

The Kinetic Model for Decolorization of Commercial Reactive Red 120 Azo Dye Aqueous Solution by the Fenton Process and Study the Effect of Inorganic Salts

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Abstract

The degradation of a commercial azo dye Reactive Red 120 (RR120) in synthetic aqueous solution using Fenton's oxidation has been studied. The influence of different reaction parameters such as pH, hydrogen peroxide, ferrous sulfate, and the RR 120 concentration on the oxidative degradation of RR 120 have been appraised. The optimal reaction conditions were determined and it was found to be pH = 3.50, $[H_2O_2] = 1.1 \times 10^{-3}$ M, $[Fe^{2+}] = 1.0 \times 10^{-4}$ M for $[RR\ 120] = 7.5 \times 10^{-5}$ M. Under optimal conditions, 96.0% decolorization efficiency of dye in aqueous solution was achieved after 15 min of reaction. The effect of azo bond loading ($L_{azo\ bond}$), from 0.25 to 1.0, and pH values from 2.5 to 5.0 were estimated on RR 120 color removal kinetic rates. A correlation between the kinetic of the color removal rates ($\ln k_2$) versus $L_{azo\ bond}$ was carried out at the different pH levels. The color removal rate increased linearly with decreasing $L_{azo\ bond}$, in the order of pH: 3.5 > 5.0 > 2.5. All the experimental data were analyzed using the first and second-order kinetic models. The second-order provides the best correlation of the data. 67% Chemical Oxygen Demand (COD) removal efficiency of the RR 120 were achieved after 15 min of reaction by fixing the initial H_2O_2/Fe^{2+} molar ratio, COD loading factor (L_{COD}), and pH at 11, 0.25 and 3.5, respectively. Also, the effects of various inorganic anions (such as Cl^- , SO_4^{2-} , CO_3^{2-} , etc.) on the oxidation efficiency of Fenton were studied. This study can benefit planners who deal with contaminated textile wastewater using chemical treatment by advanced oxidation technologies.

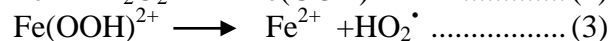
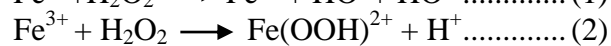
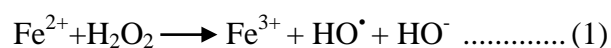
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Key words: Fenton, Kinetics, Azo dye, Advanced oxidation processes, Chemical oxygen demand.

Introduction

The textile industry is a main source of effluent industrial wastewater; due to a more consumption of water during process operations. This industrial wastewater contains chemicals such as alkalis, acids, dyes, surfactants and matter high in biological oxygen demand [1]. Thus, there is environmental effect; due to the textile industry is used more water than any other industry; globally, virtually all wastewater discharged is highly polluted. Show that the daily water consumption of an average sized textile mill about 50 gal per kg of fabric manufactured daily [2]. The most abundant of these compounds are azo dyes, which represent 70% of the world dye production. Large volumes of industrial wastewater with highly levels of azo dyes (about $250\ mg\ L^{-1}$) are daily discharged by many industries around the world in the surface water. The stability and complexity of the dye structure is more difficult to degradation when it is present

in the textile wastewater [3]. Therefore, the mineralization of dyes generated by textile industry is a main challenge and an environmental concern [4]. 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 [5]. In the last years, the problem of high toxic level of wastewater has been tried by Advanced Oxidation Processes (AOPs) [6]. AOPs are based on the in-situ generation of hydroxyl radical (HO^\bullet , $E^\circ(HO^\bullet/H_2O) = 2.80\ V$) [7]. The Fenton system is one of the most techniques used 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 [8].



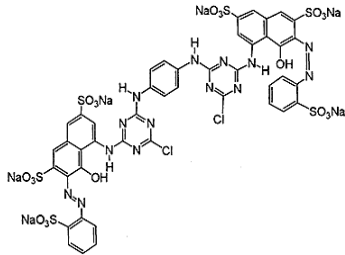
In Fenton oxidation process, hydroxyl free radical prefer to attack the azo bond ($-N=N-$) of the dye molecule by cleaving it to produce aromatic amines and inorganic ions such as NH_4^+ [9, 10]. For treatment industrial textile wastewater containing dyes; the AOPs are effective techniques for degradation aromatic compounds due to the electrophilic aromatic substitution of hydroxyl radical which then lead to open the aromatic ring [11, 12]. The goal of the other treatment is reducing the chemical oxygen demand (COD) of the industrial textile wastewater. Typically, these two targets require different chemical reagents such as H_2O_2 and Fe^{2+} according to either azo bond or COD loadings [13,14]. In this manuscript, reports of the color removal or COD removal kinetics of the Reactive Red 120 (RR 120), 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 RR 120 at optimum pH according to the color removal kinetics by fixing Fe^{2+} while varying H_2O_2 and vice versa; (2) to estimate the effects of either azobond loading factor ($L_{azobond}$) or COD loading factor (L_{COD}) at different pH values on the color removal kinetic rates or COD removal of RR 120 by Fenton oxidation process at the optimum conditions; (3) Finally, to study the effects of inorganic anions such as chloride, sulfate, carbonate and bicarbonate at optimum conditions on degradation of RR 120.

Experimental Chemicals

Reactive red 120 (RR 120) (Ciba Specialty Chemicals Inc.) was a gift from Al-Kut Textile Factory, Iraq. H_2O_2 (30% W/W), Na_2SO_3 and $FeSO_4 \cdot 7H_2O$ 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). A solution 0.062 M of ammonium metavanadate NH_4VO_3 (BDH) was prepared in 0.58 M of H_2SO_4 and used in quantification H_2O_2 concentration. 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 using distilled water. The main characteristics and chemical structure of RR 120 dye are as shown in Table (1).

