# Removal of Reactive Green Dye from Textile Waste Water by Photo Fenton Process: Modeling, Kinetic, and Thermodynamic.

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## Abstract

This work investigated the removal of the reactive green (R.G) dye from wastewater using the photo-Fenton process. Batch experiments were carried out to research the role of the Impacts of operating parameters. The dosage of $H_2O_2$; dosage $Fe^{+2}$; pH; temperature, and irradiation time were examined. Maximum decolorization efficiencies green dye were achieved at the $[H_2O_2]$=100 ppm; $[Fe^{2+}]$=20 ppm; pH 3; temperature=56 °C and irradiation time=90 min. This research focuses on modeling, kinetics and thermodynamics of the removal of pollutant (reactive green dye) of water. The results showed that the decolorization kinetic of R.G followed pseudo-first-order reaction kinetic. Also the thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ were determined using the Van't Hoff equation for the oxidation processes. The changes in Gibbs free energy showed the oxidation process under normal conditions is non-spontaneous.

**Keywords:** Wastewater Treatment, Reactive Green Dye, Advanced Oxidation, Photo-Fenton Process, RSM, Kinetic, Thermodynamic.

إزالة الصبغة الخضراء التفاعلية من مياه الصرف الصحي للنسيج عن طريق عملية فنتون الضوئية: النمذجة والحركية والديناميكية الحرارية.

تبارك عبد السجاد1، خالد مخلف موسى2

**الخلاصة:**

في هذا الدراسة حققت إزالة الصبغة الخضراء التفاعلية (R.G) من مياه الصرف باستخدام عملية -photo Fenton. أجريت تجارب دفعية لبحث دور تأثيرات معاملات التشغيل تركيز بيروكسيد الهيدروجين (H$_2$O$_2$ )؛ Fe $^2$ + ؛ pH. كما تم فحص درجة الحرارة ووقت التشعيع. تم تحقيق أقصى كفاءة لإزالة الصبغة الخضراء عند [H$_2$O$_2$] =100 ppm ؛ [Fe$^{2+}$]= 20 ppm ؛ pH 3؛ درجة الحرارة = 56 C°ووقت التشعيع = 90 دقيقة. يركز هذا البحث على النمذجة والحركية والديناميكا الحرارية لإزالة الملوثات (الصبغة الخضراء التفاعلية) من مياه الصرف. أظهرت النتائج أن حركية إزالة اللون لـ R.G تتبع حركية التفاعل من الدرجة الأولى. كما تم تحديد المعلمات الديناميكية الحرارية ΔG°,ΔH° و ΔS° باستخدام معادلة Van't Hoff لعمليات الأكسدة. أظهرت التغييرات في طاقة جيبس الحرة أن عملية الأكسدة في ظل الظروف العادية غير تلقائية.

## 1. Introduction

Dyes are colored materials that are often used in textile fibers and coloring of fabrics to permanently transfer colors to other substances by staining or immersing them. Dyes are often natural or synthetic, soluble or insoluble, and constitutes an abundant class of organic compounds[1]. Over (100,000) forms of synthetic dyes are currently used commercially and (700,000) tons of coloring are manufactured worldwide annually[2]. Synthetic colors can generally be categorized as anionic (direct, acid and reactive), cationic (basic) and non-ionic (disperse)[3]. There are two essential conditions under which a colored compound functions as a dye a chromophore presence and a uxochrome presence [4]:

Dyes are greatly used during the textile industry. Therefore, when fabrics are tinted, such as cellulose, where a sufficient number of colors are not installed on the fabric, the remaining unused colors will be discharged into wastewater[5]. For the textile industry, dye-containing wastewater has represented serious pollution problems in the world. Nearly (10-15) percent of all dyes used in various textile and other industries are discharged into wastewater worldwide. Thus, the discharge of liquid waste containing dye into the aquatic environment is not only unwelcome because of its color, but also because

many of the released dyes and their decomposition products are poisonous, carcinogenic or primarily mutant in life forms[6][7]. There are three methods for the treatment of colored materials, which include physical methods employing precipitation, adsorption and reverse osmosis, chemical methods via oxidation and reduction, and biological methods inclusive anaerobic and aerobic treatment. Sludge formation is a disadvantage of precipitation methods. Adsorption has the downside that the adsorbent has to be regenerated periodically. This entails extra expenses, and often very time-consuming procedures [8]. While different methods have been employed to treat textile dye wastewater, none of these treatments was satisfactory due to the high degree of polarity and complex molecular structure of the effluent. Promising results have been achieved using advanced oxidation processes (AOPs) for effluent from the dyeing industry in recent years. These processes are focused on the creation of highly reactive radicals, in particular hydroxyl radicals, which facilitate the destruction until mineralization of the target pollutant. The remarkable benefit of AOPs as a whole is that they neither move contaminants from one process to another nor generate large quantities of hazardous sludge[9]. There are several types of AOPs the following [10]:

1. photolysis (UV or VUV),
2. hydrogen peroxide (this includes the $H_2O_2$ + UV, Fenton: $H_2O_2$ + $Fe^{2+}/Fe^{3+}$, Fenton-like reagents: $H_2O_2$ + $Fe^{2+}$-solid/$Fe^{3+}$- solid and photo-Fenton: $H_2O_2$ + $Fe^{2+}/Fe^{3+}$ + UV),
3. ozone (this includes ozonation, photo-ozonation, ozonation + catalysis and $O_3$ + $H_2O_2$ and $O_3$ + $Fe^{2+}/Fe^3$) and
4. photocatalysis (this includes heterogeneous catalysis and photocatalysis and $TiO_2$ + CdS + combinations).

