



INTERNATIONAL JOURNAL OF PHYTOFUELS AND ALLIED SCIENCES
(A Journal of the Society for the Conservation of Phytofuels and Sciences)
(<http://www.phytofuelsciences.com>) (ISSN 2354 1784)

EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES OF CATALYTIC OXIDATION OF ORANGE G DYE IN AQUEOUS MEDIA

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ABSTRACT

The study of effect of Fenton oxidation process on the oxidation of dye was carried out to determine the efficiency and operating conditions for the application of Fenton oxidation process to treat wastewater containing an azo dye, Orange G (OG), some important operating parameters such as pH values of solutions, concentration of H_2O_2 and Fe^{2+} , temperature, ionic salt and the concentration of dye, were investigated systematically. The kinetic study was studied spectrophotometrically under pseudo-first order condition at temperature of 293-313K. The result showed that the oxidation of Orange G increases with increase in reaction temperature, pH, oxidant and catalyst concentration but decreases with increase in ionic salt. The oxidation kinetics of Orange G by Fenton Oxidation process followed the pseudo first order reaction kinetics. The rate constant in the presence of catalyst was observed to be more than the rate constant in the absence of catalyst and activation energy for catalysed and un-catalysed reaction were detected to be 83.7kJ/mol and 84.3kJ/mol respectively. The result of k_{obs} and difference in activation energy shows that catalyst enhances the oxidation reaction. These results can be a basis for fundamental knowledge for the treatment of water containing Orange G and other azo dyes by Fenton Oxidation process.

Key words: azo dye, kinetics, Fenton oxidation, thermodynamics, catalytic

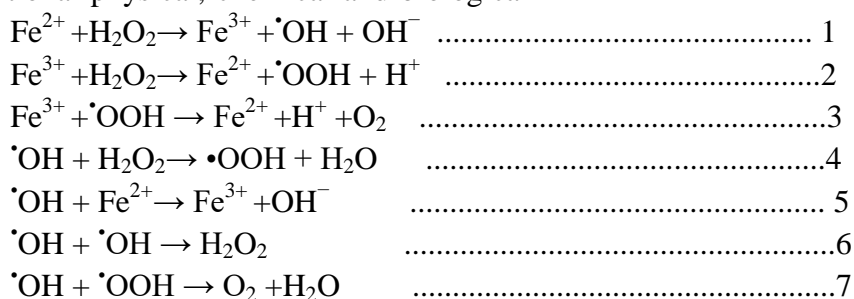
INTRODUCTION

Dye pollutants from the dyestuff manufacturing, dyeing, printing and textile industries are important sources of environmental contamination. The effluents

discharged from these industries are usually strongly colored, and the direct release of the wastewater into receiving water body will cause damage to both aquatic life and human beings due to their toxic, carcinogenic and

mutagenic effects. Azo dyes, characterized by the presence of one or more azo groups (N=N) bound to aromatic rings, are the largest and most important class of synthetic organic dyes. It has been estimated that more than 50% of all dyes in common use are azo dyes because of their chemical stability and versatility.(Neamtu *et al.*, 1999).

The complex and steady molecular structures of most of azo dyes makes them to be resistant to biological and chemical degradation. This stability results in the inefficiency of the conventional physical, chemical and biological



MATERIALS AND METHODS

Materials and Reagents

The various resources include H_2O_2 (oxidant) , FeSO_4 (catalyst), NaCl (ionic salt), H_2SO_4 , Orange G (substrate), Distilled water,, Beakers, Standard flasks, conical flasks, funnels, measuring cylinders, water bath, thermometers. The major analytical equipment used was UV-Visible spectrophotometer (Spectronic 20D) and pH meter [Crimson micro pH 200]

The oxidant and catalyst were all obtained from Shanghai Chemical Reagents Co. (Shanghai China). Orange G was obtained from Merck Chemicals Ltd. All chemicals used were of analytical grade and without any further purification. Distilled water was utilized throughout the research.

Experimental procedures

treatment methods inefficient and costly for their removal from water.(Neamtu *et al.*, 2002)Fenton's reaction is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) in an acidic medium, which was firstly discovered by Fenton in the 1890s (Lu *et al.*, 1999).

