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Decolorization of Sunzol Black DN conc. in aqueous solution by Fenton oxidation process: effect of system parameters and kinetic study

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ABSTRACT

The decolorization of Sunzol Black DN conc. (SBDN) in aqueous solution by Fenton oxidation process was studied. The effects of different reaction parameters such as initial hydrogen peroxide concentration ($[H_2O_2]_o$), initial Fe^{2+} concentration ($[Fe^{2+}]_o$), pH, temperature and the initial SBDN concentration ($[SBDN]_o$) on the decolorization of the SBDN dye have been investigated. The optimal reaction conditions were experimentally determined and it was found to be $[H_2O_2]_o = 4$ mM, $[Fe^{2+}]_o = 0.05$ mM, pH = 3.5 and $[SBDN]_o = 100$ mg/l at temperature 30°C. Under optimal condition, 94.5% decolorization efficiency of dye in aqueous solution was achieved within 90 min of reaction. The decolorization kinetics of SBDN by Fenton oxidation process followed the second-order reaction kinetics, and the apparent activation energy, was found to be 38.582 kJ/mol.

Keywords: Fenton oxidation process; Sunzol Black DN conc.; Hydroxyl radical; Kinetic

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1. Introduction

Nowadays most colorants have the purpose to satisfy the aesthetical needs of the environment and thus, thousands of dyes and pigments are produced in industrial scales [1]. Textile industry has shown a significant increase in the use of synthetic complex organic dyes as the coloring material [2] and this industry is a growing industry in Malaysia. It contributes about 22% of the total volume of industrial wastewater generated in the country [3]. Synthetic dyestuffs, one group of organic pollutants, are used extensively in textile, paper, printing industries and dye houses. It is reported that there are over 100,000 commercially available dyes with a production of over 7×10^5 metric tonnes per year [4,5]. Estimates indicate that approximately 10–20% of the synthetic textile dyes used is lost in waste streams during manufacturing or processing operations [6]. Colored effluents from textile wastewater which are discharged from textile industries pose a significant environmental pollution problem because of its high toxicity and possible accumulation in the environment. Even at low concentrations, textile wastewater is intensely colored. Reactive dyes have been identified as the most environmental problematic compounds in textile dye effluents [7,8].

Sunzol Black DN conc. (SBDN) is a reactive dye, characterized by having a reactive group, either a haloheterocycle or an activated double bond that when applied to a fibre in an alkaline dye bath, forms a chemical bond with a hydroxyl group on the cellulosic fibre. This type of dyes represent an increasing market share, currently about 20–30% of the total market for dyes, because they are used to dye cotton, which makes up about half of the world's fibre consumption. SBDN is not regarded as acutely toxic, but it can have various harmful effects. On irritation, it may cause sensitization by skin contact and eye irritation. Due to large-scale production and extensive application, reactive dyes can cause considerable

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environmental pollution and are serious health-risk factors. Therefore, removal of these dyes from wastewater is most desirable [9].

Over the past two decades, environmental regulatory requirements have become more stringent because of increased awareness of the human health and ecological risks associated with environmental contaminants. Therefore, various treatment technologies have been developed over the last 10 to 15 years in order to cost-effectively meet these requirements. One such group of technologies is commonly referred to as advanced oxidation processes (AOP). These processes generally involve generation and use of powerful but relatively nonselective transient oxidizing species, primarily the hydroxyl radical ($^\bullet OH$) and in some cases the singlet oxygen. This technology is now being widely applied in the treatment of synthetic dyes. Common AOPs involve Fenton and photo-Fenton processes, ozonation, electrochemical oxidation, photolysis with H_2O_2 and O_3, high voltage electrical discharge process, TiO_2 photocatalysis, radiolysis, water solution treatment by electronic beams or γ beam and various combinations of these methods [10].

