The Kinetic Model for Decolourization of Commercial Direct Blue 2 Azo Dye Aqueous Solution by the Fenton Process and the Effect of Inorganic Salts

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ABSTRACT

The study of Fenton's oxidation and degradation of Direct Blue 2 (DB2) as the commercial azo dye in synthetic aqueous solution has been accomplished. The optimum oxidative degradation reaction conditions were achieved as follows: pH = 3.50, $[H_2O_2]$ = 1.1×10^{-3} M, $[Fe^{2+}]$ = 1.0×10^{-4} M for [DB 2] = 1.0×10^{-4} M. Under optimal conditions, 80% of decolouration efficiency was carried out within 15 min of reaction. An engagement between the kinetics of the colour removal rates (ln k_2) versus $L_{azo\ bond}$ was carried out at the different pH levels. The colour removal rate was increased with decreasing of $L_{azo\ bond}$, in the order of pH: 3.5 > 5.0 > 2.5. The second-order kinetic model provided the best correlation of the data. Effects of various inorganic anions (such as Cl^-, SO_4^{2-}, CO_3^{2-}, etc.) was studied to enhance the oxidation efficiency of Fenton reaction. Advanced oxidation technologies were developed in this study especially with dealing with contaminated textile wastewater over the use of chemical treatment.

INTRODUCTION

The textile industry is a major source of outflowing industrial wastewater due to more exhaustion of water during process operations. This industrial wastewater contains chemicals such as alkalis, acids, dyes, surfactants and matter high in biochemical oxygen demand (Razzak & Hossain 2016). As the textile industry uses more water than any other industry globally, virtually all wastewater discharged is highly polluted. Water consumption of an average-sized textile mill about 50 gals per kg of fabric manufactured daily (Luo et al. 2016). The most plentiful of these compounds are azo dyes, which exemplify 70% of the world dye product. Large volumes of industrial wastewater with high scales of azo dyes (about 250 $mg.L^{-1}$) are every day vacuous by many industries around the world in the surface water. The stability and complexity of the dye structure make it more difficult to degrade when it is present in the textile wastewater (Garcia-Segura & Brillas 2016). Therefore, the mineralization of dyes generated by the textile industry is the main challenge and environmental concern (Holkar et al. 2016). There are several methods currently used to remove wastewater contamination in the fabric, but they are not universally applicable and are not cost-effective for all dyes (Nidheesh et al. 2013). In the last years, the problem of a high toxic level of wastewater has been tried by Advanced Oxidation Processes (AOPs) (Sharma et al. 2018). AOPs are based on the in-situ generation of

hydroxyl radical (HO•, E° (HO•/H_2O) = 2.80V) (Dewil et al. 2017). The Fenton system is one of the most used techniques to degrade different organic pollutants such as azo-dyes by hydroxyl free radical generated from the hydrogen peroxide molecules reduction with Fe^{2+} ions at acidic pH (Jin et al. 2017).

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^{2+} + H^{+} \qquad \ldots(2)$$

$$Fe(OOH)^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet} \qquad \ldots(3)$$

In Fenton oxidation process, hydroxyl free radical prefer to attack the azo bond (–N=N–) of the dye molecule by cleaving it to produce aromatic amines and inorganic ions such as NH_4^+ (Trovó et al. 2016). For the treatment of industrial textile wastewater containing dyes; the AOPs are effective techniques for degradation of aromatic compounds consequent to the electrophilic aromatic exchange of HO• which then leads to open the aromatic ring (Mousset et al. 2014). The goal of the other treatment is reducing the chemical oxygen demand of the industrial textile wastewater. Typically, these two targets require various chemical reagents like H_2O_2 and Fe^{2+} coincide to either azo bond or chemical oxygen demand loadings (Dehghani et al. 2016). This manuscript reports the colour removal or COD removal kinetics of the DB 2 which contains diazo bond, by Fenton oxidation process. The goals of this study were: (1) to determine the best molar ratio of

H_2O_2/Fe^{2+} through Fenton oxidation process of DB 2 at optimum pH according to the colour removal kinetics with constant Fe^{2+} and variable H_2O_2; (2) at the optimum conditions, estimation of the effects of either azo bond loading factor ($L_{azobond}$) or COD loading factor (L_{COD}) at different pH values in relation to the colour removal kinetic classify and COD removal of DB2 by Fenton oxidation process; (3) at optimum conditions on degradation of DB2, study the effect of the inorganic anions such as sulphate, carbonate chloride and bicarbonate

MATERIALS AND METHODS

Chemicals

Direct Blue 2 (DB2) (Ciba Specialty Chemicals Inc). H_2O_2 (30%W/W), Na_2SO_3 and $FeSO_4.7H_2O$ were obtained from Merck and BDH. NaOH (99%) and H_2SO_4 (99%) were used to adjust the pH which was purchased from Appli Chem (GmbH). To estimate the concentration of hydrogen peroxide, a solution of ammonium metavanadate NH_4VO_3 (BDH) was prepared. Its molar concentration was 0.062 M dissolved in sulfuric acid, with a concentration of 0.058 M. KCl (99%), NaCl (99%), Na_2CO_3 (99.0%), $NaHCO_3$ (98%), Na_2SO_4 (99%) and K_2SO_4 (99%) were obtained from Fluka. All solutions were prepared with distilled water. The main characteristics and chemical structure of DB 2 dye are as shown in Table 1 and Fig. 1.

Experimental Procedure

The colour removal of the azo dye DB 2 solutions was followed quantitatively by measuring the decrease in absorbance at max = 570 nm using (UV/VIS, Model SP-3000 OPTIMA) spectrophotometer. The chemical oxygen demand (COD) was determined by the method described in EPA method

410.4 (Luo et al. 2016, Razzak & Hossain 2016). H_2O_2 was quantified spectrophotometrically as described by Nogueira (Nogueira et al. 2005). The degradation of DB 2 was carried out by the Fenton process using a batch reactor (total volume of 1 L) under constant agitation with a magnetic stirrer and room temperature ranged from 35±2°C. The experiments were conducted as the following:

1. To determine the effect of the primary concentration of H_2O_2 (0.22×10^{-4} to 4.4×10^{-3} M) on the removal kinetics of DB 2 (1×10^{-4} M). The experiments were conducted with a constant concentration of iron ions (1×10^{-4} M) and pH 3.5. A desired amount of $FeSO_4.7H_2O$ was added to each experiment. Either 1 M H_2SO_4 or 1 M NaOH was used to adjust the pH at the specified value, the proper amount of H_2O_2 was added to each batch reactor. To estimate the dye decolourization, 10 mL of sample was immediately analysed at 1, 3, 5, 7, 10, 15, 20, 30, 45 and 60 min.