Several researchers investigated the advanced oxidation processes for the reduction of organic contaminants. Chen et. al.,2001 [11] examined the photodegradation of methyl orange in methanolic solution in the presence of ferric ions and $H_2O_2$ under both UV and visible irradiations. It was found that different radicals were generated under UV and visible light irradiations. Possible mechanism of the photo-Fenton reaction in methanolic solution was proposed based on experimental findings under both UV and visible light irradiations. The intermediates produced during the photo-Fenton reaction were detected. Malik et. al.,2003 [12] Studied employed the Fenton is reagent to oxidise two direct dyes, Blue 54 and Red 31. Results indicate that dyes are decomposed in a two-stage reaction. In the first stage, dyes are quickly decomposed, and somewhat less rapidly in the second stage. At the optimum initial ratio of [$Fe^{2+}$]:[ $H_2O_2$]:[dye], (97%) degradation can be achieved in (30 min) at a temperature of (30 °C), and (70%) removal of initial chemical oxygen demand (COD) is achieved after (60 min). Ertugay et. al.,2013[13] studied the treatment of a solution containing Direct Blue 71(DB71) by the Fenton oxidation process. The experimental results show that the initial concentration of $H_2O_2$, $Fe^{2+}$, DB71,

the initial pH, and the temperature had great influence on the degradation of DB71 dye and Chemical Oxygen Demand (COD) removal in a batch reactor by the Fenton is process. Under the optimal conditions (94%) color and (50.7%) COD removal efficiency of the dye in (100 mg/L) aqueous solution were achieved after 20 min of reaction. Al-Anbari et. al.,2017 [14] decoloration of the blue azo dye was investigated in simulated wastewater as a function of the solar photocatalytic process. From the results of an experiment, the optimum conditions for solar photocatalytic $V_2O_5$ were obtained to be: pH=(2), $H_2O_2$ concentration =(100mg/L), catalyst load=(500mg/L) and initial concentration of dye=(25 mg/L). The efficiency of decoloration can be achieved by using $V_2O_5$ as a solar photocatalytic to (97%). Forqan et. al.,2019 [15] used sunlight and UV radiation to compare the decolorization of brilliant reactive red dye using four processes ($H_2O_2$/sunlight, $H_2O_2$/UV, $H_2O_2$/$TiO_2$/sunlight, and $H_2O_2$/$TiO_2$/UV). The experimental results showed that decolorization percentage with $H_2O_2$/sunlight and $TiO_2$/ $H_2O_2$/sunlight were (95.7%) and (98.42%) respectively. While using $H_2O_2$/UV, $H_2O_2$/$TiO_2$ /UV, the percentage of decolorization were (97.85%) and (96.33%) respectively. The results also indicated that the sunlight is more economic and cost-effective than UV radiation.

The present work aims to evaluate the treatability of the removal efficiency of dye from simulated wastewater containing reactive green using the photo-Fenton reactor by batch modes. Minitab software is used to find the model describes the removal efficiency of dye as function of the operating variables; irradiation time, pH, hydrogen peroxide concentration, ferrous sulfate concentration, and effect of temperature. Addition, kinetic and thermodynamic studies on the reactivity of hydroxyl radicals in wastewater treatment by AOPs.

## 2. Experimental Work
### 2.1. Materials

The reactive green dye (R.G) with 630 nm wavelength with chemical structure shown in Fig.1 was supplied by Al-Hilla textile factory located in the south of Baghdad-Iraq. A stock solution of 1000ppm was prepared in 250 ml of distilled water with dissolved 0.25 g of reactive green. Ferrous sulphate $Fe^{2+}$ (India 99 % purity), hydrogen peroxide $H_2O_2$ (Germany 45% wt./wt.), hydrochloric acid (98 % purity) and NaOH were used in this work. Table 1 List of the chemicals used in this work.

