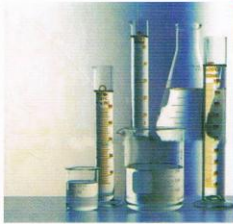


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Decolorization and Mineralization of C.I. Reactive Blue 4 and C.I. reactive Red 2 by Fenton Oxidation Process

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Abstract:

The application of Advanced Oxidation Processes (AOPs) for dyes wastewater treatment is the focus of this study. Fenton reagent as one of AOPs was applied for the minimization of organic content of colored synthetic wastewater. The reactive dyes, C.I. Reactive Blue 4 (RB4) and C.I. Reactive Red 2 (RR2) were used as the model organic pollutants. Fenton type process was examined in order to establish optimal operating conditions (pH, hydrogen peroxide (H₂O₂) and ferrous ion catalyst concentration (Fe²⁺), [Fe²⁺]/[H₂O₂] ratio, dye concentration, and temperature for maximum degradation of the investigated model colored wastewater. Degradation of studied dyes as organic pollutant was monitored on the basis of color degradation and mineralization extents of model solution, determined by UV/VIS spectrophotometer and TOC, respectively. The optimal operating conditions found were a ratio [Fe²⁺]/[H₂O₂] of 1:20, and pH 3. By using this process, almost complete color degradation of 99.8% and TOC degradation of 39.8-42.5% were achieved within 60 minutes of reaction. Pseudo-first-order degradation rate constants were found from the batch experimental data.

Keywords: Advanced Oxidation Processes (AOPs), dyes wastewater, reactive dyes, Fenton reagent, kinetic analysis

1. Introduction

Nowadays, the color of the effluent released into receiving waters has become a serious environmental problem. The discharge of pulp, paper, and textile effluents often imparts color to the receiving waters for miles downstream from the source. The color is aesthetically unpleasant and it also reduces light penetration into water decreasing the efficiency of photosynthesis in aquatic plants, thereby, having undesirable impact on their growth. In addition, some of the dyes might be toxic to some organisms.

Textile waste minimization and remediation programs around the world have demonstrated that the color problem is becoming more and more apparent as one of the major environmental tasks associated to this area. The traditional treatment techniques applied in textile wastewaters, such as coagulation/flocculation, membrane separation (ultra filtration, reverse osmosis) or elimination by activated carbon adsorption, only do a phase transfer of the pollutant, and biological treatment is not a complete solution to the problem due to biological resistance of some dyes.

In the last two decades, there has been immense research interests in the treatment of textile industry dyes with so-called "Advanced Oxidation Processes (AOPs)", not only

as a consequence of growing environmental concern tackled by legislative aspects, but also due to the success of advanced oxidation systems in overcoming the color and pollutant 'phase transfer' problem.

Advanced oxidation formed by a variety of chemicals (O₃/OH[•], O₃/H₂O₂, Fenton's reaction, modified Fenton or Fenton-like oxidation), photochemical (O₃/UVC, H₂O₂/UV, photo-Fenton, modified Photo-Fenton's oxidation) as well as near-UV-vis or solar light induced TiO₂-mediated heterogeneous photocatalytic oxidation system appear to have the ability to completely decolorize and at least partially mineralize textile industry dyes in short reaction periods without producing any exhaust gases or harmful sludge [1, 2]. Besides, no toxic and/or carcinogenic by-products have usually been observed when applying AOPs for textile dyes decolorization [3]. Among AOPs, Fenton process is very promising since the systems achieves high reaction yields, offers a cost effective source of hydroxyl radicals and it is easy to operate and maintain [4]. Fenton's reagent oxidation is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions. In an acidic environment if hydrogen peroxide is added to an aqueous system containing an organic substrate and ferrous ions, a complex redox reaction will occur [5-7]. The overall reaction is:



Fenton reagent is an attractive oxidative system for wastewater treatment due to the fact that iron is very abundant and non-toxic and hydrogen peroxide is easy to handle and environmentally safe. The renewed interest of researchers for this classical, old reactive system is today underlined by a significant number of investigations devoted to its applications in wastewater treatment [8]. The main advantage of the Fenton's reagent is its simplicity. The chemicals are readily available at moderate cost and there is no need for special equipment [9, 10]. This process could be a good option to treat and eliminate textile dyes. The process appears to have capacity to completely decolorize and partially mineralize textile industry dyes in short reaction time, as reported by some studies [4, 11-14].