Table (1)

Characteristics of Reactive red dye 120.

Properties	Value
Chemical formula	$C_{44}H_{24}Cl_2N_{14}Na_6O_{20}S_6$
Molar Mass	1470
Chemical Structure	
Functional group	Diazo
Color, λ max (nm)	Bright red, 535

Experimental Procedure

The color removal of the azo dye RR 120 solutions was followed quantitatively by measuring the decrease in absorbance at $\lambda_{max} = 535$ 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 [15]. H_2O_2 was quantified spectrophotometrically as described by Nogueira [16]. The degradation of RR 120 was carried out by Fenton process using a batch reactor (total volume of 1L) under constant agitation with a magnetic stirrer and room temperature ranged from $35 \pm 2^\circ C$. The experiments were conducted as the following:

1) To achieve the effects of the initial H_2O_2 concentration (ranging from 1.1×10^{-4} to 5.0×10^{-3} M) on the color removal (decolorization) kinetics of RR 120 (7.5×10^{-5} M), Fenton oxidation experiments were conducted at a fixed Fe^{2+} concentration of 1.0×10^{-4} M and initial pH 3.5. A desired amount of $FeSO_4 \cdot 7H_2O$ was added to each experiment. The pH was then adjusted to the required value using either (1 M H_2SO_4 or 1 M $NaOH$); the amount of H_2O_2 was calculated according to the predetermined H_2O_2 concentration; and was added to the batch reactor. For monitoring the RR 120 concentration during the color removal

process, 10 mL of sample was taken out at 1, 3, 5, 7, 10, 15, 20, 30, 45 and 60 min and were analyzed immediately.

- 2) The effects of Fe^{2+} concentration ranged from 1.0×10^{-5} to 1.0×10^{-3} M on decolorization rate of RR 120 7.5×10^{-5} M solution were studied under the optimal condition of H_2O_2 concentration of 1.1×10^{-3} M at pH 3.5.
- 3) The optimum molar ratio $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ 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 [17, 18].
- 4) Experiments were carried out at three pH values (2.5, 3.5 and 5.0) and at different L_{azobond} for the Fenton oxidation process. The color removal (decolorization) kinetic of 7.5×10^{-5} M of RR 120, was studied at different $L_{\text{azo bond}}$ (1.0, 0.75, 0.5, and 0.25) which are equivalent to H_2O_2 concentrations (5×10^{-4} ; 2.0×10^{-4} ; 3.0×10^{-4} ; and 6.0×10^{-4} M), respectively for the destruction of azo group bond at a fixed $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio of 11.
- 5) The COD removal of RR 120, was studied at different L_{COD} (1.0, 0.75, 0.5, and 0.25) at $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio equal to 11. Different H_2O_2 concentrations: 3.8×10^{-3} ; 5.2×10^{-3} ; 7.76×10^{-3} ; and 1.0×10^{-2} M equivalent to L_{COD} (1.0, 0.75, 0.5, and 0.25) were used for the COD removal, because the experimental COD concentration obtained at 7.5×10^{-5} M RR120 solution was $124 \text{ mg O}_2 \text{ L}^{-1}$ (COD = 3.64×10^{-3} M).
- 6) The effect of 1.0 % of inorganic salts on decolorization of RR 120 at (7.5×10^{-5} M) was investigated. 10 gm of inorganic salt was added to 1 L batch reactor for each experiment.
- 7) 100 μL Na_2SO_3 solution (1 M) was added to the all samples before analysis by UV-Vis to ensure removal of the residual H_2O_2 . Thus, the residual of H_2O_2 was destroyed and Fenton reactions was stopped [10, 19]. 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 [20].

Results and discussion

Results presented in following section are based on batch studies for degradation of Reactive Red 120 (RR 120) by Fenton oxidation. The parameters for color removal (decolorization) efficiencies such as loading azo bond factor ($L_{\text{azo bond}}$) or COD loading factor (L_{COD}) was studied; which are defined by Eqs. (4) and (5), respectively [10]. The stoichiometry requirements of Fenton's reagent dose should depend on the amount of available O_2 in H_2O_2 to produce hydroxyl free radical during the oxidation of azo bond and its organic intermediates [10]. Therefore, the dosage of H_2O_2 required should be based on the initial $L_{\text{azo bond}}$, L_{COD} of RR 120, and O_2 supplied by H_2O_2 , respectively.

$$L_{\text{azo bond}} = \{[\text{RR 120}]_{\text{initial}} (\text{M})\} / \text{O}_{2\text{available}} (\text{M}) \quad \dots\dots\dots (4)$$

$$L_{\text{COD}} = \{\text{COD}_{\text{initial}} (\text{M})\} / \text{O}_{2\text{available}} (\text{M}) \quad \dots\dots\dots (5)$$

Where $\text{RR 120}_{\text{initial}}$ and $\text{COD}_{\text{initial}}$ are the initial concentration and the chemical oxygen demand of RR 120 dye, respectively.

Construction of the calibration graphs

Absorption spectrum of the RR 120 dye aqueous solutions were recorded. Calibration graph of RR 120 was constructed. Into a series of 10 mL volumetric flasks an increasing volume of RR 120 working solution (0.01 M) were transferred to cover the range of the calibration graph and diluted to the mark with distilled water. The absorbance's was measured at 535 nm versus the distilled water as reagent blank as shown in Fig.(1).