Among these processes, Fenton process has been widely used [11–14] because of its relative low cost and high performance in generating $^\bullet OH$ radicals for the decomposition of refractory organic compounds. The Fenton reaction is a catalytic process for the generation of hydroxyl radicals from hydrogen peroxide, and is based on an electron transfer between H_2O_2 and iron ions acting as homogeneous catalyst. These radicals are very strong oxidizing agents capable of reacting with a wide variety of organic compounds under ambient conditions. The advantage of the Fenton's reagent is that no energy input is necessary to activate hydrogen peroxide [15]. Therefore, this method offers a cost effective source of hydroxyl radicals, using easy-to-handle reagents [16]. Fenton's reagent was found to be very effective in treating various industrial wastewater components, including aromatic amines [17], a wide variety of dyes [18], phenolic compounds [19], as well as many other substances, including pesticides [20]. The catalytic generation of hydroxyl radicals by iron ions (Fenton mechanism) is well known and can be basically described by the following reactions [21].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO^\bullet \qquad (2)$$

However, the homogeneous Fenton process requires stoichiometric amounts of Fe^{2+} and large quantities of acid, usually H_2SO_4, to produce the optimum pH (pH 3.0). After the process, the effluent must be neutralized with a base to be safely discharged [22].

The aim of this study was to investigate the influence of various parameters on the decolorization of a reactive dye called SBDN in aqueous solution by the Fenton oxidation process.

2. Materials and methods

2.1. Chemicals and reagents

The dye, Sunzol Black DN conc. (SBDN) was obtained from Oh Young Industrial Co. Ltd (Seoul, Korea). The Fe^{2+} ions were provided from solutions of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and the hydrogen peroxide (H_2O_2), 30% w/w; were all obtained from Sigma-Aldrich (M) Sdn Bhd, Malaysia. All chemicals were of analytical grade and were used without any further purification. Double distilled water was used throughout this study.

2.2. Preparation of dye solution

The dye solution was prepared by dissolving 1.0 g of SBDN in 1.0 l of distilled water to produce a stock solution of 1.0 g/l. This stock solution was diluted in accurate proportions to produce solutions of different initial concentrations.

2.3. Experimental procedure

All experiments were carried out in 250 ml-stoppered glasses (Erlenmeyer flask), which were placed in a thermostated water-bath provided with agitation at 130 rpm for 90 min. Each experimental run was performed by taking an appropriate amount of stock dye solution followed by dilution with distilled water to 200 ml and addition of pre-determined amounts of hydrogen peroxide (H_2O_2) to the flask. Solution pH values were adjusted to the desired value by using 0.10 M H_2SO_4 or 1.0 M NaOH solution. The reactions were initiated by the addition of predetermined amounts of ferrous sulfate solution to the flask. Samples were withdrawn from the reaction mixture at preset time intervals and analyzed in duplicate for the concentration of the dye left in solution.

The effect of $[H_2O_2]_o$ dosage on the SBDN decolorization was studied by varying the amount of $[H_2O_2]_o$ used (0.50 mM, 1.0 mM, 2.0 mM and 4.0 mM), while maintaining the pH, agitation speed, initial ferrous sulfate concentration, initial SBDN concentration and temperature constant at 3.36, 130 rpm, 0.050 mM, 100 mg/l and 30°C, respectively. The solutions were agitated in a thermostated water-bath shaker and analyzed periodically.

The effect of the $[Fe^{2+}]_o$ dosage in the oxidation of SBDN was also studied. Different $[Fe^{2+}]_o$ concentrations (0.010 mM, 0.025 mM, 0.050 mM and 0.10 mM) were added along with 200 ml of 100 mg/l SBDN solution with the optimum value of $[H_2O_2]_o$. The parameters of the solution were maintained at pH 3.36, 30°C and agitation speed of 130 rpm.

The effect of pH on SBDN decolorization was studied with varied initial pH of dye solution from 2.0, 2.5, 3.0, 3.5 to 4.0 using 0.10 M H_2SO_4 and 1.0 M NaOH, while maintaining agitation speed, temperature, initial concentration of dye, the optimum values of $[Fe^{2+}]_o$ and $[H_2O_2]_o$ at 130 rpm, 30°C and 100 mg/l. The flasks were agitated in a thermostated water-bath shaker for a period of 90 min while samples were withdrawn periodically for analysis.