The mechanism of Fenton's reaction was postulated/proposed by the following scheme

All tests were conducted using UV spectrophotometer to monitor the progress of the reaction Temperature control was realized through a thermostat and a magnetic stirrer was used to stir reaction solutions. At the beginning of each test, appropriate volumes of stock OG and ferrous sulphate solutions were placed into the reactor and made upto 100mL mark with deionized water. The pH value of each reaction solution was adjusted to the desired value by using the prepared 0.1M sulphuric acid or 0.1M sodium hydroxide solution. The pH was determined with a model PHS-3C pH meter. The reactions were initiated by adding calculated amounts of hydrogen peroxide to the beaker. Aliquot samples were taken from the reaction mixture periodically for UV and results were recorded immediately.

Analytical methods

The UV of OG was recorded from 200 to 800 nm using a UV/Vis spectrophotometer with a spectrometric quartz cell (1cm path length). The maximum absorbance (λ_{max}) of OG was found at 560 nm. The peak at 478 nm was attributed to the absorption of the $n \rightarrow \pi^*$ transition related to the $-N=N-$ group in OG molecule. Here the measure of OG concentration interfered not by the degradation products. Therefore, the concentration of OG in reaction mixture at different reaction times was determined by measuring the absorption intensity of solution at 560 nm and using a calibration curve. The reaction could continue after sampling, so in order to decrease the experimental error, the sampling and measurement of the absorbance of reaction solutions were finished in 1 min. (Madan, 2011)

Results and Discussion

Effect of varying substrate concentration on the oxidation of orange G with H_2O_2 in the presence of Fe^{2+} as catalyst

The effect of the variation of oxidant concentration was studied, temperature, ionic strength and pH. It was observed that the decolorization efficiency of OG decreased with increasing concentration of OG. As the concentration of OG increases from 2.6×10^{-4} to 1.3×10^{-3} M, the decolorization efficiency of OG within 30 min of reaction decreased from 96.0% to 72.8%. The relative lower concentration of $\cdot OH$ due to increasing concentration of OG while the same dosage of H_2O_2 and Fe^{2+} , led to a decreasing of the decolorization efficiency of OG. This is in line with similar report of oxidation of orange G by (Nicole *et al.*, 1990; Neamtu *et al.*, 2000)

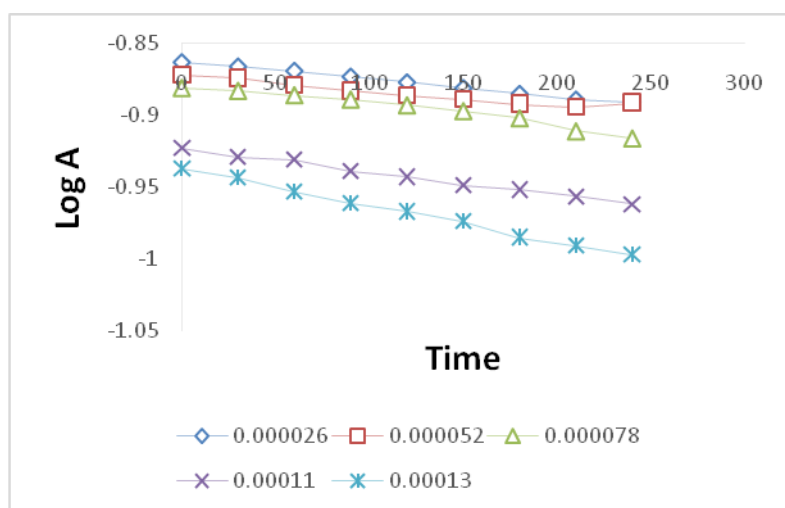


Figure 1: Graph of effect of concentration of substrate

Effect of Varying oxidant concentration on the oxidation of orange G with H_2O_2 in the presence of $Fe(II)$ ions

The effect of the variation of oxidant concentration was studied at a constant concentration of substrate, catalyst, ionic strength, pH and temperature at different

concentration of oxidant. The results are presented in Figure 2. From the figure, it can be observed that increasing the dosage of H_2O_2 from 1.0×10^{-3} to 5.0×10^{-3} M could enhance the

decolourization of OG from 74.2% to 92.5% within 30 min of reaction. This is in line with similar report of oxidation of dye by (Neamtu *et al.*, 2002).