2. For this step of oxidation, the effect of $[H_2O_2]$ was in the range of 1.0×10^{-5} to 2.5×10^{-4} M, the stock solution of $[H_2O_2]$ was 1.1×10^{-3} M and pH of the dye solution was constant at 3.5 on decolourization rate of [DB 2] = 1.0×10^{-4} M.

3. The most favourable molar ratio H_2O_2/Fe^{2+} was experimentally determined by changing either H_2O_2 or Fe^{2+} concentrations as described in the first and second steps. In the literature review, H_2O_2 and Fe^{2+} doses were determined by carrying out several experiments at different ratios of H_2O_2 and Fe^{2+} doses (Kehinde & Abdul Aziz 2014, Garcia-Segura & Brillas 2016, Luo et al. 2016).

4. Experiments were achieved at three pH values (2.5, 3.5 and 5.0) and different $L_{azobond}$ for the Fenton oxidation process. The colour removal (decolourization) kinetic
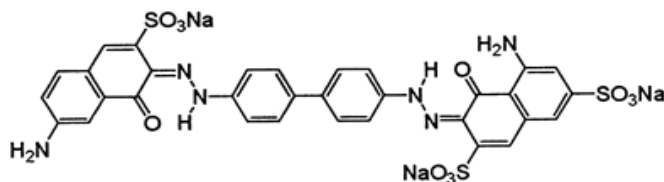

Fig. 1: Chemical structure of DB2.

Table 1: Characteristics of DB 2.

Properties	Value
Chemical formula	$C_{32}H_{12}N_6Na_3O_{11}S_3$
Molar Mass	831 g/mol
Functional group	Diazo
Color, λ max (nm)	Deep Purple, 570

of 1.0×10^{-4} M of DB 2, was studied at different $L_{azo\ bond}$ (1.0, 0.75, 0.5 and 0.25) which are equivalent to H_2O_2 concentrations (2.0×10^{-4}, 2.7×10^{-4}, 4.0×10^{-4} and 8.0×10^{-4} M), respectively for the demolition of azo group bond at a constant H_2O_2/Fe^{2+} molar ratio of 11.

5. The COD removal of DB 2, was studied at different L_{COD} (1.0, 0.75, 0.5, and 0.25) at H_2O_2/Fe^{2+} molar ratio equal to 11. Different H_2O_2 concentrations: 1.4×10^{-2}, 1.9×10^{-2}, 2.8×10^{-2} and 5.6×10^{-2} M equivalent to L_{COD} (1.0, 0.75, 0.5, and 0.25) were used for the COD removal, for the reason that the empirical COD concentration gained at 1.0×10^{-4} M DB 2 solution was 224 mg O_2 L^{-1} (COD = 7.0×10^{-3} M).

6. The effect of 1.0 % of inorganic salts on decolourization of DB 2 at (1.0×10^{-4} M) was investigated. 10 g of inorganic salt was added to 1 L batch reactor for each experiment.

7. To ensure the removal of residual hydrogen peroxide H_2O_2, 100 μL of 1.0 M sodium sulphate Na_2SO_3 solution, was added to all samples before the analysis by UV-Vis. Thus, the residual of H_2O_2 was destroyed and Fenton reactions were stopped (Holkar et al. 2016). While, to measure the COD concentration in the treated water, the interference from residual H_2O_2 was removed by addition of Na_2CO_3 (20 g/L) and placed in a water bath at 90°C for 60 min (Wu and Englehardt 2012, Nidheesh et al. 2013).

RESULTS AND DISCUSSION

Results presented here are based on the batch system of degradation of DB 2 by Fenton oxidation. The parameters for colour removal (decolourization) efficiencies such as loading azo bond factor ($L_{azo\ bond}$) or COD loading factor

(L_{COD}) were studied; which are defined by Eqs. 4 and 5, respectively (Trovó et al. 2016, Sharma et al. 2018). In oxidation processes using the Fenton's reagent, the amount of oxygen O_2 available in H_2O_2 must be measured to produce free hydroxyl radicals $HO^\bullet$ responsible for the breakdown of the azo bond and the intermediate organic compounds (Sharma et al. 2018). Therefore, the dosage of H_2O_2 required should be based on the initial $L_{azo\ bond}$, L_{COD} of DB 2, and O_2 supplied by H_2O_2, respectively.

$$L_{azo\ bond} = \{[DB\ 2]_{initial}\ (M)\}/O_{2\ available}\ (M) \qquad \ldots(4)$$

$$L_{COD} = \{COD_{initial}\ (M)\}/O_{2available}\ (M) \qquad \ldots(5)$$

Where, $DB2_{initial}$ and $COD_{initial}$ are the initial concentration and the chemical oxygen demand of DB 2 dye, respectively. Dye decolourization efficiency was calculated as follows:

$$(\%)\ Dye\ colour\ removal\ efficiency = (1 - C_t / C_0) \times 100 \qquad \ldots(6)$$

Where, C_t and C_0 (mol.L^{-1}) are the concentrations of DB 2 dye at reaction time t and 0, respectively. The chemical oxygen demand removal percentage was calculated as follows:

$$(\%)\ COD\ removal = (1 - COD_t / COD_0) \times 100 \qquad \ldots(7)$$

Where, COD_t and COD_0 are the chemical oxygen demand of DB 2 dye at reaction time t and 0, respectively.