The effect of initial SBDN concentration in the decolorization process was studied by varying the amount of $[dye]_o$ used for the experiment (25, 50, 75 and 100 mg/l) employing the optimum amounts of $[H_2O_2]_o$, $[Fe^{2+}]_o$ and pH previously determined. The reaction temperature and agitation speed were maintained at 30°C and 130 rpm.

The effect of reaction temperature was studied at 30, 40 and 50°C using 200 ml of 100 mg/l SBDN solution which was agitated with the optimum amounts and value of $[H_2O_2]_o$, $[Fe^{2+}]_o$, $[dye]_o$ and pH at 130 rpm.

2.4. Analytical method

The UV-Vis spectra of the SBDN dye were recorded from 200 to 1100 nm using a UV-Vis spectrophotometer (Shimadzu, model UV 1601, Japan) with a spectrometric quartz cell (1 cm path length). The maximum absorbance wavelength (λ_{max}) of SBDN was found to be 392 nm. Therefore, the concentration of dye in the reaction mixture at different reaction time was determined by measuring the absorption intensity at λ_{max} = 392 nm and from a calibration curve. Prior to the measurement, a calibration curve was obtained by using the standard SBDN solution with known concentrations. Because the reaction continued after sampling, the measurement of absorbance of reaction solution was done within 1 min. The decolorization efficiency of SBDN was defined as follows:

$$\text{Decolorization efficiency }(\%) = \left[1-(C_o / C_t)\right] \times 100 \tag{3}$$

where C_o (mg/l) is the initial concentration of SBDN and C_t (mg/l) is the concentration of SBDN at reaction time, *t* (min).

3. Results and discussion

3.1. Effect of the initial H_2O_2 concentration

The effect of H_2O_2 dosage on the decolorization of SBDN was examined by varying initial concentration of H_2O_2 from 0.50 mM, 1.0 mM, 2.0 mM to 4.0 mM and the results are shown in Fig. 1. It can be seen that the decolorization efficiency of the dye increases with the increase in the initial concentration of hydrogen peroxide. The decolorization efficiency increases from 30.67% to 77.54% as a consequence of increasing H_2O_2 dosage from 0.5 mM to 4 mM at 10 min of the reaction. This is due to the oxidation power of Fenton process which was improved with increasing •OH radical amount in solution obtained from the dissociation of hydrogen peroxide [23–25]. However, it can be seen that after a period of 40 min there was no appreciable increase in the decolorization efficiency as the reaction tends to equilibrium. At the reaction time of 90 min, decolorization efficiencies of 0.50, 1.0, 2.0 and 4.0 mM H_2O_2 dosage were 93.07, 94.39, 96.03 and 96.55%, respectively.

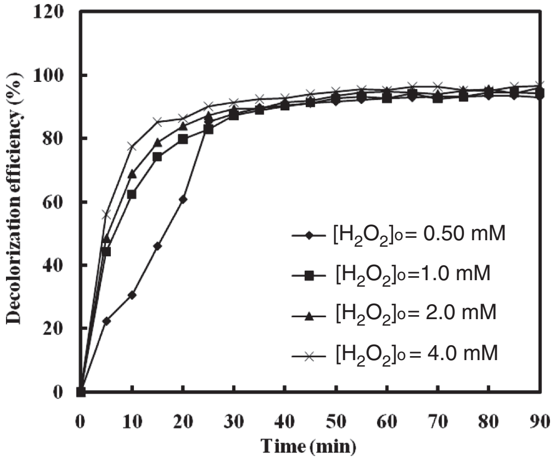

Fig. 1. Effect of initial H_2O_2 concentration on the decolorization of SBDN during Fenton oxidation process. Reaction conditions: $[dye]_o$ = 100 mg/l, $[Fe^{2+}]_o$ = 0.050 mM, pH = 3.36, *T* = 30°C and agitation speed = 130 rpm.