The concentration of the dye (RR 120) was calculated by Beer-Lambert law at the maximum wavelength ($\lambda_{\text{max}} = 535 \text{ nm}$) by the equation:

$$A = l \epsilon C \quad \dots\dots\dots (6)$$

Where A is the absorbance; l, is the path length (cm); ϵ , is the molar absorptivity ($\text{L mol}^{-1} \text{ cm}^{-1}$) and C, is the RR 120 dye concentration (M).

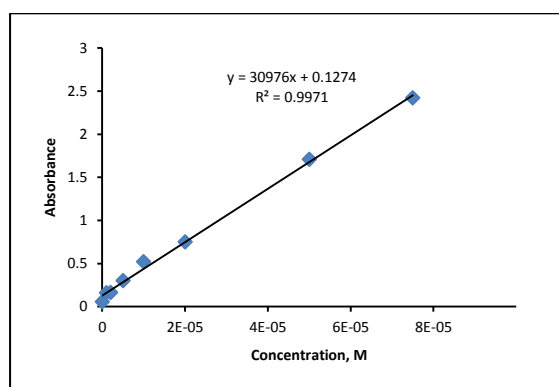


Fig.(1): Calibration graph of RR 120 dye.

Dye color removal (decolorization) efficiency was calculated as follows:

$$(\%) \text{ Dye color removal efficiency} = (1 - C_t / C_0) \times 100 \dots\dots\dots (7)$$

Where C_t and C_0 (mol L^{-1}) are the concentrations of RR 120 dye at reaction time t and 0, respectively. The chemical oxygen demand removal percentage was calculated as follows:

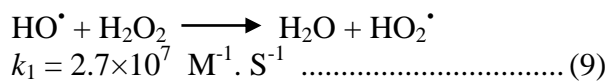
$$(\%) \text{ COD removal} = (1 - \text{COD}_t / \text{COD}_0) \times 100 \dots\dots\dots (8)$$

Where COD_t and COD_0 are the chemical oxygen demand of RR 120 dye attraction time t and 0, respectively.

Effect of the H_2O_2 dose on the removal of RR 120

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. To determine the concentration of H_2O_2 giving the maximum decolorization efficiency of RR 120, experiments were conducted, and results obtained are represented in Fig.(2). The RR 120 color removal (decolorization) with concentration of (7.5×10^{-5} M or 100.25 mg/L) was evaluated by of Fenton’s oxidation using different concentration of H_2O_2 between (1.1×10^{-4} and 5×10^{-3} M) and fixed amount of ferrous iron (1×10^{-4} M or 5.6 mg/L) to find the optimal oxidant dosage. From Fig.(2) when the hydrogen peroxide concentration was 1.1×10^{-4} M the color removal of RR 120 (40.5%) was achieved after 10 min of the reaction. However, increasing the peroxide dosage until 1.1×10^{-3} M a higher color removal was

reached (94.0%) at 10 min of Fenton oxidation. At high H_2O_2 concentration more than 1.1×10^{-3} M, the efficiency of dye removal showed no significant efficiency, which is due to the recombination of hydroxyl radicals with H_2O_2 , and scavenging of HO^\bullet radicals will occur, which can be illustrated by Eq.(9) [21]:



Therefore, 1.1×10^{-3} M H_2O_2 was chosen as the optimum concentration and used in all experiments to assess the effects of Fe^{2+} concentration on RR 120.

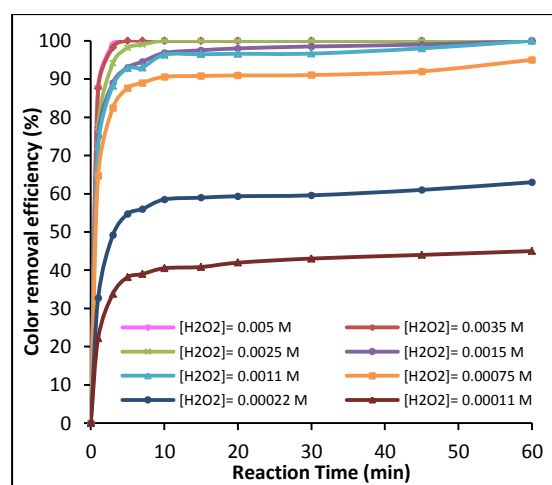


Fig.(2): RR 120 color removal efficiency by Fenton oxidation at various H_2O_2 doses.

Experimental conditions: $[\text{RR 120}] = 7.5 \times 10^{-5}$ M; $[\text{Fe}^{2+}] = 1.0 \times 10^{-4}$ M and $\text{pH} = 3.5$.

The kinetics of influence of H_2O_2 concentration on RR 120 decolorization

The kinetics of Fenton oxidation can be very complicated because of a large number of reactions occur at the same time. Two kinetic models the first-order, and the second-order have been used to fit the experimental data obtained from the color removal processes. Comparing the correlation coefficient (R^2) obtained from Table (2), it can be seen that the correlation coefficient of the first-order model was not good enough due to the low correlation coefficients, while the second-order reaction was obviously much better than based on the first-

Table (2)

First- and second- orders kinetic parameters and regression coefficients for each H_2O_2 concentration. Experimental conditions: $[RR\ 120] = 7.5 \times 10^{-5} M$; $[Fe^{2+}] = 1.0 \times 10^{-4} M$ and $pH = 3.5$.