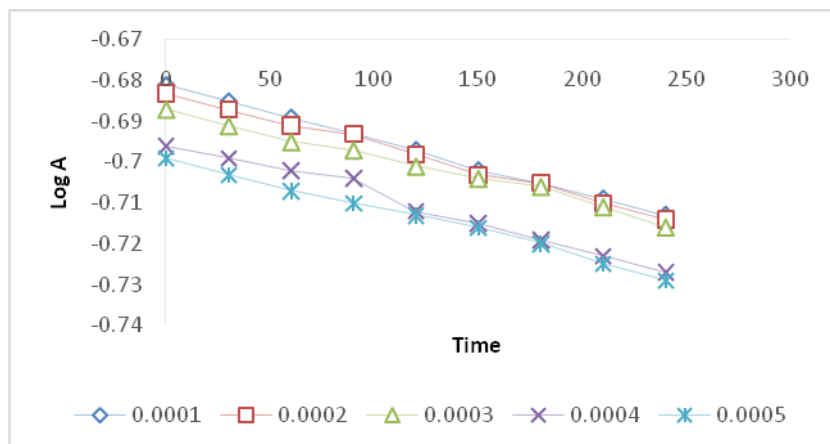


Figure 2: Graph of effect of concentration of oxidant

Effect of varying catalyst concentration on the oxidation of orange G with H_2O_2 .

The effect of catalyst concentration was studied at constant concentration of substrate, oxidant, ionic strength, pH and temperature. The plot of

log of absorbance against time for the variation of catalyst shows increase in pseudo first order constant k_{obs} as the catalyst concentration is increased. This is in line with similar report of oxidation on dye by (Malik and Saha 2002)

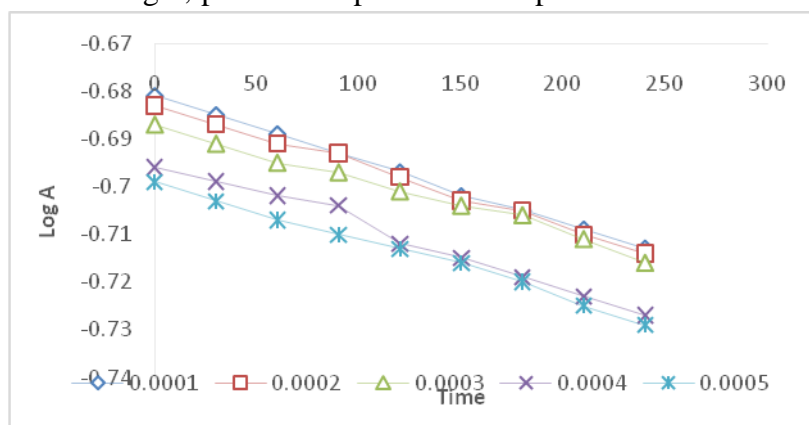


Figure 3: Graph of effect of concentration of catalyst

Effect of varying temperature on the rate of reaction for the oxidation of orange G with H_2O_2 in the presence of Fe (II) ion

The oxidation reaction was studied at different temperature ranging from 20-40°C. The concentration of the substrate oxidant, catalyst, ionic salt and pH were fixed. As can be

observed from Figure 4, raising the temperature has a positive impact on the decolorization of OG. The decolorization efficiency within 4 min of reaction increased from 80.2% to 95.1% as the temperature increases from 20 to 40°C. Additionally, the period of time required for the decolorization of OG was also much shorter at

higher temperature. This can be explained that Fenton's reaction could be accelerated by raising temperature which improved the

generation rate of $\bullet\text{OH}$ and therefore enhance the decolorization of OG. This result follows literature report (Sheng-PengSuna *et al.*, 2008).