Dyes are generally small molecules comprising two key components: the chromophore, responsible for the color, and the functional group that allows dye fixation onto the fibre. In terms of chemical structure, the azo compounds represent the largest group (around 50%) of all textile dyestuffs produced. In accordance with the number of such groups, the dyes are described as monoazo, diazo, triazo, etc dyes. The second classification of dyes which is based on their mode of application distinguish acid, reactive, metal complex, disperse, vat, mordant, direct, basic, and sulphur dyes. Most commonly in use today are the reactive and direct types for cotton, viscose-rayon dyeing and disperse types for polyester dyeing [15].

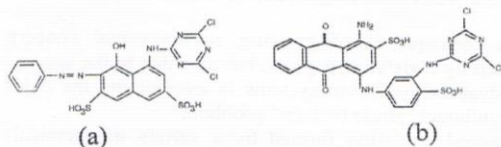


Figure 1. The chemical structure of (a) C.I. Reactive Red 2 and (b) C.I. Reactive Blue 4

Table 1. The general characteristics of dyes

Dye	C.I. Reactive Blue 4	C.I. Reactive Red 2
Chemical formula	$\text{C}_{22}\text{O}_8\text{H}_{22}\text{N}_6\text{S}_2\text{Cl}_2$	$\text{C}_{19}\text{H}_{10}\text{Cl}_2\text{N}_6\text{Na}_2\text{O}_7\text{S}_2$
Molecular weight (g/mol)	637.4	615
C.I. number	595	538
λ_{max} (nm)		

Research on textile effluent decolorization has focused on fibre reactive dyes [16] for the following reasons. Firstly, reactive dyes represent an integral market share (almost 45% of all textile dyes produced annually belong to the fibre reactive class). Secondly, these dyes have low fixation rates, which results in highly colored spent dye-baths whose treatment is inadequate in conventional wastewater treatment plants [17]. Thirdly, of special concern is the reactive dyeing process, where on average of 10 times more water is consumed for preparation,

dyeing, washing and rinsing stages than for dyeing with other dye types. Reactive dyes have been identified as the most environmental problematic compounds in textile dye effluents [18, 19].

Reactive textile dyes, namely Reactive Blue 4 (RB4) and Reactive Red 2 (RR2) were chosen as refractory model pollutants. The chemical structure and some properties of the reactive dyes are presented in Fig. 1 and Table 1. These textile dyes were selected for this study since their molecular structure are known and the dyes are frequently being applied for the dyeing of cotton and nylon (polyamide) fabrics worldwide. A dye concentration of 100 mg/L was selected in the present study as previously reported [20-22] because effluents originating from the cotton and polyamide dyeing factories are usually in the range of 10-200 mg/L.

Color removal from RB4 and RR2 which were typical of the Indonesian textile industry such as batik work on cotton were studied by using Fenton reagent. The aim of the study was to examine the effect of the major system parameters such as pH, hydrogen peroxide concentration, iron catalyst concentration, dye concentration, and iron catalyst/ H_2O_2 ratio, on the decolorization of RB4 and RR2. The efficiency of the treatment will be evaluated in terms of color degradation at certain wavelength and mineralization in the term of TOC reduction.

Fenton's reagent is a solution of hydrogen peroxide and an iron catalyst that is used to oxidize contaminants or wastewaters. The Fenton process is being increasingly used in the treatment of contaminated water. The conventional 'dark' Fenton process involves the use of one or more oxidizing agents [usually hydrogen peroxide (H_2O_2) and/or oxygen] and a catalyst (a metal salt or oxide, usually iron), while the photo-Fenton process also involves irradiation with sunlight or an artificial light source, which increases the rate of contaminant degradation by stimulating the reduction of Fe(III) to Fe(II). The reactions produce a range of free radicals, which can react with most organic compounds. Reactions involving the highly reactive hydroxyl radical are the most important, and are characteristic of all advanced oxidation processes (AOPs).