3.2. Effect of the initial Fe^{2+} concentration

In order to study the role of initial concentration of Fe^{2+} on the decolorization of SBDN, a series of experiments were conducted with different $[Fe^{2+}]_o$ from 0.010 mM to 0.10 mM and the results obtained are presented in Fig. 2. The results, Fig. 2, the effect of $[Fe^{2+}]_o$ on the decolorization of the dye by Fenton oxidation indicated that the decolorization of SBDN is remarkably dependent on the $[Fe^{2+}]_o$ at fixed $[H_2O_2]_o$ and $[dye]_o$. At a low $[Fe^{2+}]_o$ (0.010 mM), the decolorization efficiency was 46.77% at the 90 min reaction time. Whereas for 0.025 mM, 0.050 mM and 0.10 mM, the decolorization efficiency are 95.79, 95.8 and 95.77% at 90 min reaction time, respectively. The decolorization efficiency of dye increases with the increase in $[Fe^{2+}]_o$. Nevertheless, any further increase in the concentration of Fe^{2+} beyond 0.05 mM did not show

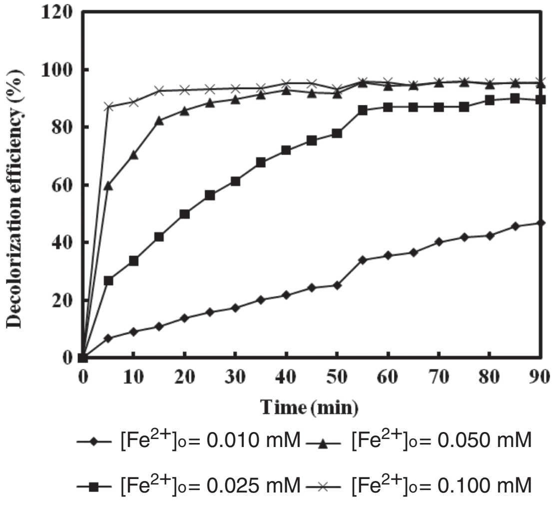

Fig. 2. Effect of initial Fe^{2+} concentration on the decolorization of SBDN during Fenton oxidation process. Reaction condition: $[dye]_o$ = 100 mg/l, $[H_2O_2]_o$ = 4.0 mM, pH = 3.36, Temperature = 30°C and agitation speed = 130 rpm.

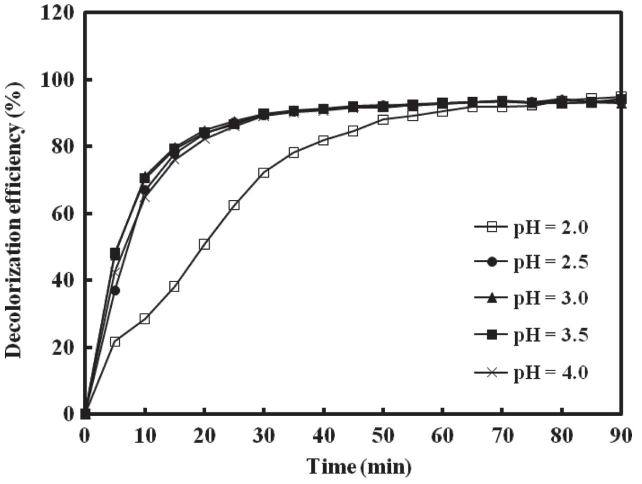

Fig. 3. Effect of pH on the decolorization of SBDN during Fenton oxidation process. Reaction conditions: $[dye]_o$ = 100 mg/l, $[H_2O_2]_o$ = 4.0 mM, $[Fe^{2+}]_o$= 0.050 mM, temperature = 30°C and agitation speed = 130 rpm.

any significant enhancement in the reaction as demonstrated by the results. Therefore, considering the need to remove Fe^{2+} from the solution before discharge, the optimal Fe^{2+} concentration was selected as 0.050 mM for the decolorization of 100 mg/l SBDN. Moreover, the work of Behnajady et al. [26] revealed that the use of a much higher concentration of Fe^{2+} could lead to the self scavenging of $^{\bullet}OH$ radical by Fe^{2+} and induce the decrease in decolorization rate of pollutants.