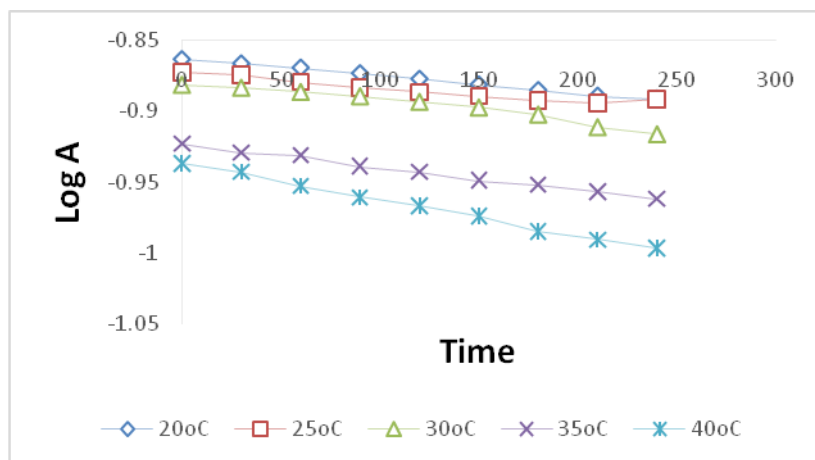


Figure 4: Effect of changes in temperature

Effect of pH, on the rate of reaction of oxidation of orange G with H_2O_2 in the presence of Fe (II) ion.

The effect of pH was studied at different pH (2 – 6), NaOH and H_2SO_4 were used to adjust the pH at different ratios. A direct influence of initial pH on the decolorization of OG could be observed and the best decolorization efficiency was obtained at pH of 4.0. As shown in figure 5 at initial pH of 6.0, the decolorization of OG almost could not be observed in 4 min of reaction. It is principally due to the formation of ferrous/ferric hydroxide complexes leading to the deactivation of ferrous catalyst, which results in a small amount of $\bullet\text{OH}$ being generated. When the initial pH was decreased from 6.0 to 4.0, the decolorization efficiency of OG within 4 min increased significantly from 0.8% to 94.7%. However, the decolorization efficiency of OG slowed down to 70.8% with further decrease of the initial pH from 4.0 to 2.0. This could be explained by the

formation of oxonium ion (i. e. H_3O^{2+}), which enhanced the stability of H_2O_2 and restricted the generation of $\bullet\text{OH}$ at low pH conditions ($\text{pH} < 3.0$) (Rongsheng *et al.*, 2004).). In addition, the scavenging of $\bullet\text{OH}$ by the excessive of H^+ is also another reason for the lower decolorization efficiency of OG at pH of 2. Herein, a suitable initial pH for the decolorization of OG by Fenton oxidation process was recommended as 4.0. This result is in line with similar report on oxidation of dye by (Sheng-PengSuna *et al.*, 2008)

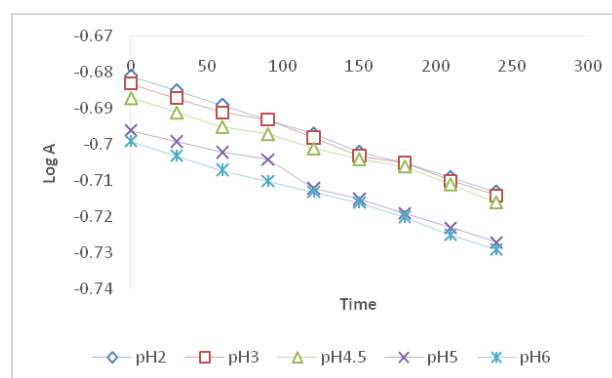


Figure 5: Graph of effect of changes in pH

Effect of variation of concentration of ionic salt on the rate of oxidation reaction with H₂O₂ in the presence of Fe (II) ion

The effect of ionic salt was studied at constant concentration of substrate, oxidant, catalyst, temperature and pH. Huge amounts of salts were used in colouring up variety of dyes on textiles and they were co-existed with dyes in effluent, which could affect the treatment of wastewater. In the present study, the effect of the presence of chloride ion (1×10^{-2} to 9×10^{-2} M) on the decolorization of OG was