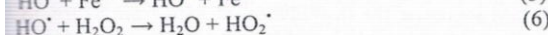
All AOPs are based mainly on hydroxyl radical chemistry. The hydroxyl radical species reacts strongly with most organic substance by hydrogen abstraction or electrophilic addition to double bonds. Free radicals further react with molecular oxygen to give a peroxy radical, initiating a sequence of oxidative degradation reactions that may lead to complete mineralization of the contaminant. In order to assess the degree of mineralization reached during AOPs, the decrease of the total organic carbon (TOC) is generally estimated. However, in the presence of real wastewaters with high organic content, these values give a global indication of the effectiveness of the treatment system adopted [23].

Production of hydroxyl radical (HO^\bullet) by Fenton reagent [24] occurs by means of addition of H_2O_2 to Fe^{2+} salts as described in (1). The ferrous ion initiates and catalyses

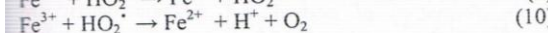
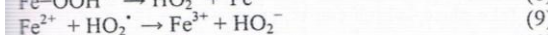
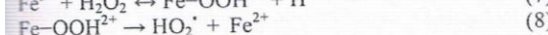
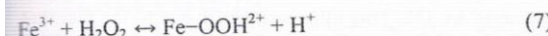
the decomposition of H_2O_2 , resulting in the generation of hydroxyl radicals, HO^\bullet [25]. Hydroxyl radicals are powerful oxidation agents that have capability to attack organic substrates (RH) rapidly and cause chemical decomposition of these compounds by hydrogen abstraction and addition to C-C unsaturated bonds [26]:



Numerous competing reactions which involve Fe^{2+} , Fe^{3+} , H_2O_2 , hydroxyl radicals, hydroperoxyl radicals and radicals derived from the substrate, may also be involved. Hydroxyl radicals may be scavenged by reacting with Fe^{2+} or hydrogen peroxide:



Fe^{3+} formed through reactions (1) and (5) can react with H_2O_2 following a radical mechanism that involves hydroxyl and hydroperoxyl radicals, with regeneration of Fe^{2+} [25, 27]:



2. Material and Methods

2.1 Chemicals and Materials

Synthetic dyes wastewater was prepared by using Reactive Blue 4 and Reactive Red 2 obtained from Fajar Setia Dyestuff in Jakarta. Hydrogen peroxide (H_2O_2 30% w/w) was acquired from Thermo Fisher Scientific Pty Ltd. Ferrous sulphate catalyst ($FeSO_4 \cdot 7 H_2O$) and other chemicals were purchased from Ajax Finechem. The initial pH of the solution was adjusted by adding diluted sulphuric acid (H_2SO_4) or sodium hydroxide (NaOH). Measurement of pH was obtained from a TPS Digital pH meter.

2.2 Experimental Details

The degradation of RB4 and RR2 dyes were carried out in batch operation. Dyes solution was prepared in distilled water. For every experiment performed, the reactor was initially loaded with 250 ml of RB4 aqueous solution, adding 5 ml of ferrous catalyst, following by adjusting pH value with 0.1 or 0.01 M of H_2SO_4 and 0.1 M of NaOH solution. Concentration of ferrous catalyst was varied within the range of 3-6 mM. Continuous mixing was maintained by means of magnetic stirrer. The reaction was initiated by adding 5 ml of H_2O_2 and the time was recorded. The reaction was terminated instantly by adding 0.5 ml of 1 N $Na_2S_2O_3$ solutions to the reaction mixture [28].

2.3 Calculation

Samples were taken periodically for analysis of color and Total Organic Carbon (TOC) degradation. Color degradation was determined by SP-8001 UV/VIS spectrophotometer while mineralization degree was determined on the basis of TOC degradation by a TOC- $V_{CPH/CPN}$ TOC Analyzer Shimadzu.

The degradation percentage of dyes is defined as follows:

$$\text{Color degradation percentage} = (1 - (c_t/c_0)) \times 100\% \quad (11)$$

where c_0 (ppm) is the initial concentration of dyes, and c_t (ppm) is the concentration of dyes at reaction time t (min). The mineralization degree is represented by (12):

$$\text{TOC degradation percentage} = (1 - (TOC_t/TOC_0)) \times 100\% \quad (12)$$

where TOC_0 (ppm) is the initial concentration of TOC, and TOC_t (ppm) is the concentration of TOC at reaction time t (min).