**Table (1):** List of chemicals used.

| Compound | Vender | Purpose |
|---|---|---|
| Hydrogen peroxide ($H_2O_2$) | Germany (45% wt/wt) | A major source for produce hydroxyl radicals in the photo Fenton process. |
| Ferrous sulfate heptahydrate (FeSO$_4$.7H$_2$O) | India (99 % purity) | The use of iron salts as a catalyst for the decomposition of hydrogen peroxide to hydroxyl radicals. |

| Hydrochloric acid (HCl) and Sodium hydroxide (NaOH) | India ( 98 % purity) | Regulate the dye solution to obtain a designed range. |
|---|---|---|
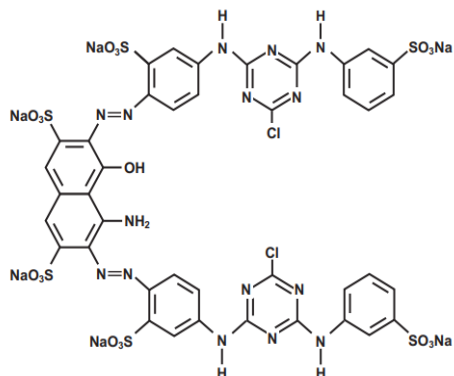


**Figure(1):** Chemical structure of Reactive green[16].

### 2.2. Photo-Fenton batch reactor:

All photo-Fenton experiments were carried out using a glass reactor of 250 ml capacity. The reaction mixture inside the reactor, consisting of 150 ml the dye solutions and the precise amount of Fenton's reagent, was continuously magnetic stirrer to provide good mixing at 200 rpm. It was equipped with two UV tubes each of 6 W were used in the initial experiments, then four UV tubes with a total intensity of 24W were used to study the effect of intensity on dye removal, as the shown batch reactor in Fig 2. addition, A digital WTW pH-72 was used to measure the pH of the treated solutions. UV spectrometer study was conducted to detect the removal of reactive green from samples using Eq. (1):

$$R = \frac{c_\circ - c_t}{c_\circ} x100\% \qquad (1)$$

Where R is the decolonization efficiency; $C_0$, and $C_t$ are the initial and final concentration of reactive green dye (mg /l), respectively.

### 2.3. The experimental design:

The experimental design used to reduce the number of experiments, the interaction among the variables and to find the optimum conditions for multi input variables [17]. Response Surface Methodology (RSM) is a powerful tool for optimizing chemical reactions or industrial processes, including factor design and evaluating regression. It helps in determining the effective factors and in building models to study interaction, and selecting optimal variable conditions for a desired response. A variety of statistical experimental designs with RSM have been used in recent years to optimize the conditions.

A well known types of RSM designs such as D-optimal design, Box-Behnken design and the central composite design (CCD) are used in process engineer [18]. The model describes the implementation system of experiments can be find by the experimental design as follows:

$$Y = B_0 + \sum_{i=1}^{q} B_i X_i + \sum_{i=1}^{q} B_{ii} X_i^2 + \sum_i \sum_j B_{ij} X_i X_j + \varepsilon \qquad (2)$$

where Y is the predicted response, $B_0$ the constant terms, $B_i$ the linear effect, $B_{ii}$ the squared effect, $B_{ij}$ represents the interaction effect and $\varepsilon$ is a random error. MINITAB software was used to design the experiments in this work.
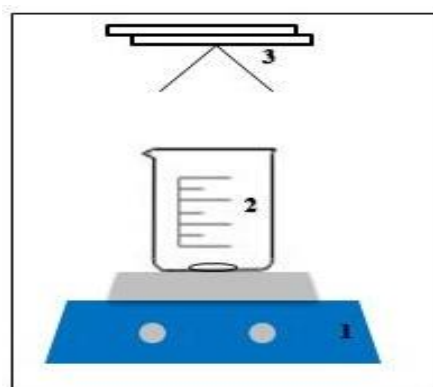


**Figure (2):** A sketch of photo-oxidation system. (1) Magnetic stirrer, (2) Glass reactor, (3) UV lamp.

## 3. Results and discussion:
### 3-1 Modeling:

In the present work, Forty-six experiments were conducted according to the statistical design of the experiments using the RSM- Box–Behnken method. The initial reactive green dye concentration of 20 ppm was used. The initial $H_2O_2$ concentration ($X_1$), initial $Fe^{+2}$($X_2$), irradiation time ($X_3$), temperature ($X_4$) and pH ($X_5$) were selected as the independent variables because they were the five important parameters affecting R.G degradation using $H_2O_2/Fe^{+2}/UV$. The efficiency of degradation R.G was considered as the response. Based on the initial screening experiments, the experimental variables ranges and levels of independent variables for the degradation of R.G by $H_2O_2/Fe^{+2}/UV$. RSM was selected to obtain the studied response as shown in Table 2 as follows:

**Table (2):** Results of the Box–Behnken experiments

| Run no. | $H_2O_2$ (ppm) $X_1$ | $Fe^{+2}$ (ppm) $X_2$ | Irradiation time (min) $X_3$ | Temperature (°C) $X_4$ | pH $X_5$ | Dye removal (%) Y |
|---|---|---|---|---|---|---|
| 1 | 25.0 | 12.5 | 20 | 42.5 | 7 | 7.3125 |
| 2 | 25.0 | 12.5 | 90 | 42.5 | 7 | 10.3125 |
| 3 | 100.0 | 12.5 | 20 | 42.5 | 7 | 9.7917 |
| 4 | 100.0 | 12.5 | 90 | 42.5 | 7 | 17.0833 |
| 5 | 62.5 | 5.0 | 55 | 42.5 | 3 | 72.2917 |
| 6 | 62.5 | 20.0 | 55 | 42.5 | 3 | 77.5000 |
| 7 | 62.5 | 5.0 | 55 | 42.5 | 10 | 5.3542 |
| 8 | 62.5 | 20.0 | 55 | 42.5 | 10 | 6.7500 |

| 9 | 25.0 | 12.5 | 55 | 25.0 | 7 | 8.7500 |
|---|------|------|----|------|---|--------|
| 10 | 100.0 | 12.5 | 55 | 25.0 | 7 | 14.4792 |
| 11 | 25.0 | 12.5 | 55 | 60.0 | 7 | 7.1875 |
| 12 | 100.0 | 12.5 | 55 | 60.0 | 7 | 14.4792 |
| 13 | 62.5 | 5.0 | 20 | 42.5 | 7 | 8.7500 |
| 14 | 62.5 | 5.0 | 90 | 42.5 | 7 | 15.0000 |
| 15 | 62.5 | 20.0 | 20 | 42.5 | 7 | 13.4375 |
| 16 | 62.5 | 20.0 | 90 | 42.5 | 7 | 17.6042 |
| 17 | 62.5 | 12.5 | 55 | 25.0 | 3 | 41.5625 |
| 18 | 62.5 | 12.5 | 55 | 25.0 | 10 | 12.3958 |
| 19 | 62.5 | 12.5 | 55 | 60.0 | 3 | 81.6667 |
| 20 | 62.5 | 12.5 | 55 | 60.0 | 10 | 312514. |
| 21 | 25.0 | 5.0 | 55 | 42.5 | 7 | 4.0625 |
| 22 | 100.0 | 5.0 | 55 | 42.5 | 7 | 10427. |
| 23 | 25.0 | 20.0 | 55 | 42.5 | 7 | 18755. |
| 24 | 100.0 | 20.0 | 55 | 42.5 | 7 | 18.1250 |
| 25 | 62.5 | 12.5 | 20 | 42.5 | 3 | 60.3125 |
| 26 | 62.5 | 12.5 | 90 | 42.5 | 3 | 79.0625 |
| 27 | 62.5 | 12.5 | 20 | 42.5 | 10 | 5.6250 |
| 28 | 62.5 | 12.5 | 90 | 42.5 | 10 | 7.7083 |
| 29 | 62.5 | 5.0 | 55 | 25.0 | 7 | 22926. |
| 30 | 62.5 | 20.0 | 55 | 25.0 | 7 | 10.8333 |
| 31 | 62.5 | 5.0 | 55 | 60.0 | 7 | 14588. |
| 32 | 62.5 | 20.0 | 55 | 60.0 | 7 | 8.0208 |
| 33 | 62.5 | 12.5 | 20 | 25.0 | 7 | 10.8333 |
| 34 | 62.5 | 12.5 | 90 | 25.0 | 7 | 16.5625 |
| 35 | 62.5 | 12.5 | 20 | 60.0 | 7 | 5.2708 |
| 36 | 62.5 | 12.5 | 90 | 60.0 | 7 | 12.3958 |
| 37 | 25.0 | 12.5 | 55 | 42.5 | 3 | 70.2083 |
| 38 | 100.0 | 12.5 | 55 | 42.5 | 3 | 81.6667 |
| 39 | 25.0 | 12.5 | 55 | 42.5 | 10 | 11.8750 |
| 40 | 100.0 | 12.5 | 55 | 42.5 | 10 | 13.9583 |
| 41 | 62.5 | 12.5 | 55 | 42.5 | 7 | 9.2708 |
| 42 | 62.5 | 12.5 | 55 | 42.5 | 7 | 9.3213 |
| 43 | 62.5 | 12.5 | 55 | 42.5 | 7 | 9.5333 |
| 44 | 62.5 | 12.5 | 55 | 42.5 | 7 | 9.2464 |
| 45 | 62.5 | 12.5 | 55 | 42.5 | 7 | 9.2103 |
| 46 | 62.5 | 12.5 | 55 | 42.5 | 7 | 9.1083 |

From the experimental results presented in Table 2, the mathematical correlations of dye removal (Y) response which is related to the quadratic and interaction effects of the operational parameters, is revealed in Eq. (3) as follows:

Dye removal (%): $Y = 71.1 - 0.161 X_1 + 0.09 X_2 + 0.187 X_3 + 1.704 X_4 - 23.39 X_5 + 0.00069 X_1^2 + 0.0066 X_2^2 + 0.00082 X_3^2 - 0.00512 X_4^2 + 2.090 X_5^2 + 0.00880 X_1*X_2 + 0.00120 X_1*X_3 + 0.00250 X_1*X_4 - 0.0178 X_1*X_5 - 0.00198 X_2*X_3 + 0.0005 X_2*X_4 - 0.0662 X_2*X_5 + 0.00057 X_3* X_4 - 0.0350 X_3*X_5 - 0.2071 X_4* X_5$         ($R^2 = 0.9796$)         (3)

Experimental results had been analyzed using Portable Statgraphics Centurion 15.2.11.0 statistical software to approximate the response of dependent variables and to obtain the optimum conditions of the operating variables. Moreover, the statistical significance was analyzed by (ANOVA)[19] as shown in Table 3.