Effect of the H_2O_2 Dose on the Removal of DB 2

In the Fenton process, hydrogen peroxide plays an essential role in contaminant removal efficiency. Therefore, it was necessary to find the optimum hydrogen peroxide concentrations. The decolourization of 1.0×10^{-4} M DB 2 was evaluated in the range of (0.22×10^{-4} and 4.5×10^{-3} M) H_2O_2 and constant amount of ferrous iron (1×10^{-4} M or 5.6 mg/L) to find the optimal oxidant dosage. The effect of hydrogen peroxide
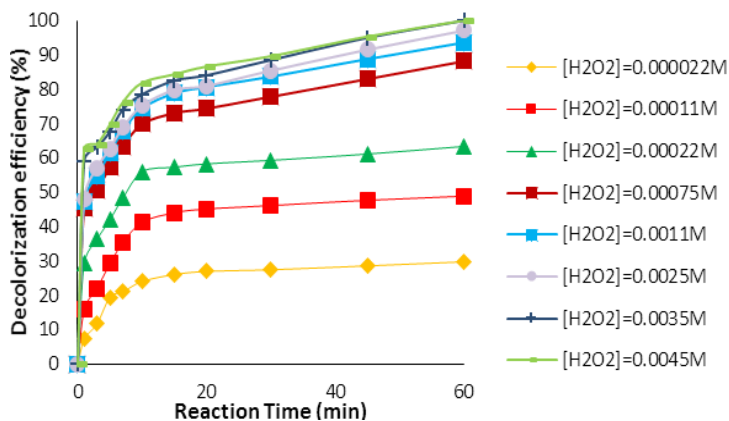

Fig. 2: DB 2 reaction time effect on decolourization of dye by Fenton oxidation at various H_2O_2 doses. Experimental conditions: [DB 2] = 1.0×10^{-4} M, [Fe^{2+}] = 1.0×10^{-4} M and pH = 3.5.

concentration and reaction time are shown in Fig. 2. At the concentration of 0.22×10^{-4} M, the colour removal of DB 2 was 24.0 % after 10 min of the reaction. However, the increment of peroxide dosage till 1.1×10^{-3} M, a colour removal was reached at a higher level of 74.0%. The concentration of 1.1×10^{-3} M H_2O_2 was selected as the best concentration and used in all experiments to estimate the effects of Fe^{2+} concentration on DB 2. At H_2O_2 concentration of higher than 1.1×10^{-3} M, the decolourization efficiency of dye solution showed little considerable efficiency, which may be due to the reaction of hydroxyl radicals with H_2O_2 and scavenging of $HO^{\bullet}$ radicals takes place as shown in Eq. 8 (Liu et al. 2017).

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad k_1 = 2.7 \times 10^7 \text{ M}^{-1}.\text{S}^{-1} \dots(8)$$
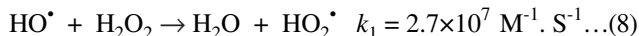
The kinetics of influence of H_2O_2 concentration on DB 2 decolourization

Because of different side reactions occurring at the same time, the kinetic study of Fenton oxidation is highly complicated. Two models of kinetic studies were experimented to achieve the kinetics parameters. The first and second-order reaction, have been tested to fit the experimental data obtained from the colour removal experiments. The correlation coefficient

(R^2) was used in the comparison of the two models. The data of Table 2 illustrate that the first-order model was not useful enough for proper parameter selection may due to the low correlation parameters, while the second-order reaction was much better. The results illustrated that the colour removal kinetics of DB 2 followed the second-order model very well.

Fig. 3 shows that the DB 2 colour removal kinetic rates at constant iron ions of 1.0×10^{-4} M increase with the H_2O_2 concentration in two steps. The first step was at the small amount of H_2O_2 ranged 0.22×10^{-4} to 1.1×10^{-3} M, the DB 2 colour removal kinetics increased slowly with a rate constant, k = 2×10^6 $[H_2O_2]$ + 416.97 and with higher correlation coefficient value of R^2 = 0.9715. The second step was at the concentration of H_2O_2 was increased from 1.1×10^{-3} to 4.5×10^{-3} M, DB 2 colour removal kinetics was increased, and a rate constant K = 372437 $[H_2O_2]$ + 2014.7 and correlation coefficient R^2 was decreased to a value of 0.8561 (Fig. 3). The positive effect of DB 2 colour removal kinetics values was observed with a high concentration of H_2O_2 may be due to the high production of hydroxyl free radical. When H_2O_2 concentration was larger than 1.1×10^{-3} M (Fig. 3), the DB 2 colour removal kinetics was linearly increased, the

Table 2: First and second orders kinetic parameters and correlation coefficients for each H_2O_2 concentration. Experimental conditions: $[Fe^{2+}]$ = 1.0×10^{-4} M, pH= 3.5 and [DB 2] = 1.0×10^{-4} M.

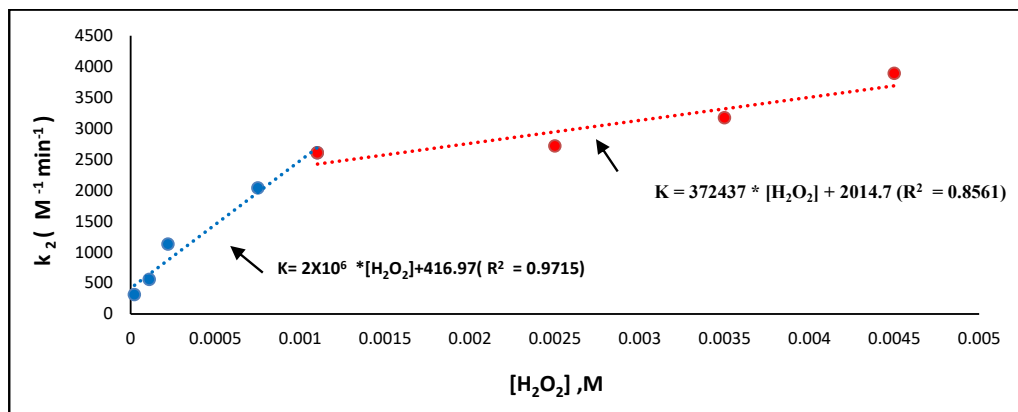| $[H_2O_2]$ (M)	H_2O_2/Fe^{+2}	First-order		Second-order	
		K_1 (min^{-1})	R^2	K_2 (M^{-1}.min^{-1})	R^2
4.5×10^{-3}	45	0.1355	0.7649	3890	0.9233
3.5×10^{-3}	35	0.1227	0.7472	3171	0.9124
2.5×10^{-3}	25	0.1171	0.8322	2714	0.9547
1.1×10^{-3}	11	0.1148	0.8418	2604	0.9567
7.5×10^{-4}	7.5	0.0994	0.8186	2035	0.9343
2.2×10^{-4}	2.2	0.0704	0.8799	1128	0.9468
1.1×10^{-4}	1.1	0.0737	0.8786	556	0.9332
0.22×10^{-4}	0.22	0.0268	0.9168	312	0.9323