3. Results and Discussion

3.1 Effect of pH

Fenton oxidation as indicated by Eq. (1) is known as a highly pH dependent process since pH plays an important role in the mechanism of HO^\bullet production in the Fenton's reaction [6]. The hydroxyl radicals can be efficiently formed especially under acidic conditions [4]. To find the optimum pH for maximum degradation of the aqueous dye solutions, reactions were carried out at different pH values in the range of 2-7, by adding either H_2SO_4 or NaOH. The effect of pH on decolorization of dyes by Fenton process is shown in Fig. 2. This figure shows that pH significantly influences the dyes degradation.

At pH of more than 5, as can be shown from the figure, a very low color degradation of less than 5% was produced. At high pH, ferrous ions are unstable and they would easily form ferric ions which have a tendency to produce a colloidal ferric hydroxo complex. The generation of HO^\bullet gets slower because of the formation of this species. In the latter form, the iron catalytically decomposes the H_2O_2 into oxygen and water, without forming hydroxyl radicals, as suggested by the reaction in Eq. (6) through Eq. (10).

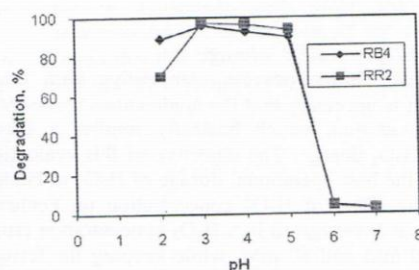


Figure 2. Effect of pH on the degradation percentage of dyes. Operating conditions: $[H_2O_2] = 30\text{mM}$, $[Fe] = 4\text{mM}$, reaction time 60 min, $[RB4] = 100\text{ppm}$, $[RR2] = 100\text{ppm}$, $T = 25^\circ\text{C}$.

Decolorization and Mineralization of C.I. Reactive Blue 4 and C.I. reactive Red 2 by Fenton Oxidation Process

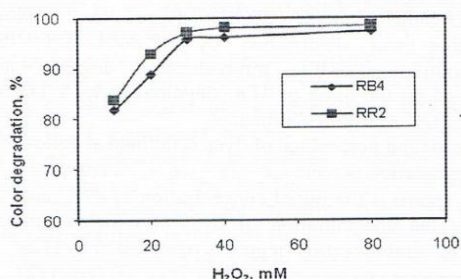


Figure 3. Effect of H₂O₂ dosage on the color degradation percentage of dyes. Operating conditions: pH = 3, [Fe²⁺] = 4mM, [RB4] = 100 ppm, [RR2] = 100 ppm, T = 25°C.

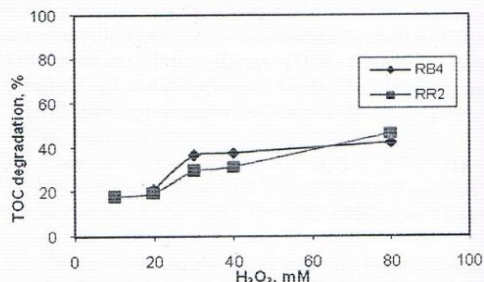


Figure 4. Effect of H₂O₂ dosage on the TOC degradation percentage of dyes. Operating conditions: pH = 3, [Fe²⁺] = 4mM, [RB4] = 100 ppm, [RR2] = 100 ppm, T = 25°C.

In contrast, at pH 2-5, the degradation percentage obtained was greater than 70%. Under these conditions, sufficient HO• are produced and Fe²⁺ is still highly soluble in water at pH between 2-5 [29]. In this study, the highest color removal was achieved at pH 3, where the degradations were 95.5 and 97.3% for RB4 and RR2, respectively which agrees with the findings of Gulkaya et al. [30] who found that the highest removal efficiency was attained at pH of 3 in Fenton's treatment of a carpet dyeing wastewater.

In another study [16] of Fenton type process for minimization of organic content in colored wastewater, two reactive dyes namely C.I Reactive Blue 49 with anthraquinone chromophore and C.I. Reactive Blue 137 with azo chromophore were used as model organic pollutants, and the best results were also achieved at pH of 3 with the color removals of 92-98.5%. Arslan-Alaton et al. also used the optimum pH of 3 for Fenton reactions in their research on the effect of Fenton treatment on aerobic, anoxic and anaerobic processes of advanced oxidation of acid and reactive dyes [29].