**Table (3):** ANOVA test results for the photo-Fenton process

| Source | Sum of Squares | Df | Mean Square | F-Ratio | P-Value |
|--------|----------------|----|-------------|---------|---------|
| **Main effects** | | | | | |
| Irradiation Time (min) | 63.7065 | 2 | 289.3 | 11.51 | 0.002 |
| Hydrogen Peroxide (ppm) | 27.2294 | 2 | 189.1 | 7.53 | 0.011 |
| Ferrous Sulphate (ppm) | 25.287 | 2 | 126.644 | 3.08 | 0.0584 |
| pH | 170.468 | 2 | 14875.4 | 492.0 | 0.000 |
| Temperature | 23094.4 | 2 | 11547.2 | 281.10 | 0.000 |
| Residual | 1437.76 | 35 | | | |
| Total corrected | 26460.8 | 45 | | | |

According to different variables, the ANOVA table decomposes the variability in dye removal (%). The contribution of each factor is measured having removed the effects of all other factors. The P-values check each of the variables for their statistical significance. Since P-values are less than 0.05, these factors have a statistically important impact on dye Removal (%) at the 95.0% confidence level. The experimental and predicted results were drawn and found that the correlation coefficient ($R^2$) of (0.9796) demonstrates how well the model fits the experimental data.

Through Table 2, the maximum efficiency of removal dye achieved at 81.67%. This can be explained by looking at the circumstances of the experience, hydrogen peroxide and ferrous ions are important parameters that affect the photo Fenton process through the impact on produce hydroxyl

radicals. where the increase of hydroxyl radicals is proportional to the amount of hydrogen peroxide and ferrous ions used on acidic environments. Also, the higher temperature increased the reaction rate between hydrogen peroxide and ferrous ions, thus increasing the rate of generation of oxidizing species such as •OH radical.



**Figure (3):** Samples of wastewater before and after treatment.

## 3-2 Kinetic Models

An approximation kinetics models for decolorization of dye solution can be assume due to the complexity of the process. Equations 4 and 5 describe the first order model and second order model respectively to find which kinetic model best fit the experimental data [20]

$$\ln \frac{[C_\circ]}{[C_t]} = K_1 t \qquad (4)$$

$$\frac{1}{[C_t]} - \frac{1}{[C_\circ]} = K_2 t \qquad (5)$$

$C_\circ$ = initial concentration of dye mg/l (before treatment).

$C_t$ = Concentration of dye at specified time (after treatment).

t = time in minute.

$K_1$ = the first order rate constant (min$^{-1}$).

$K_2$ = the second order rate constant (Lmg$^{-1}$min$^{-1}$).

The decolorization kinetic study for reactive green dye was conducted using a photo-Fenton oxidation process for specific irradiation time. The data were examined through the (Fig. 4-9) and (Tables 4-6) for hydrogen peroxide concentration, pH and temperature to check if the system fit the pseudo-first-order kinetics or second-order kinetics. The slopes of the Fig. were used to evaluate the values of the rate constants of the first-order ($K_1$) and second-order kinetic equations ($K_2$) then provide better $R^2$ values for both models.

The •OH concentration is the driving force of the oxidation rate of the contaminant, so it's very important to understand of the factors controlling the •OH concentration in the UV / $H_2O_2$/$Fe^{+2}$ system. Furthermore, the consumption rate of $H_2O_2$ does not match the rate of hydroxyl radicals generation because iron oxides can decompose hydrogen peroxide to water and oxygen via non-radical pathways [21]. The analysis of the effect of $H_2O_2$ on the kinetics was discussed using first and second order models where all findings were described in (Fig. 4 and 5) and the results are tabulated in Table 4. Through the findings and to match the best experimental data, we compare the coefficient of