$[H_2O_2]$ (M)	H_2O_2/Fe^{2+}	First-order		Second-order	
		K1 (min^{-1})	R^2	K2 ($M^{-1} min^{-1}$)	R^2
5.0×10^{-3}	50	1.0423	0.9088	596468	0.9722
3.5×10^{-3}	35	0.8883	0.8868	297841	0.9848
2.5×10^{-3}	25	0.6354	0.9053	202419	0.9458
1.5×10^{-3}	15	0.3058	0.8485	44238	0.9694
1.1×10^{-3}	11	0.2487	0.7511	20879	0.9434
7.5×10^{-4}	7.5	0.2084	0.7606	13811	0.9370
2.2×10^{-4}	2.2	0.0768	0.7367	1889.9	0.8159
1.1×10^{-4}	1.1	0.0448	0.7067	885.19	0.7543

order. The results illustrated that the color removal kinetics of RR 120 followed the second-order model very well. Fig.(3) shows that the RR 120 color removal kinetic rates at affixed Fe^{2+} concentration of $1.0 \times 10^{-4} M$ increase with the H_2O_2 concentration in two different steps: (1) For the lowest amount of H_2O_2 ranged from 1.1×10^{-4} to $1.1 \times 10^{-3} M$, the RR 120 color removal kinetics increased slowly with a slope of 2.0×10^7 ; and higher regression coefficient value ($R^2 = 0.9969$). (2) while, increasing the H_2O_2 from 1.1×10^{-3} to $5.0 \times 10^{-3} M$, RR 120 color removal kinetics increases with a higher slope of 1.0×10^8 and lower correlation coefficient value ($R^2 = 0.9814$) Fig.(3), the positive effect on the RR 120 color removal kinetics values at high H_2O_2 concentration is because of the higher production of hydroxyl free radical. When H_2O_2 concentration was greater than $1.1 \times 10^{-3} M$ Fig.(3), the RR 120 color removal kinetics increased linearly with the H_2O_2 concentration with lower regression coefficient value. It suggests that the overdosed H_2O_2 was scavenging hydroxyl free radicals excessively (Eq. 9). Therefore, $1.1 \times 10^{-3} M$ H_2O_2 was chosen as the optimum concentration on RR 120 color removal kinetics.

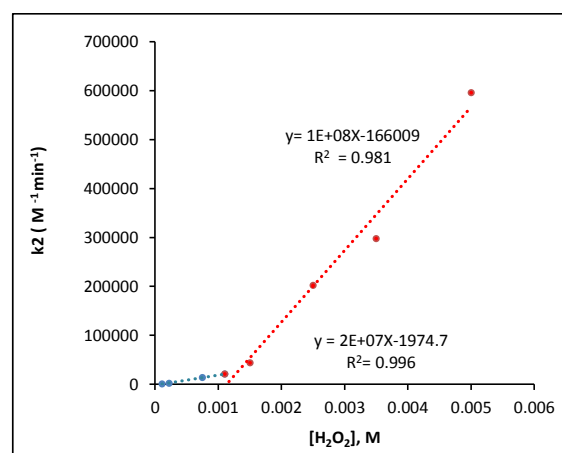
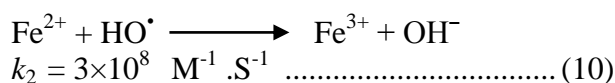


Fig.(3): Correlations between the second-order kinetic constants versus H_2O_2 concentrations, during RR 120 color removal by Fenton oxidation. Experimental conditions: $[RR\ 120] = 7.5 \times 10^{-5} M$; $[Fe^{2+}] = 1.0 \times 10^{-4} M$ and $pH = 3.5$.

Effect of Fe^{2+} doses on the removal of RR 120

The influence of Fe^{2+} (catalyst) concentration on the removal of RR 120 was examined by using the different Fe^{2+} concentrations from 1.0×10^{-5} to $1.0 \times 10^{-3} M$ while H_2O_2 concentration was fixed at $1.1 \times 10^{-3} M$. As can be observed in Fig.(4), the removal rate for RR 120 was enhanced by increasing the Fe^{2+} concentration from 1.0×10^{-5} to $1.0 \times 10^{-4} M$ and the color removal from 43.9% and 94.0% respectively was achieved at 10 min of the reaction. This is due to the fact that Fe^{2+} plays very important role in initiating the decompositions of H_2O_2 to generate hydroxyl free radicals in the Fenton process, which reacted with RR 120 instantly; resulting in the increase of RR 120 degradation [9]. Contrariwise, further increasing the Fe^{2+} concentration higher than $1.0 \times 10^{-4} M$, there is no significant enhancement in Fenton oxidation. The observed decrease in RR 120 decomposition rate upon increasing the Fe^{2+} concentration may be attributed to the role of Fe^{2+} as scavenger of hydroxyl radicals (Eq.(10)). Therefore, the optimal Fe^{2+} concentration for the removal of RR 120 was $1.0 \times 10^{-4} M$.



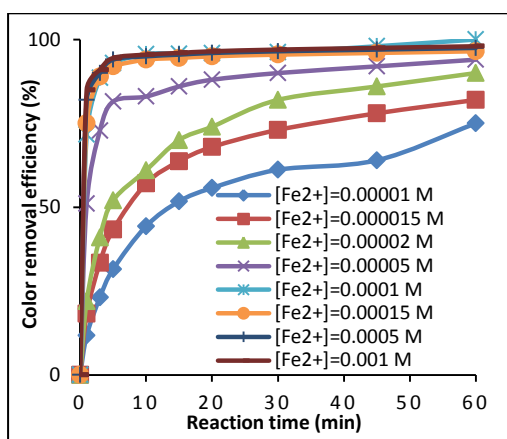


Fig.(4): RR 120 color removal by Fenton oxidation at various Fe^{2+} concentrations. Experimental conditions: $[RR\ 120] = 7.5 \times 10^{-5} M$; $[H_2O_2] = 1.1 \times 10^{-3} M$ and $pH=3.5$.

