H}^+ \\
\text{FeOH}^{2+} + \text{H}_2\text{O}_2 &\leftrightarrow \text{Fe}^{II}(-\text{OH})(\text{HO}_2)^+ + \text{H}^+ \\
\text{Fe}^{II}(\text{HO}_2)^{2+} &\longrightarrow \text{Fe}^{2+} + \text{HO}_2\cdot \\
\text{Fe}^{II}(-\text{OH})(\text{HO}_2)^+ &\longrightarrow \text{Fe}^{2+} + \text{HO}_2\cdot + \text{OH}^- 
\end{align*}
\]

On the other hand, an excess amount of the catalyst within the reaction mixture can also lead to lower efficiencies due to consumption of available •OH through scavenging reactions. This clearly inhibits the process [37] and decreases the pollutant management [12].

\[
\text{Fe}^{2+} + \cdot\text{OH} \longrightarrow \text{Fe}^{3+} + \text{OH}^- 
\]
This necessitates the determination of the mass ratio required to overcome the scavenging phenomenon. To establish the optimum mass ratio of \((H_2O_2):(Fe^{3+})\), the iron masses studied were in the range of 0.21–5.1, 3.8–91.0 and 8.6–206 mg for 20, 510 and 1000 mg L\(^{-1}\), respectively. Correspondingly, the ratio of 5–15 was maintained using a mass of \(H_2O_2\) ranging from 4.26–1030 mg. This mass ratio was similar to values reported in literature, i.e. 1.63 to 15.25 [15,40,43,45].

In light of the above analysis, it can be concluded that the optimum process conditions for the Fenton-like oxidation of the RBB are: \((H_2O_2):(COD) = 12\) and \((H_2O_2):(Fe^{3+}) = 20\) for COD reduction at all concentrations. For TOC reduction below a concentration of 500 mg L\(^{-1}\), a ratio of \((H_2O_2):(COD) = 7\) favours the process; at a higher concentration, a ratio of 12 results in improved TOC reduction. For the ratio \((H_2O_2):(Fe^{3+})\), a value of 12.5 is most suitable for concentrations lower than 500 mg L\(^{-1}\) and 20 for concentrations exceeding 500 mg L\(^{-1}\).

It is also of interest to note that the mineralisation values (TOC) obtained for treating an effluent were always lower than the degradation results (COD). Furthermore, the high efficiencies reported do not necessarily imply completion of oxidation [35]. The concern for wastewater mineralisation (an indicator of converting the carbons and heteroatom components of the organic compound to inorganic species) [46] is informed by the fact that the toxicity of some degradation by-products is more hazardous and persistent than the starting dye [2]. For the RBB dye, the reaction intermediates of oxidation are mainly carboxylic acid groups [23,47]. These by-products subsequently react with \(•OH\) to finally become mineralised. However, some of these carboxylic acids are recalcitrant and resist radical attack leading to observed low mineralisation [48]. Hence, high degradation and colour removal efficiencies must be complemented with mineralisation analysis [23].

In this work, the complete degradation of the wastewater was attained using the stoichiometric theoretical amounts of the Fenton reagents. Hence, the research findings negate the need for further remediation. If the degradation had been incomplete, then to attain complete degradation would have been costly and not attractive as it is generally expensive using advanced oxidation processes. This is due to the consumption of chemical reagents (catalysts and oxidisers) higher than stoichiometric quantities, which increase with treatment time [49]. The energy requirements for other AOPs further increase the operational cost. The radiation (electricity) requirement for photocatalytic reactors, have been reported by Bandara et al. [50] to gulf about 60% of the total operating cost. In light of this, AOPs have been employed to partially pre-treatment the wastewater to minimally mineralise in order to avoid unnecessary expenditure of chemicals and energy, thereby lowering the treatment cost considerably [51].

A comparison between current studies with similar reported results suggests that optimisation indeed enhanced the process. This can be seen when a comparison is made with other advanced oxidation processes. For instance, in the work of Lucas and Peres [2], 21.6% TOC removal was obtained, 28% after 480 min [6] and 51% by Arslan and Balcıoğlu [19]. Therefore, the optimised conventional Fenton oxidation is potentially a more attractive in dye treatment. This is against the backdrop that UV light, although it aids in generating more radicals, actually does not destroy the formic acid formed but slightly photo-decomposes it [23]. This might account for the observed mineralisation. This was seen in the case of a photo-Fenton reaction of RBB reported by Lucas and Peres [2], where only 46.4% was mineralised, while for Huang et al. [23], 70% of the COD was reduced. Low COD removal is an indicator that the TOC removal would be less than 40% as COD removal in the studies analysed and irrespective of initial concentration (20–10,000 mg L\(^{-1}\)) all achieved higher than 70% COD removal.

A comparison of the present experimental findings and literature values revealed that conventional Fenton-like oxidation is an effective approach for complete decolourisation, achieving the minimum discharge level for COD and appreciable TOC reduction. This suggests the effectiveness of Fenton-like oxidation under optimised operating conditions for Batik cottage industry effluents typically containing RBB in concentration ranges of 300–1000 mg L\(^{-1}\). It should be noted that the comparison was limited to only advanced oxidation processes; other processes were not considered as the indices of evaluating their process efficiencies differs. In advanced oxidation processes, mineralisation (i.e. complete destruction of the organic compound) is the specific objective while for other technologies, the amount adsorbed, retained or degraded is the target.

**Conclusions**

Mineralisation (TOC reduction), degradation (COD reduction) and colour abatement of a RBB solution at varied concentrations ranging from 20–1000 mg L\(^{-1}\) was performed based upon D-optimal statistical design by Fenton-like peroxidation. Varied working conditions were investigated with the aim of optimising the process and response surface methodology was employed to study the interactive effects of four specific variables (initial dye concentration, \((Dye)_{o}\); molar ratio of oxidant to dye COD, \((H_2O_2):(COD)\); weight ratio of the oxidant to the catalyst, \((H_2O_2):(Fe^{3+})\) and reaction time, \((t_r)\)).

The empirical equations derived from the experimental data adequately described the process throughout the examined regions. This indicates the suitability of the model and the success of the response surface methodology (RSM) in optimising the conditions of the Fenton-like oxidation treatment of RBB solutions. Also, the ANOVA showed a high coefficient of determination (<90%) and thus satisfactorily explained the process.
For concentrations of 20, 510 and 1000 mg L\(^{-1}\), the optimum %TOC reduction and oxidation time were found to be 44% for 95 min, 52% for 52.5 min and 68% for 10 min corresponding to 67, 81 and 75% COD reduction efficiencies, respectively. However, for the 20, 510 and 1000 mg L\(^{-1}\) concentrations, the optimum %COD reduction and oxidation times were 89% for 95 min, 91% for 10 min and 84% for 95 min, respectively. The determined \(R^2\) and \(R^2_{adj}\) correlation coefficients for the model equations were 0.9936 and 0.9718 for colour, 0.9750 and 0.9388 for COD and 0.9160 and 0.8579 for %TOC removal.

References