Fig. 3: Correlations among the second order kinetic constants versus H_2O_2 used, obtained during DB 2 decolourization by Fenton process. Initial conditions: $[Fe^{2+}] = 1 \times 10^{-4}$ M, pH= 3.5 and [DB 2] = 1.0×10^{-4} M.

regression coefficient value was decreased at the same time. It suggests that the overdosed H_2O_2 was scavenging hydroxyl free radicals excessively (Eq. 8). Consequently, 1.1×10^{-3} M H_2O_2 was selected as the optimum concentration on DB 2 colour removal kinetics.

Effect of Fe^{2+} Doses on the Removal of DB 2

The influence of Fe^{2+} stimulation on the removal of DB 2 was examined using the different Fe^{2+} concentrations. The $[Fe^{2+}]$ were in range of 1.0×10^{-5} to 2.5×10^{-4} M with constant H_2O_2 concentration of 1.1×10^{-3} M. Increase of the concentration of $[Fe^{2+}]$ from 1.0×10^{-5} to 1.0×10^{-4} M had the positive effect on the removal rate for DB 2 (Fig. 4). The colour removal was increased from 22.0 % to 74.0 % at 10 min of the reaction, that effect may be due to the activity of Fe^{2+} in initiating the degradation of H_2O_2 to generate hydroxyl free radicals as a part of Fenton process. These radicals can reacted with DB 2 instantly, that lead to DB 2 degradation (Lucas & Peres 2006). When the concentration of Fe^{2+} was increased to higher than 1.0×10^{-4} M, a slight increase in the decomposition rate may have occurred and that improved the function of Fe^{2+} as a scavenger of HO^{*} (Eq. 9). Hence, the optimum Fe^{2+} concentration of the removal of DB 2 was selected as 1.0×10^{-4} M.

$$Fe^{2+} + HO^{\bullet} \quad Fe^{3+} + OH^{-} \quad k_2 = 3 \times 10^{8} \ M^{-1}.S^{-1} \quad \dots (9)$$

The Kinetics of Influence of Fe^{2+} Concentration on DB 2 Colour Removal

Two kinetic models were studied to estimate the effect of Fe^{2+} concentrations on the decomposition kinetics of DB 2. Table 3 shows the kinetic parameters of the study. The regression coefficient (R^2) values of the second-order reaction were higher than the first-order and we concluded that the colour removal kinetics of DB 2 obeys to the second-order kinetics model. The correlation between the second-order kinetics of the DB 2 colour removal and different Fe^{2+} concentrations (from 1.5×10^{-5} to 2.5×10^{-4} M) are presented in Fig. 5. Fig. 5 elucidates that the DB 2 colour removal kinetic average increase with the increase of Fe^{2+} in two varied steps as well: (1) At low concentration of Fe^{2+} ranged from 1.5×10^{-5} to 1.0×10^{-4} M, the DB 2 colour removal kinetics was increased clearly with a slope of 3.0×10^{7}. (2) At high concentration of Fe^{2+} (from 1.5×10^{-4} to 2.5×10^{-4} M), DB 2 colour removal kinetics increased also but the slope (9.0×10^{6}) was decreased. At low colour removal kinetics in the second step in comparison with the first step, the proposition may lead to that Fe^{2+} was higher than the need for consumption amount of $HO^{\bullet}$ (Eq. 10). Thus, the amount of hydroxyl free radicals available to oxidize DB 2 dye became very low. The positive effect of Fe^{2+} on the DB 2 colour removal kinetics assured that Fe^{2+} stimulate by fast dissociation of H_2O_2 into $HO^{\bullet}$ radicals;
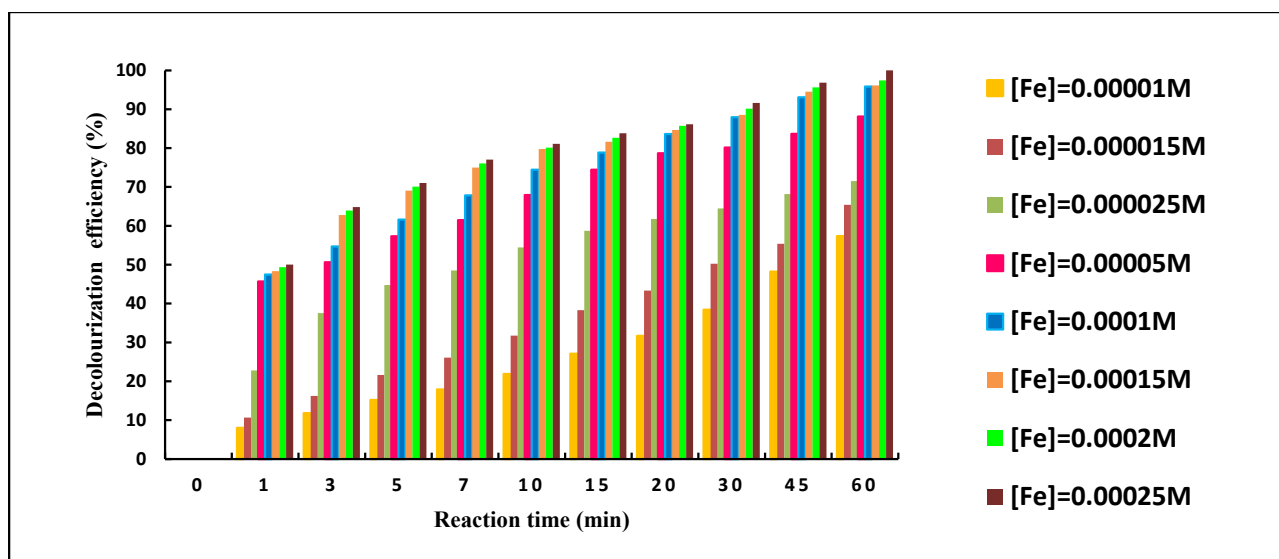