The kinetics of influence of Fe^{2+} concentration on RR120 color removal

To evaluate the effect of Fe^{2+} concentrations on decolorization kinetics of RR 120, two kinetic models were studied. Table(3) shows that the value of the regression coefficient (R^2) values of the second-order kinetic is the highest in the predominantly of the first order and this shows that the color removal kinetics of RR 120 follow the second-order kinetics model. The correlation between second-order kinetics of the RR 120 color removal and different Fe^{2+} concentrations (from 1.0×10^{-5} to $1.0 \times 10^{-3} M$) are presented in Fig.(5). Fig.(5) elucidates that the RR 120 color removal kinetic rates increase with the Fe^{2+} concentration in two different steps as well: (1) For the lowest dose of Fe^{2+} ranged from (1.0×10^{-5} to $1.0 \times 10^{-4} M$), the RR 120 color removal kinetics increased sharply with a slope of (2.0×10^8); (2) whilst increasing the concentration of Fe^{2+} (from 1.0×10^{-4} to $1.0 \times 10^{-3} M$), RR 120 color removal kinetics increased too with slower slope of (1.0×10^7). The slower color removal kinetics in the second step than the first step suggests that Fe^{2+} is overdosed by consumption considerable amount of hydroxyl free radicals (Eq.(10)). Thus, the amount of hydroxyl free radicals available to oxidize RR 120 dye will be very low. The positive effect of Fe^{2+} on the RR 120 color removal kinetics assured that Fe^{2+} acts as catalyst by rapid dissociation of H_2O_2 into HO^\bullet radicals; due to Fe^{2+} not able to oxidize organic molecules. When Fe^{2+} dose is

more than $1.0 \times 10^{-4} M$ Fig.(5); the RR 120 color removal kinetics rate increased linearly with lower intensity by scavenging HO^\bullet radicals. Thus, $1.0 \times 10^{-4} M$ Fe^{2+} was chosen as optimum concentration.

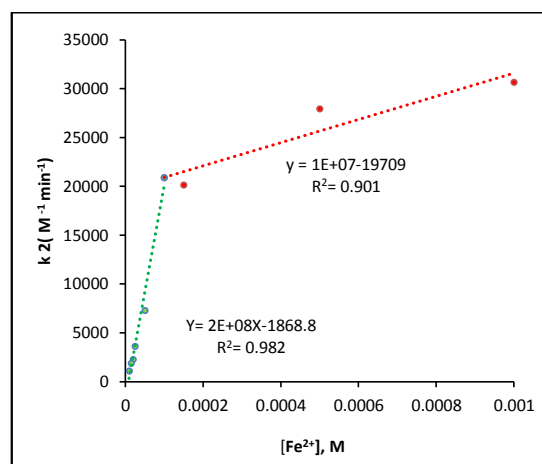


Fig.(5): Correlations between the second-order kinetic constants versus Fe^{2+} concentrations, during RR 120 color removal by Fenton oxidation. Experimental conditions: $[RR\ 120] = 7.5 \times 10^{-5} M$; $[H_2O_2] = 1.1 \times 10^{-3} M$ and $pH = 3.5$.

Table (3)

First- and second- orders kinetic parameters and regression coefficients for each Fe^{2+} concentrations. Experimental conditions: $[RR\ 120] = 7.5 \times 10^{-5} M$; $[H_2O_2] = 1.1 \times 10^{-3} M$ and $pH= 3.5$.

[Fe^{2+}] (M)	H_2O_2 / Fe^{2+}	First order		Second order	
		KI(min^{-1})	R^2	K2 ($M^{-1} min^{-1}$)	R^2
1.0×10^{-5}	110	0.0563	0.968	1112.3	0.9906
1.5×10^{-5}	73	0.0814	0.9533	1895.6	0.9906
2.0×10^{-5}	55	0.0909	0.9002	2264.9	0.9588
2.5×10^{-5}	44	0.1202	0.9197	3629.6	0.9876
5.0×10^{-5}	22	0.7526	0.1629	7296.7	0.8574
1.0×10^{-4}	11	0.2487	0.7511	20879	0.9434
1.5×10^{-4}	7.3	0.2405	0.7156	20146	0.9306
5.0×10^{-4}	2.2	0.2495	0.6783	27944	0.9025
1.0×10^{-3}	1.1	0.2517	0.6546	30655	0.9056

Influence of H_2O_2/Fe^{2+} molar ratio on RR 120 decolorization kinetics

Concentrations of H_2O_2 and Fe^{2+} are important parameters to optimize for the determination of the ratio H_2O_2/Fe^{2+} to accomplish maximum color removal efficiency of RR 120 from aqueous solutions and this ratio has been used in the following experiments. Several studies have been

reported the optimum molar ratio of H_2O_2/Fe^{2+} was disparate for color removal of azo dyes. For example the molar ratio of H_2O_2/Fe^{2+} was 20:1 for C.I. Reactive Blue 4 and C.I. Reactive Red 2 [22], while the ratio was 40:1 for Reactive Black 5 [23]. These differences may be attributed to various oxidation mechanisms during the Fenton oxidation process of different azodyes. From the results which were listed in Table (2) and Table (3) the optimum concentrations for H_2O_2 and Fe^{2+} were 1.1×10^{-3} M and 1.0×10^{-4} M, respectively. Therefore, the experimental optimal H_2O_2/Fe^{2+} molar ratio of 11 was chosen and was used in the next experiments.