3.3. Effect of pH

The pH of solutions is the key parameter of the treatment efficiency for Fenton's reagent, which controls the production rate of hydroxyl radical and the concentration of Fe^{2+} [27]. The effect of initial pH value of solutions on the decolorization of SBDN was studied in the pH range of 2.0–4.0 and the results are shown in Fig. 3. The results indicated that the decolorization of dye was significantly influenced by the pH of the solution. There is no optimal pH-value but an optimal pH range from 3.0 to 3.5. At this range, there is a 90% decolorization of SBDN at 35 min reaction compared to the percentage decolorization (78%) obtained at pH 2.0 in 35 min. This is because, at low pH (2.0), the reaction could be slowed down because hydrogen peroxide can stay stable probably by solvating a proton to form an oxonium ion (Eq. 4). An oxonium ion ($H_3O_2^+$) makes hydrogen peroxide electrophilic to enhance the stability and presumably to reduce substantially the reactivity with ferrous ion.

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \tag{4}$$

$$^{\bullet}OH + H^+ + e^- \rightarrow H_2O \tag{5}$$

At the same time, the formed complex species $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ also react more slowly with hydrogen peroxide. In addition, the scavenging effect of the $^{\bullet}OH$ radical by H^+ is severe [28] as shown in Eq. 5.

3.4. Effect of temperature

The effect of temperature on the decolorization of SBDN was studied at different temperatures of 30°C, 40°C and 50°C and the results are shown in Fig. 4. It can be seen that temperature exerts a strong effect on the decolorization rate of SBDN and the decolorization was accelerated by increase in temperature. From the figure, it is indicated that temperature at 50°C gives the highest decolorization efficiency compare to 40°C and 30°C. This is because higher temperature increases the reaction rate between hydrogen peroxide and any form of ferrous/ferric ions (chelated or not), thus increasing the rate of generation of oxidizing species such as $^{\bullet}OH$ radical or high-valence iron species [28]. At the same time, at higher temperatures the amount of hydrogen peroxide needed could be reduced [26].

3.5. Effect of the initial concentration of SBDN

The decolorization of different concentrations of SBDN was studied and the results are shown in Fig. 5.

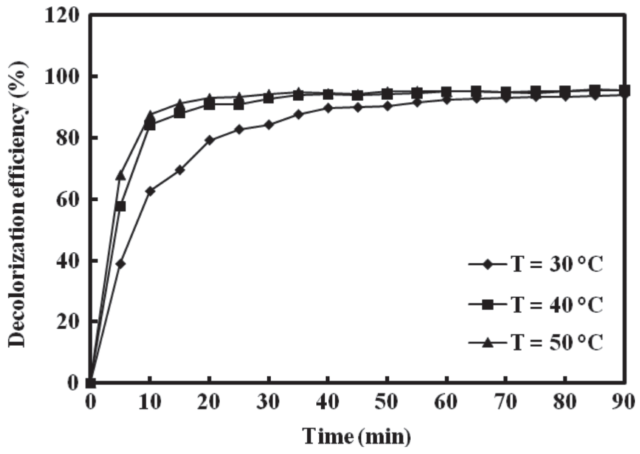

Fig. 4. Effect of temperature on the decolorization of SBDN by Fenton oxidation. Reaction conditions: $[\text{dye}]_o$ = 100 mg/l, $[H_2O_2]_o$ = 4.0 mM, $[Fe^{2+}]_o$ = 0.050 mM, agitation speed = 130 rpm and pH = 3.50.

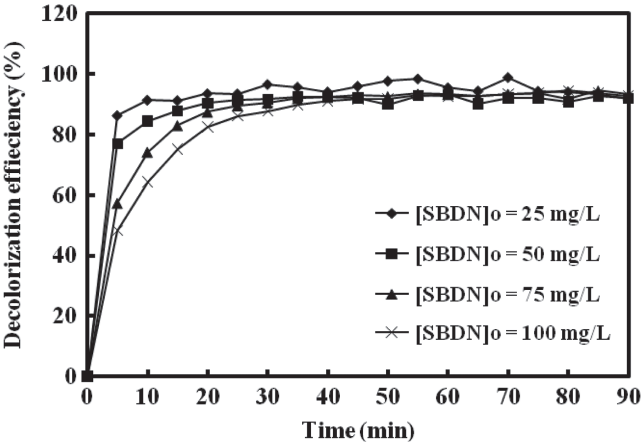

Fig. 5. Effect of initial SBDN concentration on its decolorization during Fenton process. Reaction conditions: $[H_2O_2]_o$ = 4.0 mM, $[Fe^{2+}]_o$ = 0.050 mM, temperature = 30°C, agitation speed = 130 rpm and pH = 3.50.