Fig. 4: DB 2 Decolourization by Fenton's reagent oxidation at different Fe^{+2} concentrations. Experimental conditions: $[H_2O_2] = 1.1 \times 10^{-3}$ M, pH=3.5 and [DB 2] = 1.0×10^{-4} M.
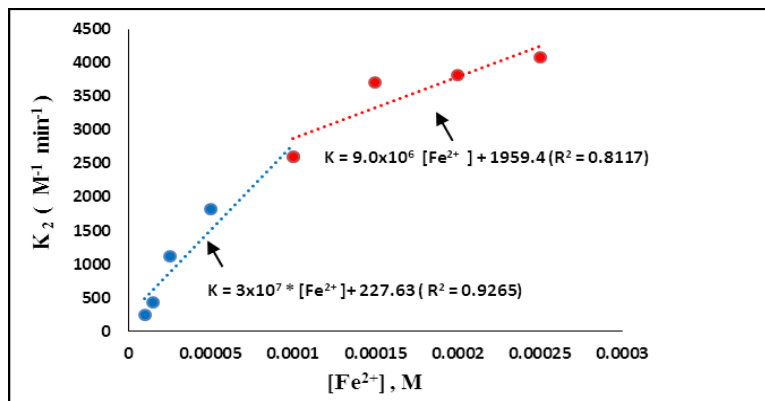
Fig. 5: Correlation between the second-order kinetic constants versus Fe^{2+} used found during DB 2 decolourization by Fenton process. Primary conditions: $[H_2O_2] = 1.1 \times 10^{-3}$ M, pH = 3.5 and [DB 2] = 1.0×10^{-4} M

Table 3: First and second-order kinetic parameters and regression coefficients for each Fe^{2+} concentrations. Experimental conditions: [DB 2] = 1.0×10^{-4} M, $[H_2O_2] = 1.1 \times 10^{-3}$ M and pH = 3.5.

$[Fe^{+2}]$ (M)	H_2O_2/Fe^{2+}	First-order		Second-order	
		K_1 (min^{-1})	R^2	K_2 (M^{-1}. min^{-1})	R^2
1.0×10^{-5}	110	0.0223	0.9259	255	0.9446
1.5×10^{-5}	73	0.0353	0.9524	435	0.9733
2.5×10^{-5}	44	0.0719	0.8826	1126	0.9449
5.0×10^{-5}	22	0.0922	0.7821	1820	0.9064
1.0×10^{-4}	11	0.1148	0.8418	2604	0.9567
1.5×10^{-4}	7.3	0.1403	0.8541	3707	0.9765
2.0×10^{-4}	5.5	0.1422	0.8443	3820	0.9724
2.5×10^{-4}	4.4	0.1471	0.8489	4085	0.9764

that may be due to the Fe^{2+} not capable to oxidize organic molecules. When Fe^{2+} dose is more than 1.0×10^{-4} M (Fig. 5); the DB 2 colour removal kinetics rate increased linearly with lower intensity by scavenging HO• radicals. Thus, 1.0×10^{-4} M Fe^{2+} was selected as the optimum concentration.

H_2O_2/Fe^{2+} Molar Ratio Effect on DB 2 Decolourization Kinetics

Concentrations of H_2O_2 over Fe^{2+} are important parameters to optimize for the determination of the ratio H_2O_2/Fe^{2+} to achieve the maximum Decolourization efficiency of DB 2 from aqueous solutions. The ratio has been used in the following experiments. Several studies have reported that the effect of the optimum molar ratio of Fenton reagent H_2O_2/Fe^{2+} was disparate for colour removal of azo dyes. For a perfect example, the ratio of H_2O_2/Fe^{2+} was 20:1 for C.I. Reactive Blue 4 and C.I. Reactive Red 2 (Agustina and Ang 2012), while the ratio was 40:1 for Reactive Black 5 (Lucas & Peres 2006, Dewil et al. 2017). These variations likely attributed to different proposed oxidation mechanisms

during the Fenton oxidation process of different azo dyes. Table 2 and Table 3 show the results obtained in this study, the optimum concentrations of H_2O_2 and Fe^{2+} were 1.1×10^{-3} M and 1.0×10^{-4} M, respectively. Consequently, the experimental optimum H_2O_2/Fe^{2+} molar ratio of 11 was selected for the next experiments.

Effect of pH and $L_{azo\ bond}$ on DB 2 Color Removal Kinetics

The pH effect on the Decolourization of DB 2 was achieved by a series of experiments conducted at three initial pH values 2.5, 3.5 and 5 (Fig. 6). The reaction time was 60 min and constant concentration of $H_2O_2 = 1.1 \times 10^{-3}$ M and $Fe^{2+} = 1.0 \times 10^{-4}$ M. pH of 2.5 had the negative effect on HO• radical production in the reaction of H_2O_2 with Fe^{2+} Eq. (1), This may be attributed to HO• scavenging by H+ ions; which elucidate the decrease of the colour removal efficiency at pH 2.5 (Esteves et al. 2016, Jin et al. 2017). On the other hand, at pH 3.5, the Decolourization efficiency of DB 2 rapidly increased with the increase in pH, at pH 3.5 almost

100% of Decolourization efficiency was achieved (Fig. 6). The main reason is that more Fe(OH)$^+$ is formed, which has much higher activity compared to Fe^{2+} in the Fenton process (Lopez-Alvarez et al. 2012, Trovó et al. 2016). Besides, at higher pH (pH 5), the precipitation of ferric hydroxide happen, causing the reduction in the dissolving Fe^{3+} ions. Aside from, in such circumstances, H$_2$O$_2$ is less stable, resulting in less HO$^\bullet$ radicals formed, decreasing the removal efficiency of Fenton oxidation (Mousset et al. 2014, Jin et al. 2017). Therefore, the pH 3.5 was chosen the optimum pH of Fenton oxidation process. At molar ratio of H$_2$O$_2$/Fe^{2+} equal to 11,

the effect of four $L_{azo bond}$ operator values (0.25, 0.5, 0.75, and 1.0) was evaluated.