Effect of pH and $L_{azo\ bond}$ on RR 120 color removal kinetics

To investigate the influence of pH on the color removal of RR 120 a series of experiments was conducted at three initial pH values (2.5, 3.5 and 5) as shown in Figure 6. The reaction was done for 60 min under controlled pH condition with constant concentration of H_2O_2 (1.1×10^{-3} M) and Fe^{2+} (1.0×10^{-4} M). At pH 2.5 the reaction of H_2O_2 with Fe^{2+} (Eq. (1)) is earnestly affected resulting the reduction in HO^\bullet radical production. This may be attributed to HO^\bullet scavenging by H^+ ions; which elucidate the decrease of the color removal efficiency at pH 2.5 [24]. On the other hand, at pH 3.5, the decolorization efficiency of RR 120 rapidly increased with the increase in pH; at pH 3.5 almost 100% of color removal efficiency was observed Fig.(6). The main reason is that more $Fe(OH)^+$ is formed; which has much higher activity compared to Fe^{2+} in Fenton process [25]. In addition, 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_2O_2 is less stable, resulting less HO^\bullet radicals are formed, decreasing the removal efficiency of Fenton oxidation. [13]. Therefore, the pH 3.5 is the optimum pH for Fenton oxidation process. The effect of four $L_{azo\ bond}$ factor values (0.25, 0.5, 0.75, and 1.0) at molar ratio H_2O_2/Fe^{2+} equal to 11 was evaluated. From the experimental data as shown in Table (4); the four levels of $L_{azo\ bond}$ are symbolized well by the second-order kinetic model. From Table(4)

there is significant difference in RR 120 color removal rates at each pH and $L_{azo\ bond}$ was observed.

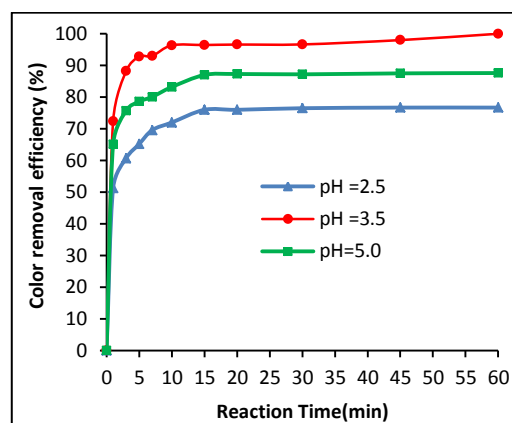


Fig.(6) Effect of pH on the color removal efficiency of RR 120 by Fenton process.

Experimental conditions:

$$[RR\ 120] = 7.5 \times 10^{-5}\ M; [Fe^{2+}] = 1.0 \times 10^{-4}\ M; [H_2O_2] = 1.1 \times 10^{-3}\ M.$$

Also, Table (4) shows that the best color removal rates of RR 120 dye take place at pH 3.5. Our results are in harmony with previous work for assessment the color removal of Amido black 10B [26] and Terasil Red R [27]. The best RR 120 color removal rates were obtained at the lowest $L_{azo\ bond}$ factor 0.25 and higher k_2 values; due to the lower $L_{azo\ bond}$ factor represented a higher amount of H_2O_2 concentration per mole of RR 120 and coincides with the higher O_2 concentration able to be used for oxidizing the RR 120 dye. Fig.(7) presents a linear correlation between the second-order kinetic model k_2 value and the $L_{azo\ bond}$ at each pH value.

Table (4)

Second-order kinetic model and regression coefficients for each pH and $L_{azo\ bond}$ value during Fenton oxidation of 7.5×10^{-5} M RR 120.

pH	$L_{azo\ bond}$	$L_{azo\ bond}$	$L_{azo\ bond}$	$L_{azo\ bond}$
	1.0	0.75	0.5	0.25
2.5	$k_2=66.81$ $R^2=0.641$	$k_2=82.6$ $R^2=0.770$	$k_2=150$ $R^2=0.654$	$k_2=465.3$ $R^2=0.751$
3.5	$k_2=651.5$ $R^2=0.986$	$k_2=818.21$ $R^2=0.981$	$k_2=1327.5$ $R^2=0.982$	$k_2=4244.6$ $R^2=0.986$
5.0	$k_2=284.2$ $R^2=0.771$	$k_2=329.6$ $R^2=0.726$	$k_2=353.4$ $R^2=0.627$	$k_2=1787.5$ $R^2=0.888$

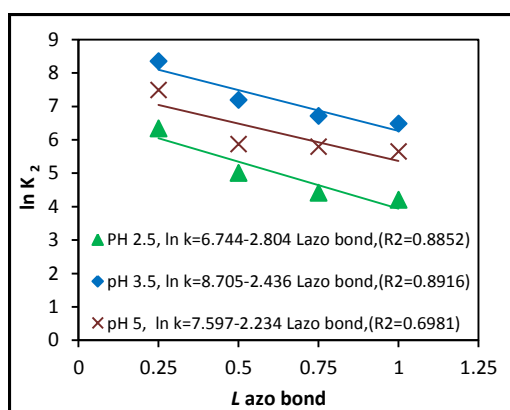


Fig.(7): Correlations between $\ln k_2$ of the color removal rates versus L_{azo} bond at different pH values obtained during Fenton oxidation of 7.5×10^{-5} M RR 120.