The initial pH value has to be in acidic range to generate the maximum amount of OH• [31]. Besides, the hydrogen peroxide and ferrous ion are more stable in low pH. Therefore, in order to attain a high degradation of dyes, further experiments in this study were conducted at pH of 3.

3.2 Effect of H₂O₂ and Fe²⁺ dosage

To make the Fenton process competitive with other processes, it is necessary that the applications represent a low cost operation, which basically implies a better control of H₂O₂ dosage. The objective of this evaluation is to select the best operational dosage of H₂O₂ in Fenton process. The effect of H₂O₂ concentration on Fenton's treatment was investigated in a H₂O₂ concentration range between 10 mM and 80 mM, while keeping the ferrous ion dose, pH, and temperature constant at 4 mM, 3, and 25°C, respectively. Fig. 3 shows the relationship between the degradation of dyes and the initial concentration of H₂O₂ in the Fenton process.

As seen from Fig. 3, the addition of H₂O₂ from 10 mM to 30 mM increases the degradation of RB4 from 81.9% to 95.9% and the degradation of RR2 from 83.8% to 97.3% for 60 minutes of reaction. The increase in the decolorization is due to the increase in hydroxyl radical concentration by addition of H₂O₂. Further increase from 30 mM to 40 mM causes no significant change in color degradation. Doubling the concentration H₂O₂ to 80 mM only improved by 1%. This little increase is due to the fact that at a higher H₂O₂ concentration scavenging of OH radicals will take place, which can be expressed by (6). The result is the formation of perhydroxyl radicals which are significantly less reactive than hydroxyl radicals and thus influence the degradation of dyes [32].

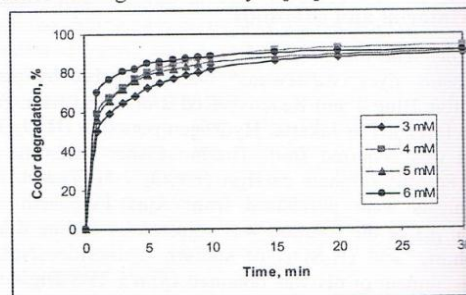


Figure 5. Effect of ferrous ion dosage on the degradation percentage of RB4. Operation conditions: [H₂O₂] = 30mM, pH = 3, [RB4] = 100 ppm, T = 25°C

TOC degradation also increases with increasing H₂O₂ concentration, due to increase in the formation of OH•. By using the concentration of 80 mM, the TOC degradations of 42.3% and 46.4% were achieved in RR2 and RB4, respectively. TOC degradations are always lower than color degradation, as can be observed from Fig. 3 and 4. Similar results were reported by Kusic et al. [16] who found that mineralization was considerably lower than the decolorization.

Decolorization and Mineralization of C.I. Reactive Blue 4 and C.I. reactive Red 2 by Fenton Oxidation Process

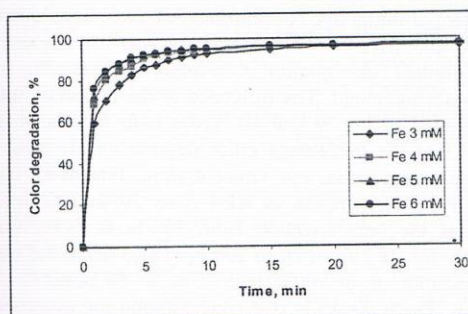


Figure 6. Effect of ferrous ion dosage on the degradation percentage of RR2. Operating conditions: $[H_2O_2] = 30\text{ mM}$, $\text{pH} = 3$, $[\text{RR2}] = 100\text{ ppm}$, $T = 25^\circ\text{C}$

The amount of ferrous ion is one of the main parameters influencing the Fenton process. In general, advanced oxidation of organic compounds is fast when ferrous ion is present at a concentration varying between 2 and 5 mM, e.g. a concentration range where sufficient HO^\cdot are produced and Fe^{2+} is still highly soluble in water at $\text{pH} 2\text{--}5$ [29]. Iron solubility is one of the obvious aspects in Fenton oxidation because the rate of hydroxyl radical formation is directly proportional to Fe^{2+} concentration according to Eq. (1).