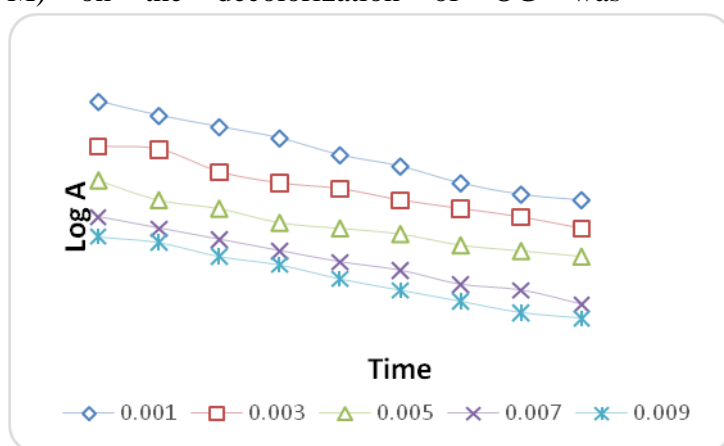


Figure 6: Effect of ionic salt presence

3.2 Kinetic Study

In the present study zero, first and second orders of reaction kinetics were used to study oxidation kinetics of orange G by Fenton oxidation process. The individual expression is as presented in equation 1, 2 & 3.

Zero order kinetics

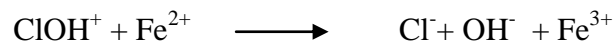
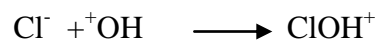
$$\frac{dA}{dt} = k_0 \quad (1)$$

First order kinetics

$$\frac{dA}{dt} = -k_1 A \quad (2)$$

Second order kinetics

investigated and the results are presented in Figure 6. It was observed that chloride ion had a negative impact on the decolorization of OG by Fenton oxidation. This is due to the scavenging effect of Cl⁻



This is in line with similar report on oxidation by (Walter and Huren 1995; Sheng-Peng Suna *et al.*, 2008)

$$\frac{dA}{dt} = -k_2 A^2 \quad (3)$$

Where C is the concentration of orange G, k_0 , k_1 and k_2 represent the apparent kinetic rate constants of zero, first and second order reaction kinetics respectively; T is the reaction time.

By integrating the (Equations 1-3), we obtained Equations 4- 6.

$$A_t = A_0 - k_0 t \quad (4)$$

$$A_t = A_0 e^{-k_1 t} \quad (5)$$

$$\frac{1}{A_t} - \frac{1}{A_0} = k_2 t \quad (6)$$

Where A_t is the concentration of OG at reaction time t .

Data analysis based on the zero-, first- and second order kinetic reaction for the oxidation of OG in Fenton oxidation process was conducted and the results are presented in Table 1. The graph of data for each equation are shown in figures 7a, 7b and 7c for zero-,

first- and second order respectively. The regression coefficients (R^2) of each graph shows that of pseudo first order reaction kinetics higher than that of pseudo second or zero order which confirms that the catalytic oxidation of orange G is a pseudo first order reaction. (Wang *et al.*, 2002; Roberts, 2002)

Table 1: Data analysis based on the Zero, First and Second order reaction kinetics

Zero order		First order		Second order	
Abs	Time(s)	Log Abs	Time(s)	1/Abs	Time(s)
0.132	0	-0.881	0	-1.135	0
0.13	30	-0.885	30	-1.13	30
0.128	60	-0.892	60	-1.121	60
0.125	90	-0.904	90	-1.106	90
0.123	120	-0.912	120	-1.097	120