correlation between the two models. It was indicated that from Table 4 the $R^2$ for $K_1$ is higher than $K_2$ suggested that the pseudo-first-order equation that more suit the data than the pseudo-second-order equation. The rate constant $K_1$ increases until the limit (0.110305min$^{-1}$) is reached at 100ppm of $H_2O_2$, implying that the optimum $H_2O_2$ concentration for this series of experiments is 100ppm.
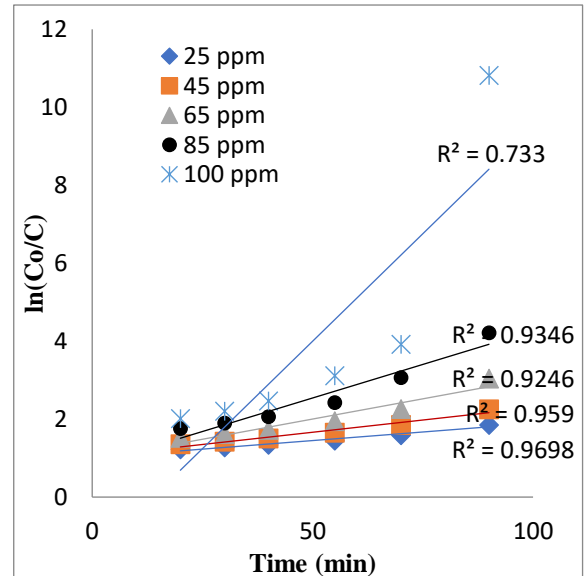


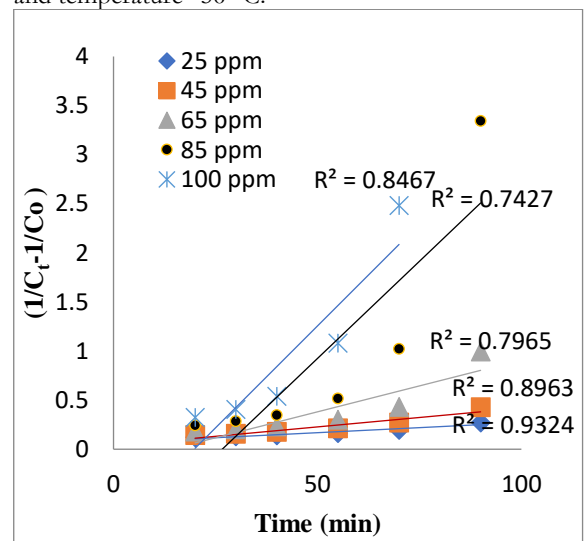**Figure (4):** The Pseudo-first-order rate constant for reactive green dye removal, $Fe^{+2}$=20 ppm, pH =3, and temperature=56 °C.



**Figure (5):** The Pseudo-second-order rate constant for reactive green dye removal, $Fe^{+2}$=20 ppm, pH =3, and temperature=56 °C.

Table 4 shows the slopes of lines in Fig. 4 and 5 which are represented First order and second order rate constants with different $H_2O_2$ concentrations.

**Table (4):** First order and second order rate constants with different $H_2O_2$ concentrations.

| $H_2O_2$ ppm | First order | | Second order | |
|---|---|---|---|---|
| | $K_1$ 1/min | $R^2$ | $K_2$ L/mg.min | $R^2$ |
| 25 | 0.008806 | 0.9698 | 0.002053 | 0.9324 |

| 45 | 0.01256 | 0.959 | 0.003835 | 0.8963 |
| 65 | 0.020743 | 0.9246 | 0.010565 | 0.7965 |
| 85 | 0.034422 | 0.9346 | 0.039591 | 0.7427 |
| 100 | 0.110305 | 0.733 | 0.041515 | 0.8467 |

The effect of pH on kinetic rate constants in the experimental condition was analyzed for R.G degradation of $[H_2O_2]$ =100 ppm, $[Fe^{2+}]$ = 20 ppm and temperature = 56 °C at various pH values. The ln (C/Co) and (1/C$_t$-1/Co ) vs. time plots were drawn and analyzed in Fig. 6 and 7. The pseudo-firs-order kinetic model produced slightly better $R^2$ values than those for the second order, the $K_2$ values were lower than $K_1$ values, suggesting the reaction corresponded well with first order kinetics rather than second order. Consequently, the photo-Fenton process tends to follow decolorization R.G is firs-first-order kinetic. As shown in Table 5, the optimal solution pH was found at pH 3.0, where the constant of reaction rate approaches its maximal value (0.110305 min$^{-1}$).
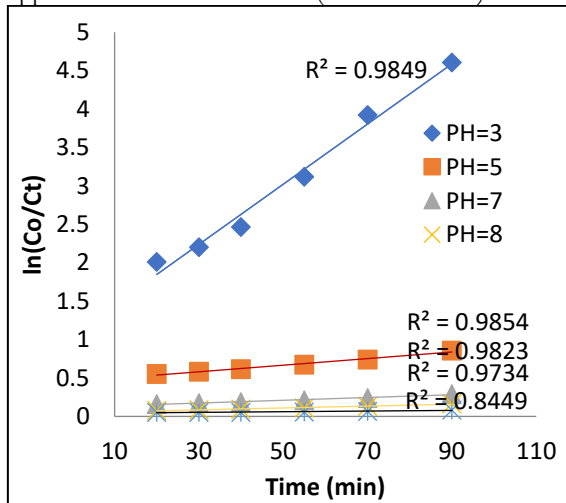