The effect of the addition of Fe^{2+} ion the color degradation of RB4 and RR2 were studied by using the concentration range of Fe^{2+} from 3-6 mM while keeping H_2O_2 concentration constant of 30 mM. The results are shown in Fig. 5 and 6. The results indicate that the color degradation increases with increasing initial Fe^{2+} concentration especially in the first 10 minutes of reaction. When using RB4 (Fig. 5), the addition of Fe^{2+} from 3 to 4 mM raises color removal from 89.8% to 94.5% for 30 minutes of reaction. However, at Fe^{2+} of 6 mM, color degradation dropped to 91.7%. For RR2 (Fig. 6), the addition of Fe^{2+} from 3 to 4 mM gives slightly higher color removal from 96.6% to 97.3% for 30 minutes of reaction. But the color degradation remains constant with further increase of Fe^{2+} concentration. The lower degradation capacity of Fe^{2+} at small concentration is probably due to the lowest OH^\cdot radical production available for oxidation. On the other hand, the excess of Fe^{2+} may scavenge the formed hydroxyl radical as illustrated in Eq. (5), which would decrease the color degradation.

The results are in accordance with literature [33], with increasing ferrous salt concentration, degradation rate of organic compound also increases, but only to that level where further addition of iron becomes inefficient. The concentration of Fe^{2+} 4mM can be used as an optimum dosage within the treatment process.

3.3 Effect of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ratio

Both, the ferrous ion (Fe^{2+}) and H_2O_2 not only react to form hydroxyl radicals by reaction in Eq. (1), but are also scavengers of hydroxyl radicals by reactions (5) and (6). The ratio of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ should affect the rates of

hydroxyl radical production and scavenging. Hence it is important to use the optimum $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ratio [3].

Arslan-Alaton et.al [29], in their examination on acid and reactive dyes, reported that the most suitable $[\text{Fe}^{2+}]:[\text{H}_2\text{O}_2]$ molar ratio was found to be 1:5 at Fe^{2+} and H_2O_2 concentrations of 4 and 20 mM, respectively. Other reported studies gave the best ratio of 1:4.9 for decolorization of azo Reactive Black 5 by Fenton process [34]. Another related investigation conducted with the Fenton's reagent, an optimum molar ratio of 1:4 was established for the treatment of simulated acid dyebath effluent bearing azo and anthraquinone dyes [35]. In yet another study, the optimum molar ratios were determined as 1:5 and 1:7 for the Fenton oxidation of Disperse Blue 106 and Disperse Yellow 54, respectively [36]. However, Kusic et al. found that the best TOC removal for the treatment of RB49 (Reactive Blue 49) by Fenton process was obtained when using the molar ratio of 1:20 with the ferrous concentration of 0.5 mM. The differences in treatment efficiencies may be attributed to the differences in their molecular structures and molar concentrations applied.

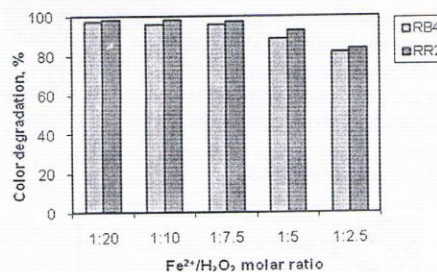


Figure 7. Effect of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ratio on the color degradation percentage of RB4 and RR2. Operating conditions: $[\text{Fe}^{2+}] = 4\text{ M}$, $[\text{RB4}] = 100\text{ ppm}$, $[\text{RR2}] = 100\text{ ppm}$ $\text{pH} = 3$, $T = 25^\circ\text{C}$

To observe the optimal initial concentration ratio of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ on the degradation of dye, the fixed concentration 4 mM of ferrous ion and concentration 100 ppm of dyes were studied while varying concentration of hydrogen peroxide to give molar ratios 1:2.5-1:20. In this study, it is clear that the best $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ratio is at the value 1:20, as demonstrated in Fig. 7 and 8. The results are in agreement with other studies using Fenton treatment on the degradation of azo reactive dyes which found that the effective system condition was established at a iron-to-hydrogen peroxide of 1:20 [4].