COD removal of RR120 at different L_{COD} factors

Although homogeneous catalytic process removed the color of azo-dye solution, the RR120 azo dye has not been mineralized, completely. For this reason it is necessary consider complementary information about the degradation of the organic pollutants [28]. Chemical oxygen demand (COD) gives an average measure of the oxidation state of the organic byproducts generated during the degradation of dye RR 120 [29]. Under the best pH of 3.5 and mole ratio of H_2O_2/Fe^{2+} equal to 11 which were determined formerly, experiments using four different L_{COD} values (0.25, 0.5, 0.75, 1.0) were performed to investigate the efficiency of Fenton process on COD removal kinetics of RR120 is shown in Fig.(8). The COD removal increases with decreasing L_{COD} because the theoretical amount of the concentration of H_2O_2 and Fe^{2+} it has increase. At the maximum ($L_{COD} = 1.0$) was observed 55.7% of COD removal were accomplished after 15 min while at the minimum ($L_{COD} = 0.25$) was observed 67% of COD removal were achieved after the same time. These results show there was residual H_2O_2 in solution after 15 min of Fenton's oxidation reaction Fig.(9), perhaps all the Fe^{2+} was converted to Fe^{3+} , decreasing the reaction rate with H_2O_2 , since a slower consumption of H_2O_2 was observed Fig.(9). The results of consumption of H_2O_2 showed that for Fenton oxidation, the 81.6% H_2O_2 was consumed after 15 min at $L_{COD} = 1.0$ while only about 43% H_2O_2 was consumed at $L_{COD} = 0.25$.

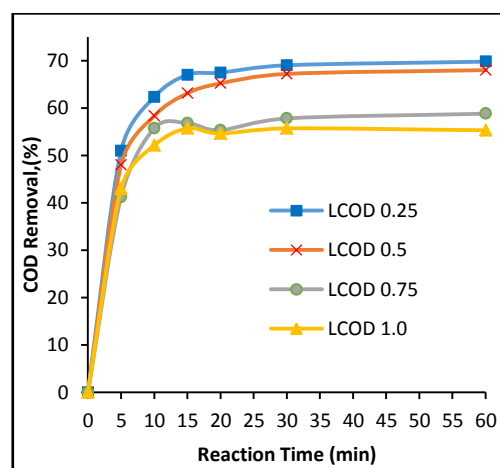


Fig.(8): Correlation between the COD removal of 7.5×10^{-5} M RR 120 ($COD = 124 \text{ mg O}_2 \text{ L}^{-1}$) versus reaction time. Experimental conditions: $pH=3.5$ and molar ratio $H_2O_2/Fe^{2+}=11$.

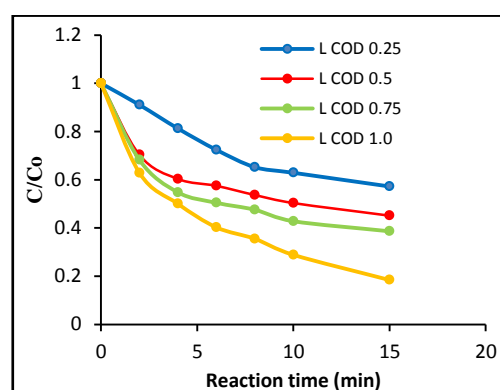


Fig.(9): The consumption of H_2O_2 using different L_{COD} factor. Experimental conditions: $[RR\ 120] = 7.5 \times 10^{-5}$ M $pH=3.5$ and molar ratio $H_2O_2/Fe^{2+}=11$.

Effect of RR 120 concentration on color removal kinetics

The color removal efficiency of different concentrations of RR 120 was studied. It was observed from Fig.(10) that the color removal of dye increases with the decrease in initial RR 120 concentration. As the concentration of dye decrease from 1.5×10^{-4} M to 5.0×10^{-5} M, the decolorization efficiency of dye increase from 45% to 96% within the first 10 min of reaction. A decrease in the concentration of RR 120 dye reveals that little dye molecules will be available to scavenging by HO^\bullet radicals which lead to increase in the color removal efficiency of RR 120 [30].

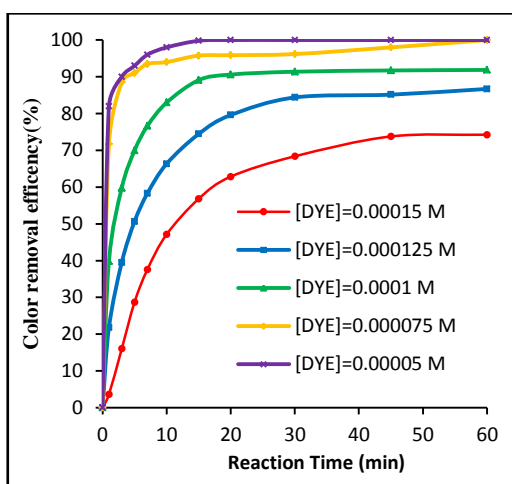


Fig.(10): Effect of initial RR120 concentration on its color removal efficiency during Fenton oxidation. Experimental conditions: $[H_2O_2] = 1.1 \times 10^{-3} M$; $[Fe^{2+}] = 1.0 \times 10^{-4} M$ and $pH = 3.5$.

Table (5) presents the second-order kinetic rates of color removal of RR 120 at various RR 120 concentrations. Also, Table (5) shows the effect of different $[H_2O_2]/[dye]$ ratios as a function of color removal kinetics of RR 120. It is obvious that the color removal kinetics increase with the decrease in RR 120 concentration in two different steps. A tenuous increase in color removal kinetic rate (from 611.8 to 4728.5 $M^{-1} min^{-1}$) 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 a acute increase in color removal kinetic rate (from 4728.5 to 50971 $M^{-1} min^{-1}$). Furthermore, the efficiency of RR 120 color removal, increases with decreasing $[H_2O_2]/[RR\ 120]$ molar ratio, which points out that a higher concentration of RR 120 was removed by using smaller dose of H_2O_2 Fig.(10).