Table 4 shows four levels of $L_{azo bond}$ and symbolized well by the second-order kinetic model. The results elucidate the significant difference in DB 2 colour removal rates at every pH and $L_{azo bond}$. The results in Table 4 approved the selection of pH 3 in Decolourization rates of DB 2 dye. The data were in harmony with previous literatures for assessment of the colour removal of Amido black 10B and Terasil Red R (Dehghani et al. 2016). The best DB 2 colour removal rates were found at the smallest $L_{azo bond}$ factor of 0.25 and higher
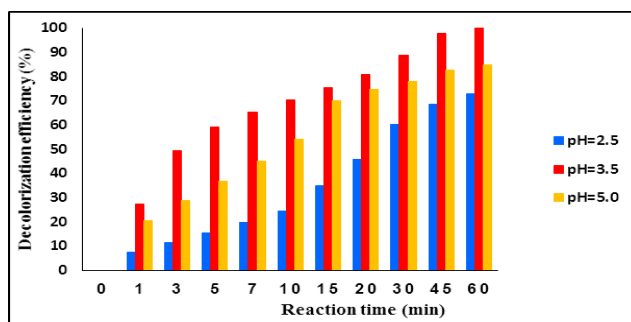

Fig. 6: Effect of pH on the colour removal efficiency of DB 2 by Fenton process. Experimental conditions; [Fe^{2+}] = 1.0×10^{-4} M, [H$_2$O$_2$] =1.1× 10^{-3} M and [DB2] = 1.0×10^{-4} M.
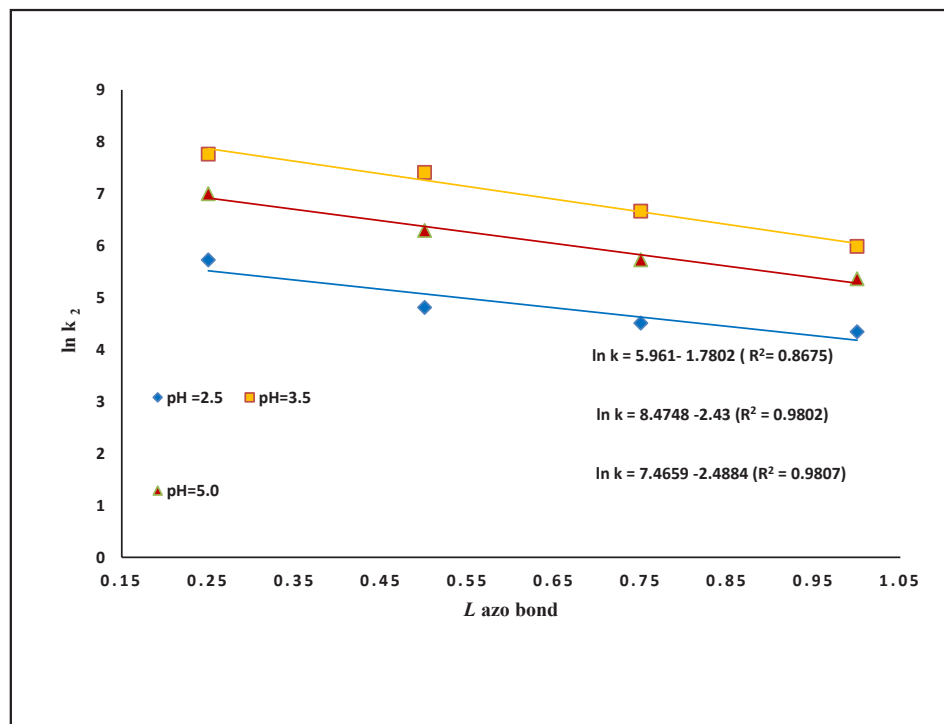

Fig. 7: Correlations between ln k$_2$ of the colour removal rates versus $L_{azo bond}$ at different pH values obtained during Fenton oxidation of 1.0 × 10^{-4} M DB 2.

Table 4: Second–order kinetic model and regression parameters for every pH and $L_{azo\ bond}$ value during Fenton oxidation of 1.0×10^{-4} M DB 2.

pH	$L_{azo\ bond}$ 1.0	$L_{azo\ bond}$ 0.75	$L_{azo\ bond}$ 0.5	$L_{azo\ bond}$ 0.25
2.5	$k_2 = 77$ $R^2 = 0.8967$	$k_2 = 91$ $R^2 = 0.970$	$k_2 = 123$ $R^2 = 0.929$	$k_2 = 307$ $R^2 = 0.8675$
3.5	$k_2 = 398$ $R^2 = 0.9895$	$k_2 = 784$ $R^2 = 0.989$	$k_2 = 1654$ $R^2 = 0.986$	$k_2 = 2351$ $R^2 = 0.98$
5.0	$k_2 = 1098$ $R^2 = 0.920$	$k_2 = 542$ $R^2 = 0.94$	$k_2 = 308$ $R^2 = 0.933$	$k_2 = 214$ $R^2 = 0.911$

k_2 values, due to the smaller $L_{azo\ bond}$ factor represented a greater amount of H_2O_2 concentration per mole of DB 2 and coincides with the larger O_2 concentration able to be used for oxidizing the DB 2 dye. Fig. 7 presents a linear relation between the second-order kinetic ln k_2 value and the $L_{azo\ bond}$ at each pH value.