It was observed that the decolorization of dye increases with the decrease in initial SBDN concentration. As the concentration of dye increase from 25 to 100 mg/l, the decolorization efficiency of dye decreased from 93% to 82% within the first of 20 min of reaction. Increase in the concentration of the dye implies that more dye molecules will be available to be scavenged by the same amount of $^{\bullet}$OH generated, which lead to a decrease in the decolorization efficiency of SBDN [29].

3.6. Kinetic study

The kinetics of SBDN decolorization by Fenton oxidation process under various reaction conditions was investigated. In the present study, zero-, first- and second-order reactions kinetics were used to study the decolorization kinetics of SBDN by Fenton oxidation process. The expressions guiding the reaction kinetics are presented below:

Zero-order reaction kinetics:

$$dC_A/dt = -k_0 \tag{6}$$

First-order reaction kinetics:

$$dC_A/dt = -k_1 C_A \tag{7}$$

Second order reaction kinetics:

$$dC_A/dt = k_2 {C_A}^2 \tag{8}$$

where C_A is the concentration of SBDN, k_0 (mg/l min^{-1}), k_1 (min^{-1}) and k_2 (l/mg min^{-1}) represent the apparent kinetic rate constants of zero-, first- and second-order reaction kinetics, respectively and t is the reaction time [30].

Integrating Eqs. (6)–(8), the following equations could be obtained.

$$C_A = -C_o k_o t \tag{9}$$

$$\ln\left(C_{Ao}/C_A\right) = k_1 t \tag{10}$$

$$1/C_A - 1/C_{Ao} = k_2 t \tag{11}$$

where C_A is the concentration of SBDN at reaction time, t.

Regression analysis based on the zero-, first- and second-order reaction kinetics for the decolorization of SBDN in Fenton oxidation process was conducted to investigate the best reaction conditions which best fit the process and second-order reaction was more favored. The results of the regression analysis are shown in Table 1. The results obtained at the optimum experimental conditions, Table 1 serial numbers 7, 11, 12, 14 and 20, show that the values of the regression coefficients for: (a) zeroth order is in the range of 0.4985 to 0.6548 with an average of 0.5663; (b) first order is in the range of 0.8122 to 0.9087 with an average of 0.8412; and (c) second order is in the range of 0.9097 to 0.9846 with an average of 0.9628. These results indicate that the second order reaction kinetics best described the decolorization of the SBDN via Fenton process.

To study the effect of temperature on the kinetics and to allow for the determination of the Arrhenius-type dependence of the kinetic constant, k, the reaction temperature was varied from 30–50°C. The obtained results are shown in Table 1 (serial numbers 14 to 16) with a

Table 1
The zero-, first- and second-order kinetic rate constants for the decolorization of SBDN at different reaction conditions