Decolorization and Mineralization of C.I. Reactive Blue 4 and C.I. reactive Red 2 by Fenton Oxidation Process

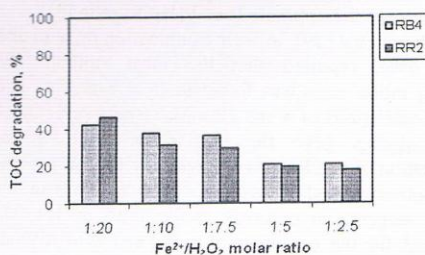


Figure 8. Effect of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ratio on the TOC degradation percentage of RB4 and RR2. Operating conditions: $[\text{Fe}^{2+}] = 4\text{mM}$, $[\text{RB4}] = 100\text{ ppm}$, $[\text{RR2}] = 100\text{ ppm}$, $\text{pH} = 3$, $T = 25^\circ\text{C}$

Fig. 7 and 8 also shows consistently that mineralization of 17.8-46.4% obtained are significantly lower in comparison to decolorization of 81.9-98.5%, in the investigated range. The highest RR2 color degradation of 98.5% and the highest TOC removal of 46.4% were attained in $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ molar ratio of 1:20. The highest RB4 color degradation of 97.4% and the highest TOC removal of 42.3% were achieved by the same $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ molar ratio. The degree of degradation is different for each of the two dyes. This indicates that molecular structure is an important factor that influences the effectiveness of dye degradation by Fenton process.

3.4 Effect of dye concentration

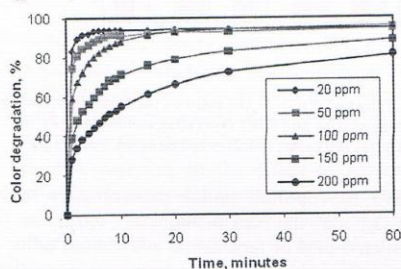


Figure 9. Effect of dye concentration on the degradation percentage of RB4. Operating conditions: $[\text{Fe}^{2+}] = 4\text{mM}$, $[\text{H}_2\text{O}_2] = 30\text{mM}$, $\text{pH} = 3$, $T = 25^\circ\text{C}$.

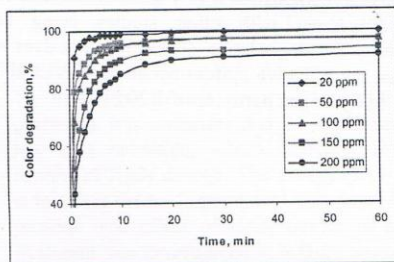


Figure 10. Effect of dye concentration on the degradation percentage of RR2. Operating conditions: $[\text{Fe}^{2+}] = 4\text{mM}$, $[\text{H}_2\text{O}_2] = 30\text{mM}$, $\text{pH} = 3$, $T = 25^\circ\text{C}$.

The effect of initial dye concentration of aqueous solution of RB4 and RR2 on Fenton process was investigated, since pollutant concentration is an important parameter in wastewater treatment. The influence of the concentration is illustrated in Fig. 9 and 10. From both figures, it is evident that the percentage color degradation decreases with increasing initial dye concentration. Increasing the initial dye concentration of RB4 from 20 to 200 ppm decreases the decolorization from 94.5% to 81%, and similarly for RR2 from 20 to 200 ppm also decreases the decolorization from 100% to 91.5%, in 60 minutes of reaction. The increase in dye concentration increases the number of dye molecules and not the OH radical concentration and so the removal ability decreases.

3.5 Effect of temperature

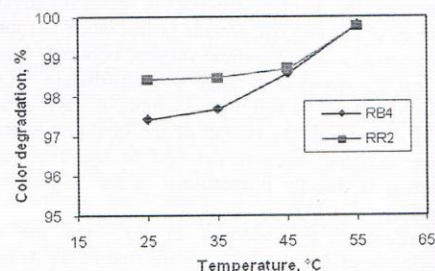


Figure 11. Effect of temperature on the degradation percentage of. Operating conditions: $[\text{Fe}^{2+}] = 4\text{mM}$, $[\text{H}_2\text{O}_2] = 80\text{mM}$, $[\text{RB4}] = 100\text{ ppm}$, $[\text{RR2}] = 100\text{ ppm}$, $\text{pH} = 3$

As a practical matter, most commercial applications of Fenton's Reagent occur at temperatures between 20-40°C [37]. A temperature range of 25-55°C was studied in order to observe the effect of temperature on the Fenton's treatment and the results are shown in Fig. 11 and 12. As can be seen from the figure, both color removal and TOC removal increase with increasing temperature. The results indicated that raising the temperature from 25 to 55° has a positive effect on the dyes degradation. At 55°C, the color degradations are 99.8% for both RB4 and RR2, and while their TOC degradations are only 42.5 and 39.8% for RB4 and RR2, respectively.