Table (5)

Second-order kinetic constants and regression coefficients for each RR120 concentration during Fenton oxidation
Experimental conditions: $[Fe^{2+}] = 1.0 \times 10^{-4} M$; $[H_2O_2] = 1.1 \times 10^{-3} M$ and $pH=3.5$.

[RR120] (M)	$[H_2O_2]/[RR\ 120]$	$K_2 (M^{-1} min^{-1})$	R^2
1.5×10^{-4}	7.3	611.89	0.9932
1.25×10^{-4}	8.8	1544.6	0.9983
1.0×10^{-4}	11	4728.5	0.9977
7.5×10^{-5}	14.6	20879	0.9434
5×10^{-5}	22	50971	0.9671

The influence of inorganic ions on RR 120 color removal by Fenton oxidation

The influence of some inorganic anions on the color removal of RR 120 was tested in the optimum conditions. To simulate an aqueous solution containing RR 120 at concentration of ($110.3\ mg\ L^{-1}$; $7.5 \times 10^{-5} M$) in the presence of 1.0 % of inorganic salt used in this study. Consequently, we intend to assess the color removal of RR 120 by the Fenton oxidation process containing high doses of selected inorganic salts; due to a large quantity of anions are predominantly present in industrial textile wastewater. Fenton oxidation is highly sensitive to inorganic anions which remain in the aqueous solution [31]. In this research, the influences of chloride, sulfate, carbonate and bicarbonate on the Fenton process were evaluated. Fig.(11) show the effect of the studied anions on the RR120 degradation by Fenton oxidation process. Anions suppress the degradation of RR 120 in the following sequence:

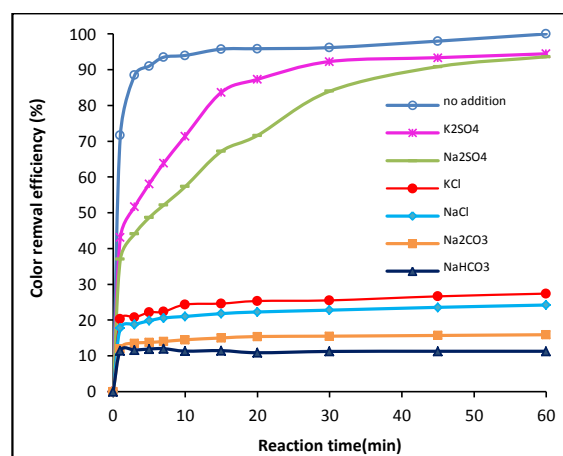
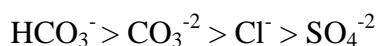
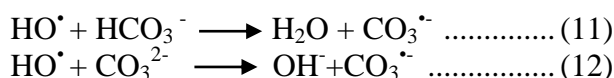


Fig.(11): Effect of addition of 1.0% inorganic anionic on RR 120 color removal efficiency. Experimental conditions: $[RR\ 120] = 7.5 \times 10^{-5} M$; $[Fe^{2+}] = 1.0 \times 10^{-4} M$; $[H_2O_2] = 1.1 \times 10^{-3} M$ and $pH=3.5$.

The addition of inorganic anions displayed various inhibiting behaviors in Fenton process treatment. The influence of the addition of HCO_3^- and CO_3^{2-} may be attributed to a decrease of the rate of generation of hydroxyl radicals because the formation of $CO_3^{\cdot-}$ (Eqs. (11) and (12)).



The radical $\text{CO}_3^{\cdot-}$ is less reactive than HO^{\cdot} radicals. In the case of Cl^- it also has a great effect on the decomposition of RR120 because it reacts with Fe^{2+} forming complex and free radical less effective than the radical of hydroxyl (Eqs. (13) and (14)) [32].



The salts of the sulfate ion appear to have less effect on the Fenton process, where sulfate ion react with Fe^{2+} and HO^{\cdot} , a component HO^{\cdot} (Eqs. (15) and (16)) [33].



Conclusions

In this study, the characteristic of COD and color removal of azo dye by Fenton process treatment was evaluated for Reactive Red 120 in aqueous solution. It has been selected amongst azo dyes due to its high solubility in aquatic environment and it is widely used from Al-Kut textile factory. The degradation of RR 120 aqueous solution strongly depends on the system parameters such as pH, hydrogen peroxide and ferrous catalyst concentration, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ mole ratio, and dye concentration. Based on the result, the following conclusions were derived:

1. The experiments showed that RR 120 at a concentration of 7.5×10^{-5} M can be degraded using the optimum $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio was determined to be 11.
2. The COD removal increases with decreasing L_{COD} . The maximum ($L_{\text{COD}} 1.0$) was observed 55.7% of COD removal were achieved after 15 min while at the minimum ($L_{\text{COD}} 0.25$) was observed 67%
3. of COD removal were achieved after the same time.
4. The optimum conditions were obtained at pH of 3.5 and the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio of 11. Under the optimum condition, almost complete color degradation resulted for RR 120.
5. This research has shown that removal efficiency of the Fenton oxidation process can be decreased in the presence of 1.0 % of inorganic salt according to the following sequence: $\text{HCO}_3^- > \text{CO}_3^{2-} > \text{Cl}^- > \text{SO}_4^{2-}$.

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