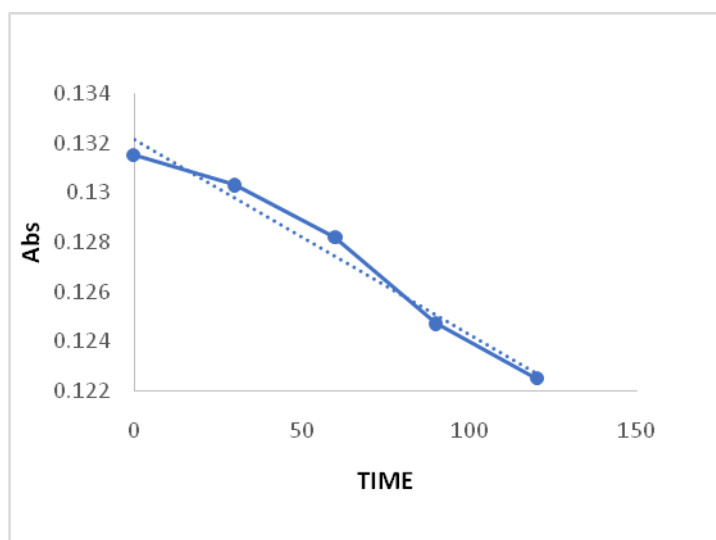


Figure 7a A against time

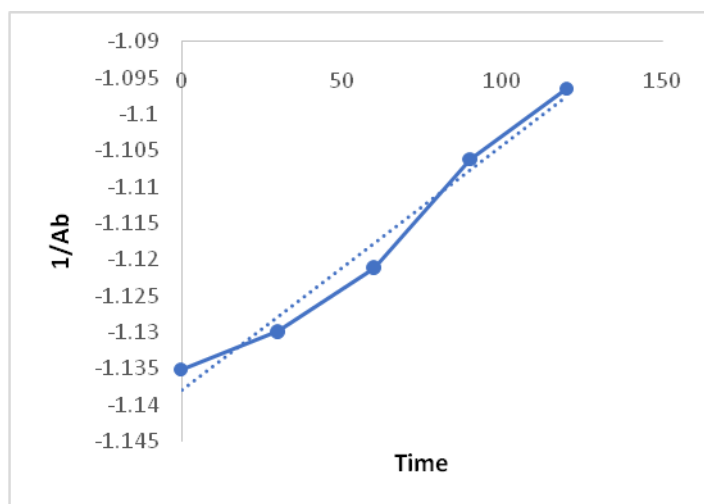


Figure 7b 1/ab against time

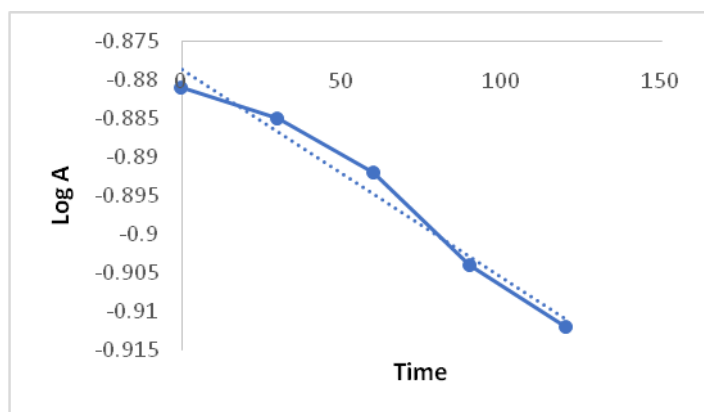


Figure 7c Log A against time

Thermodynamics of Oxidation reaction

Variation of temperature on the rate of oxidation for thermodynamic data in the presence of Fe(II) ions

The variation of the catalytic oxidation capacity with temperature is usually used to give an

account of the favourability of the oxidation process. The data obtained recorded in table 2 showed that the absorbance decreases with increasing temperature from 293– 313K. The free energy change (ΔG) was evaluated to confirm nature of oxidation. Vinodgopal, et al (1996)

Table 2: Thermodynamic data of the oxidation process in the presence of Fe (II) ions

T ($^{\circ}$ K)	1/T (K^{-1})	A_T	$K_2 = (A_0 - A_T)/A_T$	Lnk2
293	0.0034	0.1291	0.057	- 2.8647
298	0.0033	0.1279	0.067	- 2.7031
303	0.0033	0.1199	0.097	-

				2.3330
308	0.0032	0.1069	0.1052	- 2.2519
313	0.0031	0.0971	0.2303	- 1.4684

Thermodynamic parameters were calculated by the Van't Hoff Equation as in the case of a similar report by (M Neamtu *et al.*, 2002).

$$\ln k_2 = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (7)$$

The thermodynamic activation parameters were calculated as follows: The enthalpy of activation (ΔH^\ddagger) = Ea- RT (8)

Where the temperature T= 313K. The entropy of activation (ΔS^\ddagger) in each reaction was then evaluated as follows:

$$k = \frac{kT}{h} \cdot e^{-\Delta S^\ddagger/RT} \cdot e^{\Delta H^\ddagger/RT} = Ae^{-Ea/RT} \quad (9)$$

$$A = \frac{KT}{h} \cdot e^{\Delta s^\ddagger/RT} \quad (10)$$

(Where K= Boltzmann constant, R= gas constant and h= planks constant)

$$\text{Log}A = \frac{\log KT}{h} + \frac{\Delta S^\ddagger}{R} \quad (11)$$

$$\Delta S^\ddagger = 2.303R \left(\log_{10}A - \frac{\log_{10}KT}{h} \right) \quad (12)$$