COD Removal of RR120 at Different L_{COD} Factors

Although homogeneous catalytic process decolorized the DB 2, the DB 2 azo dye was not completely mineralized. For this reason it is necessary to consider complementary information about the degradation of the organic pollutants (O'Dell 1939, Holkar et al. 2016). Chemical oxygen demand (COD) gives an average measure of the oxidation state of the organic by-products generated during the degradation of DB 2 (Orhon & Çokgör 1997) . Under the optimal conditions of pH 3.5 and H_2O_2/Fe^{2+} ratio of 11, experiments using four varied L_{COD} values (0.25, 0.5, 0.75, 1.0) were performed to examine the efficiency of Fenton reagent on COD removal kinetics of DB 2 (Fig. 8). The COD removal increases with decreasing L_{COD} because the hypothetical amount of the concentration of H_2O_2 and Fe^{2+} was increased. At the
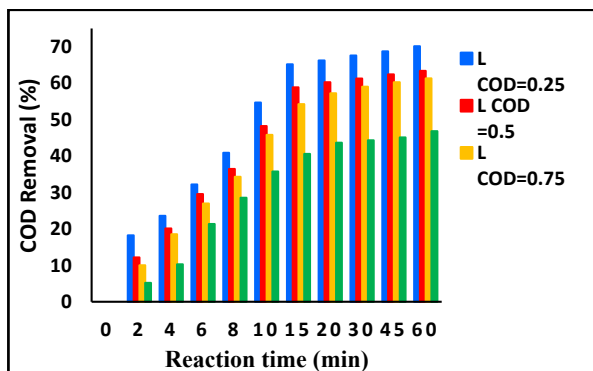

Fig . 8: Correlation between the COD removal of 1.0×10^{-4} M DB 2 (COD = 224 mg O_2 . L^{-1}) versus reaction time. Experimental conditions: pH = 3.5 and molar ratio H_2O_2 /Fe^{2+} = 11.
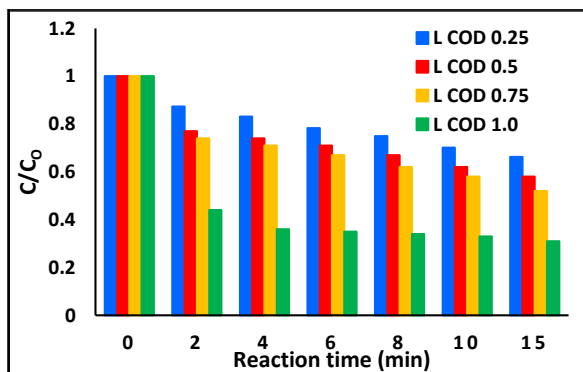

Fig. 9: The consumption of H_2O_2 using different. $L_{COD\ factor}$ Experimental conditions [DB2] = 1.0×10^{-4} M pH = 3.5.

maximum (L_{COD} = 1.0) 41% of COD was removed at 15 min while at the minimum (L_{COD} = 0.25) 65% of COD was removed at the same time. These results approved that there was a residual amount of H_2O_2 in solution after 15 min of Fenton's oxidation reaction (Fig. 9). Although, all the Fe^{2+} was transformed to Fe^{3+}, and that may decrease the reaction rate of Fe^{2+} with H_2O_2, low amount of H_2O_2 was consumed (Fig. 9). The results of consuming the H_2O_2 showed that the 82 % H_2O_2 was consumed after 15 min at L_{COD} = 1.0 while only about 43% H_2O_2 was consumed at L_{COD} = 0.25.

Effect of DB 2 Concentration on Colour Removal Kinetics

The colour removal efficiency at different concentrations of DB 2 was studied. The result was observed that the decolourization of dye increases with the decrease of primary DB 2 concentration (Fig. 10). As the concentration of dye decreased from 1.5×10^{-4} M to 5.0×10^{-5} M, the decolourization efficiency of dye increased from 43% to 93 % within the first 10 min of reaction. A decrease in the concentration of DB 2 dye reveals that lesser dye molecules will be available to scavenging by $HO^\bullet$ radicals which lead to an increase in the colour removal efficiency of DB 2 (Javaid & Qazi 2019) . Table 5 represents the second-order kinetic rates of colour removal of DB 2 at various DB 2 concentrations. Also, Table 5 shows the effect of different $[H_2O_2]/[DB\ 2]$ ratios with an increase of colour removal kinetics combined with fact that the colour removal kinetics inversely proportional with DB 2 concentration in two varied steps.

A tenuous increase in colour removal kinetic rate (from 407 to 2604 $M^{-1}\ min^{-1}$) occurred when the ratio H_2O_2/dye increases from 7.3 to 11. However, increasing the H_2O_2/dye ratio from 11 to 22, there was an acute increase in colour removal kinetic rate (from 2604 to 23415 $M^{-1}\ min^{-1}$). Furthermore, the efficiency of DB2 colour removal increases with decreasing H_2O_2/DB 2 molar ratio, which points out that a higher concentration of DB 2 was removed by using a smaller dose of H_2O_2 (Fig. 10).

The Influence of Inorganic Ions on DB 2 Colour Removal by Fenton Oxidation

The influence of some inorganic anions on the colour removal of DB 2 was tested at the optimum conditions. The experiments were designed to decompose (1.0×10^{-4} M) DB 2 in the presence of 1.0 % of inorganic salt used in this study.

Due to the expectation of the existence of a large number of anions in industrial textile wastewater, consequently, we intend to assess the decolourization of DB 2 in high doses of selected inorganic salts. The existence of inorganic anions
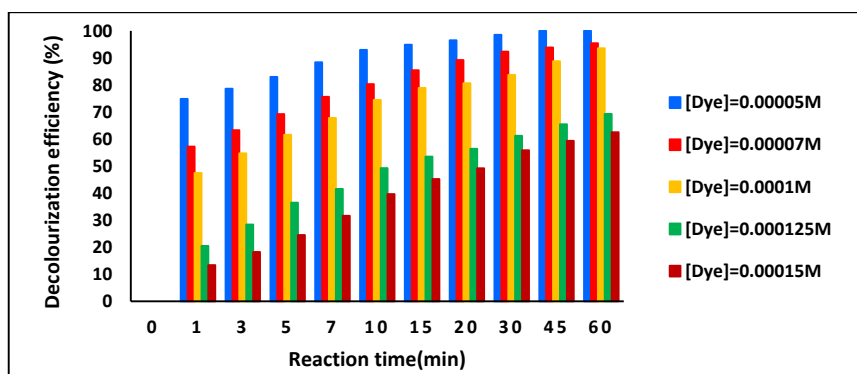

Fig. 10: Effect of initial DB 2 concentration on its colour removal efficiency during Fenton oxidation. Experimental conditions: $[H_2O_2]$ =1.1×10^{-3}M, $[Fe^{2+}]$ =1.0×10^{-4} M and pH = 3.5.