No	$[SBDN]_o$ (mg/l)	pH	$[H_2O_2]_o$ (mM)	$[Fe^{2+}]_o$ (mM)	Temp (°C)	Zero-order		First-order		Second-order	
						k_o (mg/l min^{-1})	R^2	k_1 (min^{-1})	R^2	k_2 (l/mg min^{-1})	R^2
1	100	3.36	0.5	0.05	30	7.4193	0.794	0.2429	0.8941	0.0122	0.9507
2	100	3.36	1	0.05	30	5.5325	0.6387	0.209	0.9128	0.0122	0.9823
3	100	3.36	2	0.05	30	5.2418	0.583	0.2179	0.9028	0.0152	0.9819
4	100	3.36	4	0.05	30	4.8168	0.5012	0.2183	0.8485	0.0178	0.9861
5	100	3.36	4	0.01	30	2.605	0.9685	0.0322	0.9565	0.0004	0.9343
6	100	3.36	4	0.025	30	6.347	0.9257	0.1588	0.9834	0.005	0.8612
7*	100	3.36	4	0.05	30	4.2895	0.4985	0.1902	0.8334	0.0145	0.9097
8	100	3.36	4	0.10	30	3.5503	0.2851	0.1567	0.5452	0.0149	0.8133
9	100	2.00	4	0.05	30	7.3625	0.9116	0.208	0.9214	0.0081	0.9334
10	100	2.50	4	0.05	30	5.5095	0.5893	0.2029	0.8395	0.0117	0.9778
11*	100	3.00	4	0.05	30	5.0324	0.5444	0.1923	0.8122	0.0115	0.9589
12*	100	3.50	4	0.05	30	5.0765	0.5531	0.1931	0.8285	0.0114	0.9714
13	100	4.00	4	0.05	30	5.4000	0.6006	0.2000	0.8555	0.0114	0.9772
14*	100	3.50	4	0.05	30	1.1126	0.6548	0.0393	0.9087	0.0021	0.9835
15	100	3.50	4	0.05	40	1.6777	0.5538	0.0632	0.8146	0.0041	0.9784
16	100	3.50	4	0.05	50	1.8558	0.6011	0.0728	0.828	0.0054	0.9507
17	25	3.50	4	0.05	30	7.041	0.6433	0.7761	0.7405	0.1403	0.8532
18	50	3.50	4	0.05	30	7.2659	0.5028	0.5723	0.7326	0.1034	0.9513
19	75	3.50	4	0.05	30	8.3266	0.7543	0.3408	0.962	0.0294	0.7206
20*	100	3.50	4	0.05	30	7.6393	0.5806	0.3396	0.823	0.0203	0.9846

*Optimum experimental conditions.

clear indication that rate constant, k of SBDN decolorization is significantly affected by reaction temperature and increased with the increase in reaction temperature. According to the apparent kinetic rate constants at different temperatures, the apparent activation energy, E_a, for the decolorization of SBDN by Fenton oxidation was computed from the Arrhenius equation.

$$k = A\exp\left(-E_a/RT\right) \tag{12}$$

where A is pre-exponential (or frequency) factor, E_a is the activation energy (J/mol), R is the ideal gas constant (8.3124 J/(mol K)), T is the reaction absolute temperature (K).

A and E_a in Eq. 12 for the process can be evaluated from the intercept and slope of the Arrhenius plot of ln(k) versus 1/T, which in this case had a correlation coefficient of 0.9534. The apparent activation energy, E_a, obtained from the Arrhenius type plot (Figure not shown) was found to be 38.582 kJ/mol, and A value is 9.980×10^3 l/(mg min). The value of the activation energy, E_a obtained in this study is in good agreement with other study applied for azo dyes [30]. Therefore, the Arrhenius forms of the SBDN decolorization can be described as:

$$k = 9.98 \times 10^3 \exp\left(-38.582 \times 10^3/RT\right) \tag{13}$$

4. Conclusions

The decolorization of Sunzol Black DN conc. (SBDN) using Fenton oxidation process was studied. It was found that the solution pH, the initial H_2O_2 concentration, the initial Fe^{2+} concentration, the initial dye concentration and the temperature are the main factors that have strong influences on the decolorization of SBDN by Fenton oxidation process. The optimal operation parameters for the Fenton oxidation of SBDN were 4.0 mM $[H_2O_2]_o$, 0.050 mM $[Fe^{2+}]_o$ for 100 mg/l $[\text{dye}]_o$ at an initial pH of 3.50 with 30°C temperature. Under this condition, 94.5% decolorization efficiency of the SBDN dye in aqueous solution was achieved after 70 min reaction. The kinetic study indicated that the decolorization kinetics of SBDN followed the second-order kinetic. The apparent activation energy E_a, for the decolorization of SBDN by Fenton oxidation was determined to be 38.582 kJ/mol.

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