**Figure (6):** The Pseudo-first-order rate constant for reactive green dye removal, $Fe^{+2}$=20 ppm, $H_2O_2$=100 ppm, and temperature=56 °C.
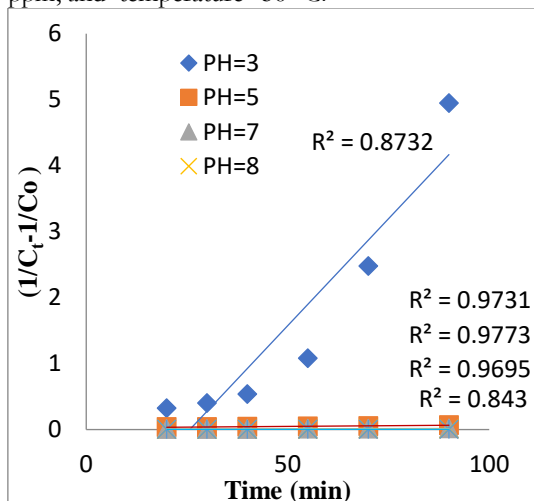


**Figure (7):**The Pseudo-second-order rate constant for reactive green dye removal, $Fe^{+2}$=20 ppm, $H_2O_2$=100 ppm, and temperature=56 °C

Table 5 is showing the slopes of lines in Fig. 6 and 7 which are represented first order and second order rate constants with different pH. The pH effected the

process due to its effected on both the charges of dye and solution.

**Table (5):** First order and second order rate constants with different PH.

| pH | First order | | Second order | |
|---|---|---|---|---|
| | $K_1$ 1/min | $R^2$ | $K_2$ L/mg.min | $R^2$ |
| 3 | 0.110305 | 0.9849 | 0.041515 | 0.8732 |
| 5 | 0.00429 | 0.9854 | 0.000433 | 0.9731 |
| 7 | 0.001804 | 0.9823 | 0.000113 | 0.9773 |
| 8 | 0.001232 | 0.9734 | 0.000007 | 0.9695 |
| 10 | 0.00042 | 0.8449 | 0.000002 | 0.843 |

Table 6 concludes that the first order kinetic model has the best fits from the experiment data at different temperatures of 25,35,45,56 and 60 °C with other test conditions at $[H_2O_2]$ = 100 ppm, $[Fe^{2+}]$ =20 ppm and pH 3 for R.G dye. The results obtained show the values of $K_1$ and $K_2$ explained the constant $K_1$ values of the first order model rose from 0.008173-0.04005 for temperature 25 and 60 °C with a strong indication that R.G degradation is greatly impacted by the temperature of the reaction and increased with temperature rise. Fig. 8 and 9 show the results.
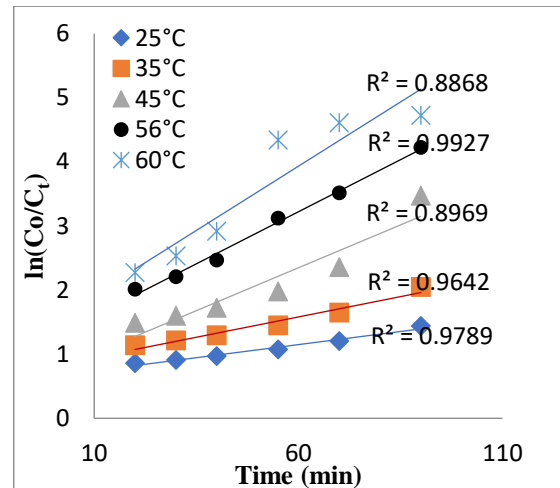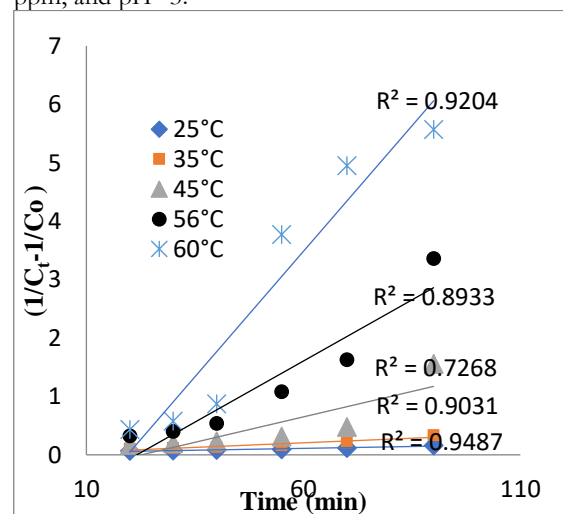


**Figure (8):** The Pseudo-first-order rate constant for reactive green dye removal, $Fe^{+2}$=20 ppm, $H_2O_2$=100 ppm, and pH=3.