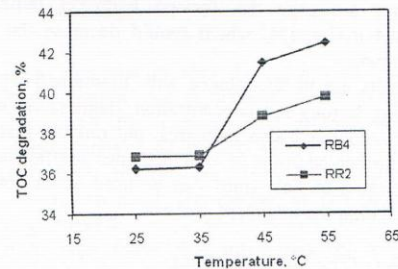


Figure 12. Effect of temperature on the TOC degradation. Operating conditions: $[\text{Fe}^{2+}] = 4\text{mM}$, $[\text{H}_2\text{O}_2] = 80\text{mM}$, $[\text{RB4}] = 100\text{ ppm}$, $[\text{RR2}] = 100\text{ ppm}$, $\text{pH} = 3$

No optimal temperature in this study was detected as opposed to the literature reports [38, 39] in which 30°C are stated as optimal temperature for Fenton's oxidation. An optimal temperature was also reported on the treatment of acid dyebath effluent by Fenton process [35], but at 50°C with 30% COD removal and 99% color removal.

Although the above reports quoted different optimal temperatures, what common in them is that removal performance declined above the optimal value due to hydrogen peroxide decomposition into oxygen and water being very significant at above 40–50°C, which is not observed in this study. In our study, there was only little change in the TOC degradation between 45 and 55°C. However, our observation was in agreement with the finding of Dutta et al. [40] who stated that there was practically no difference in the extent of degradation of reaction in the temperature between 40 and 55°C. Gulkaya et al. [30] also reported that efficiency of oxidation increased as the temperature increased from 25 to 50°C. The latter also reported that there was no change in the TOC removal between 50 to 70°C in their study on Fenton's treatment of carpet dyeing wastewater.

3.6 Kinetic analysis

In all experiments the disappearance of color during the first 10 minutes of oxidation could be described as a first-order reaction kinetics with regard to dye concentrations. Assuming pseudo-first order reaction kinetics for reactive dye degradation in aqueous solution, the decolorization rate constant, k_d , was determined from the slope of the semi logarithmic plot of color (absorbance A) versus treatment time t as shown in the following equation:

$$\ln A/A_0 = -k_d t \quad (13)$$

A pseudo-first-order kinetics was used to describe the degradation of dyes in this study as reports in other literatures [19, 41, 42]. Rate constants for the pseudo-first-order decolorization (k_d) are presented in Table 2. The fastest degradation of RB4 was achieved at 55°C. Different with the RB4, the fastest degradation for RR2 was achieved at 35°C. The rates of decolorization depend on chemical characteristics of studied dyes.

Table 2. Rate constants for the pseudo-first order decolourisation, k_d

Dye	Temperature, °C	k_d (min ⁻¹)	R ²
RB4	25	0,113	0,897
	35	0,119	0,901
	45	0,145	0,943
	55	0,335	0,967
RR2	25	0,153	0,961
	35	0,180	0,984
	45	0,067	0,972

It can be seen from the table that the rate of RB4 increased with increasing temperature. Similar results reported by Sun et al. [41] who state that the decolorization efficiency and rate of the azo dye direct Blue 15 increased with the raising of temperature from 20 to 40°C. This is because Fenton's reactions can be accelerated at high temperature and more OH• is formed [43]. However, it is convenient for the application of Fenton oxidation process to treat the contaminated wastewater since the discharge dye wastewater is normal with a high temperature.

4. Conclusion

The degradation of RB4 and RR2 aqueous solutions strongly depends on the system parameters such as pH, hydrogen peroxide and iron catalyst concentration, iron catalyst/H₂O₂ ratio, dye concentration, and temperature. It is found that the optimum conditions were obtained at pH of 3, the [Fe²⁺]/[H₂O₂] ratio of 1: 20, and temperature of 55°C. Under the optimum condition, almost complete color degradation resulted for both RB4 and RR2, while the TOC degradation was only 42.5% and 39.8% for RB4 and RR2, respectively, for 60 minutes reaction time and at an initial dye concentration of 100 ppm for both dyes. Additionally, it was also found that increasing temperature from 25 to 55°C can enhance the color and TOC degradation of both dyes. Pseudo-first-order degradation rate constants were found during the first 10 minutes of reaction.

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