All calculations were at T = 313K with the values of the constants given as; K = 1.38066 x 10⁻²³Jk⁻¹, h=6.62608 x 10⁻³⁴JS and R = 8.3145JK⁻¹mol⁻¹ as obtained from literature.

$$\text{Hence, } \Delta S^\ddagger = 2.303R(\log_{10}A - 12.81) \quad (13)$$

$$\text{Also } \Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (14)$$

The values of the various Arrhenius activation and thermodynamic parameters are recorded in Table 3 and 5 respectively in the presence and absence of catalyst

Table 3: Arrhenius and thermodynamic activation parameters for the catalytic oxidation of orange G dye with H₂O₂ in the presence of Fe(II) ions

Dye	EakJ/mol	ΔH kJ/mol	ΔS J/K/mol	ΔG kJ/mol
	83.7	-2.47	-20.4	6.431

Variation of temperature on the rate of oxidation for thermodynamic data in the absence of Fe(II) ions

The variation of temperature on the rate of oxidation for thermodynamic data in the absence of

Fe(II) ions was also carried out .The

result is presented in table 4

Table 4: Thermodynamic data of the oxidation process in the absence of Fe (II) ions

T (°K)	1/T (K ⁻¹)	A _T	K ₂ = (A _O - A _T)/A _T	Lnk2
293	0.0034	0.1285	0.0669	-2.705
298	0.0033	0.1253	0.0718	-2.634
303	0.0033	0.1213	0.0841	-2.476
308	0.0032	0.1091	0.1052	-2.252
313	0.0031	0.1007	0.1480	-1.375

Table 5: Arrhenius and thermodynamic activation parameters for the oxidation of orange G dye with H₂O₂ in the absence Fe(II) ions

Dye	EakJ/mol	ΔH kJ/mol	ΔS J/K/mol	ΔG kJ/mol
Orange G	84.6	-2.5	-21.5	6.721

DISCUSSION

The oxidation of orange G in aqueous solution by Fenton process have been studied at different experimental conditions, including different pH value of solutions, dosages of H₂O₂ and presence/absence of Fe²⁺, temperature, ionic salt and different dye concentration. The oxidation of orange G showed that increase in temperature, oxidant concentration, catalyst concentration and substrate concentration enhanced the decolourization efficiency of orange G with or without catalyst but the presence of ionic salt had a negative impact on the decolourization of orange G this is due to the scavenging effect of Cl⁻, while the presence of acidic pH enhances the oxidation of orange the basic pH inhibits it.

It is principally due to the formation of ferrous/ferric hydroxide complexes leading to the deactivation of ferrous catalyst, which resulted in the amount of ·OH generated being very small. The kinetic study indicated that oxidation of followed the first order kinetics with respect to orange G. The calculated Ea. are 83.4 kJ/mol and 85.2 kJ/mol in both catalyzed and un-catalyzed reaction respectively. There is no mean difference, hence the presence of catalyst, Fe (II)ion is insignificant. Generally, the reaction activation energy of ordinary thermal reaction is usually between 60kJ/mol and 250KJ/mol (Chen and Zhu, orange G. The result implies that the oxidation of orange G in aqueous solution by Fenton oxidation process requires lower activation energy and can be

easily achieved (Yongsheng and Yongsheng 2004; Vinodgopal, 1996).

CONCLUSION

The oxidation capacity of Fenton process has been carried out. The experimental values obtained shows that the oxidation capacity of Fenton process depends on various effects such as temperature, substrate concentration, oxidant concentration, catalyst concentration, ionic strength and pH. It was found that increased concentration of oxidant, catalyst, substrate and temperature leads to increased rate of reaction while the ionic salt affects the reaction negatively. It was also found that the best medium for the oxidation of orange G is between pH 4-4.5 i.e. acidic medium. The thermodynamics of the oxidation indicates that the process is exothermic due to the negative value of ΔH . The positive value of ΔG indicates that the oxidation is likely not spontaneous.

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