Table 5: Second-order kinetic constants and regression coefficients for each DB 2 concentration during Fenton oxidation Experimental conditions: $[Fe^{2+}]$ = 1.0×10^{-4} M, $[H_2O_2]$ = 1.1×10^{-3} M and pH=3.5.

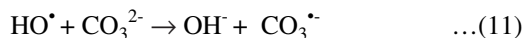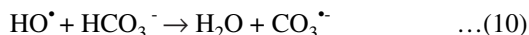| [DB 2] (M)	$[H_2O_2]/[DB\ 2]$	K_2 ($M^{-1}\ min^{-1}$)	R^2
1.5×10^{-4}	7.3	407	0.9819
1.25×10^{-4}	8.8	716	0.9714
1.0×10^{-4}	11	2604	0.9567
7.0×10^{-5}	15.7	7326	0.9501
5.0×10^{-5}	22	23415	0.94
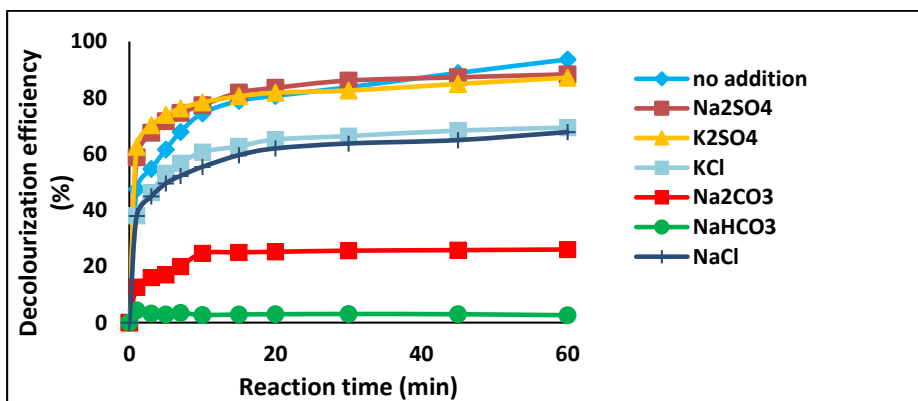
Fig: 11: Effect of addition of 1.0% inorganic anionic on DB 2 colour removal efficiency. Experimental conditions: pH = 3.5, [DB 2] = 1.0×10^{-4}M, [H_2O_2] = 1.1×10^{-3} M and [Fe^{2+}] = 1.0×10^{-4} M.

in the aqueous solution had a high effect on Fenton oxidation (Oliveira et al. 2015). In this research, the influence of carbonate, bicarbonate, sulphate and chloride on the Fenton process was evaluated. Fig. 11 shows the effect of the studied anions on the DB 2 degradation by Fenton oxidation process. Anions inhibit the degradation of DB 2 in the following order: $HCO_3^- > CO_3^{2-} > Cl^- > SO_4^{2-}$

The addition of inorganic salts displayed various suppressed behaviours in Fenton process treatment. The influence of the addition of HCO_3^- and CO_3^{2-} may be attributed to a decrease in the average of production of $HO^\bullet$ because of the formation of $CO_3^{\bullet-}$ as shown in Eqs. (10) and (11).

$$HO^\bullet + HCO_3^- \rightarrow H_2O + CO_3^{\bullet-} \qquad \ldots(10)$$

$$HO^\bullet + CO_3^{2-} \rightarrow OH^- + CO_3^{\bullet-} \qquad \ldots(11)$$

The radical $CO_3^{\bullet-}$ is less reactive than $HO^\bullet$ radicals. In the case of Cl^-, it also has a great effect on the decomposition of DB 2 because it reacts with Fe^{2+} forming complex and free radical less effective than the radical of hydroxyl as shown in Eqs. (12) and (13).

$$Fe^{2+} + Cl^- \rightarrow FeCl^+ \qquad \ldots(12)$$

$$Cl^- + HO^\bullet \rightarrow ClOH^{\bullet-} \qquad \ldots(13)$$
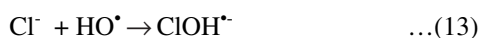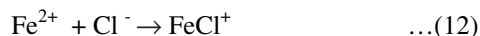
The salts of the sulphate ion appear to have less effect on the Fenton process, where sulphate ion reacts with Fe^{2+} and $HO^\bullet$, a component $HO^\bullet$ [Eqs. (14) and (15)] (Kehinde and Abdul Aziz 2014).

$$Fe^{2+} + SO_4^{2-} \rightarrow FeSO_4 \qquad \ldots(14)$$

$$HSO_4 + HO^* \rightarrow SO_4^{\bullet-} + H_2O \qquad \ldots(15)$$
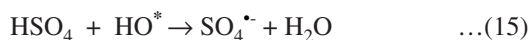
CONCLUSIONS

The parameters for loading azo bond factor ($L_{\text{azo bond}}$) or COD loading factor (L_{COD}) were highly effective parameters of colour removal (decolourization) efficiencies using the

batch system by Fenton oxidation. The results obeyed that the overdosed H_2O_2 was scavenging hydroxyl free radicals. The influence of the addition of HCO_3^- and CO_3^{2-} may be attributed to a decrease in the average of production of $HO^\bullet$ because of the formation of $CO_3^{\bullet-}$. The radical $CO_3^{\bullet-}$ is less reactive than $HO^\bullet$ radicals and the salts of the sulphate ion appear to have less effect on the Fenton process.

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