**Figure(9):** The Pseudo-second-order constant for reactive green dye removal, $Fe^{+2}$=20 ppm, $H_2O_2$=100 ppm, and pH=3.

Table 6 is showing the slopes of lines in Fig. 8 and 9 which are represented first order and second order rate constants with different temperature. The temperature greatly improves the mass transfer due to decreasing the viscosity of solution and increasing the mobility of particles.

**Table (6):** First order and second order rate constants with different Temperature.

| Temperature °C | First order | | Second order | |
|---|---|---|---|---|
| | $K_1$ 1/min | $R^2$ | $K_2$ L/mg.min | $R^2$ |
| 25 | 0.008173 | 0.9789 | 0.001283 | 0.9487 |
| 35 | 0.012668 | 0.9642 | 0.003128 | 0.9031 |
| 45 | 0.026748 | 0.8969 | 0.017403 | 0.7268 |
| 56 | 0.032475 | 0.9927 | 0.041839 | 0.8933 |
| 60 | 0.040058 | 0.8868 | 0.085893 | 0.9204 |

## 3-3 Thermodynamic study

The thermodynamic parameters are important for a better understanding of the effect of temperature such as standard Gibbs free energy change, $(\Delta G°)$, standard enthalpy change, $(\Delta H°)$, and standard entropy change, $(\Delta S°)$[22]. According to Van't Hoff equation (Eq.6), to determine Standard enthalpy $(\Delta H°)$ and Standard entropy$(\Delta S°)$, plot ln Keq vs 1/T, the resulting straight line will have a slope equal to $\Delta H°/R$ and intercept equal to $\Delta S°/R$ .

$$\ln K_{eq} = \Delta S°/R - \Delta H°/RT \qquad (6)$$

Where R is the gas constant, Keq is a thermodynamic equilibrium constant. Gibbs free energy $(\Delta G°)$ are calculated using the following equations [23].

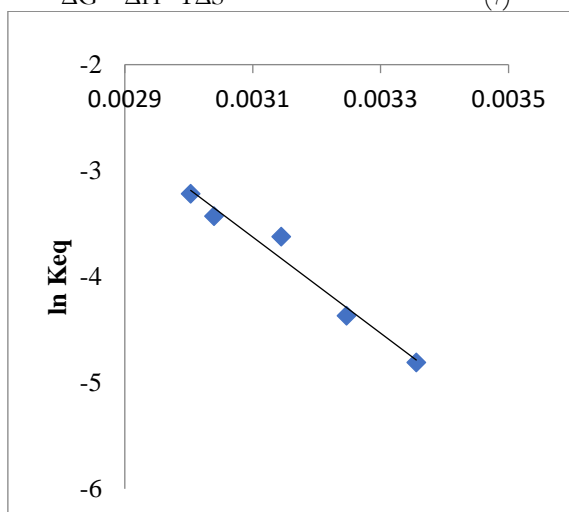$$\Delta G° = \Delta H° - T\Delta S° \qquad (7)$$



**Figure (10):** Van't Hoff plot for thermodynamic study.

Fig. 10 and Table 7 display thermodynamic parameters for the decolorization calculations. The positive entropy change value $(\Delta S°)$ shows that an increased disturbance exists during R.G oxidation. The positive value of (37.705 kJ/mol) for $\Delta H°$ refers to an endothermic reaction whereas the positive $\Delta G°$ values indicate that this reactive green dye is non-spontaneous to the photo-Fenton process. that interpenetrated as the transition state formed between the reactive green dye molecules and the intermediates of reaction (i.e. hydroxyl radicals) are be highly solvated due to The $\Delta H°, \Delta S°$ and $\Delta G°$ are positive values, [24].

**Table (7):** The thermodynamic parameters for the R.G dye decolorization.

| Temperature (K) | Keq 1/min | $\Delta H°$ (kJ/mol) | $\Delta G°$ (kJ/mol) | $\Delta S°$ (kJ/mol K) |
|---|---|---|---|---|
| 298 | 0.008173 | | 11.85588 | |
| 308 | 0.012668 | | 10.98845 | |
| 318 | 0.026748 | 37.7054 | 10.12101 | 0.086743 |
| 329 | 0.032475 | | 9.166836 | |
| 333 | 0.040058 | | 8.819863 | |

## 4. Conclusions:

The results indicated that the used process is efficient process under acidic conditions pH=3, $[H_2O_2]$= 100 ppm, $[Fe^{2+}]$=20 ppm, irradiation time=90 min and temperature 56 °C. The study presented the results of the thermodynamics and kinetics of the R.G decolorization process by photo-Fenton. A model of pseudo first order is describing the kinetics of R.G decolorization. The reaction characteristic of the oxidation process was evaluated as thermodynamically spontaneous under natural conditions. The positive value of $\Delta S°$(+30.853 kJ/mol K) indicated the increased randomness in the Fenton oxidation process. As also depicted the positive value $\Delta H°$ values of (+9.295 kJ/mol) that the processes were endothermic in nature.

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