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RESEARCH ARTICLE

Photokinetics of the oxidation of Coomassie Brilliant Blue by Potassium dichromate in acidic medium

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Abstract

Discharge of colored effluents (without decoloration), originated from textile industries create acute problems in the surroundings environment.Not alone they damage marine life by reducing the concentration of dissolved oxygen in water yet also reduce the access of sun light in the beneath aquatic herbs , weeds and plants. Therefore, it is essential to remove the colored effluent from wastewater .In this study, an oxidant (potassium dichromate) was used in different media to remove the acidic triphenyl methane azo type of dye (Coomassie brilliant Blue R-250) from textile wastewater content. For this purpose, the dye has been investigated spectrophotometrically . The percent decolorization was monitored at the Λ_{max} (530nm)in aqueous medium. Removal efficiency of CBB R-250 was observed to be sensitive to operational parameters such as initial concentration of dye and oxidizing agent, pH (acidic or basic) and temperature . The interaction of dye and oxidant was also monitored under the influence of different buffers and studied their control. Effect of the above parameters were investigated and it is conclusively stated that at moderate concentration of oxidant in acidic medium, at high temperature (313K) and low pH, decolorization of CBB R-250 dye was favoured. Spectrophotometric methods were adopted for the measurement of rate constant (k) for the decolorization of CBB R-250 and it was found to be 8.0×10^{-3} mole L^{-1} sec^{-1}.The rate law of the reaction mechanism is Rate =k $[H^+]^2$ [CBB]$[K_2Cr_2O_7]$,where order of reaction with respect to dye was found to be first order reaction, with respect to oxidant it was first order reaction and with respect to HCl it was noticed to follow second order kinetics. Various activation parameters were (Ea)=17.068kJmol^{-1}, ($\Delta H^{\neq}$)= -32.391kJmol^{-1}, Entropy ($\Delta S^{\neq}$)=-288.837J.K^{-1} and ($\Delta G^{\neq}$)=-32.500kJmol^{-1} respectively.

INTRODUCTION

Many researchers and scientists have been working on the disposal of organic dyes from the effluents of textile industry ,these effluents always find their way into our lives through rivers and irrigation system. Various techniques were adapted like biological, physical and chemical . These include adsorption techniques (Dursun and Tepe , 2011), advance chemical oxidation (Rauf ,2005) , sonolytic degradation (Rayaroth , 2015), microbial decolorization(Kannan , 2013) ,membrane filtration, chemical coagulation, flocculation (Azmi , 1998) ,and electrochemical process (Bouyakoub , 2011)for the treatment of dye wastewater, most of the processes used are costly and are comparatively expansive to eradicate this dilemma but these are comparatively expansive. The Coomassie brilliant blue belongs to the class of triphenylmethane azo dyes shows greater solubility in water in the form of its sodium salt, and its solutions are stable when stored. The Coomassie blue interact with proteins with the involvement of Vander Waals forces and hydrogen bonding. The increment of temperature causes the mechanism faster as with the rise of temperature the speed of the molecules of the dye and proteins increases. In addition, the collision chance of the sulfonic (SO_3^-) group of dyes and protonated (NH_3^+) groups of proteins enhances at boiling temperature, that result in faster staining of the bands of proteins(Smejkal G B ,2004).All these facts reveal well the interacting ability of CBB .AOPs methods involve interaction of highly active hydroxyl radicals with the organic dyes (Rauf ,2005) which gave us the concept of the collision of the dye molecule with oxidant in high sun light exposure .The oxidation process was monitored by variation of physical conditions of the medium and finally this mechanism was assembled.

Experimental

Materials and methods

The experiments are performed according to the sequence:(i) preparation of solutions, (ii) Spectrokinetic measurements, (iii) data analysis (iv) spectral analysis

Preparation of solutions

Working concentration of Coomassie blue solution(sodium salt) = 1.0×10^{-5} $molL^{-1}$, Working concentration of Potassium dichromate solution = 0.01 $molL^{-1}$, HCl = 0.1 $molL^{-1}$ and NaCl = 0.01 $molL^{-1}$ in reaction mixture , were prepared in deionized water. Necessary dilutions were freshly made at the time of kinetics measurements.

Kinetic studies

Initially, each kinetic run was made by keeping one reactant varied and the others taken as constant. Photokinetics were measured by the absorbance of a mixture of solutions with respect to time at each constant I min time intervals up to 30 min , temperature was maintained constant.The absorption spectrum of CBB was scanned for absorption maximum peak at a wavelength of 530 nm (Azmat R , 2011) .

Analysis of data measurement

The plot of absorbance vs time gives rate of reaction. The plot of ln Abs verses time gives the observed rate constant and the values of the slopes gave its values .

Results and discussion

The decolorization of CBB R-250 dye by oxidizing agent $K_2Cr_2O_7$ was investigated . The effects of parameters such as pH ,temperature concentration changes and reaction time on chemical color removal were determined and compared. The kinetic constants were also determined. The dye decolorization was carried out directly in spectrophotometer cuvette . In this study influences of different parameters were measured spectrophotomerically. Spectral measurements were based at 530 nm in the visible range . The decolorization rate was calculated by,

$$r = A_0 - A_t / A_0 \text{ x}100$$

r , rate of decolorization

A_0 , initial absorbance

A_t ,absorbance at time t

Since the decolorization rate of CBB with $K_2Cr_2O_7$ was slow in aqueous medium Table 1 and our observation was that acidic medium enhanced it therefore the reaction was monitored in acid medium .

Effect of the dye concentration

The oxidation initiates the dye degradation, the photocatalytic features contribute towards the dye degradation .The results indicate that the decolorization rate was immense at low concentration of dye and a significant decolorization decrease resulted at high concentration of dye Table 2 and 3 ,which could be due to the scarce solubility of dye at high concentrations in aqueous medium also at high concentrations the chances of the absorption of light photons by dye itself enhanced instead of the dichromate ions absorbing it . The reaction was carried out in the day time between 11 am-12 pm , at this time the high exposure to light is evident , consequently the oxidation of the dye occurred in photo excitation atmosphere. The Cr^{+6} ion in the high concentration of weak reducing agent (H^+) undergoes 1electron transfer and form Cr^{+5}ion , Equation (3)which is enormously reactive chromium ion and very transient, hydrolyze back to to Cr^{+6} Equation (4)and free radical super oxygen anion (reactive oxygen species in the presence of high sun light exposure ,the hydrolysis of Cr^{+5} ion takes place in acidic medium(Lushchak O V , 2008), Equation (4) . The super active oxygen anion radicals oxidize and consequent decolorization of the dye which mainly occurs at chromospheres rather than the dye structure (Agarwal K , 2013 , Ackerlay D F ,2006) Equation (5) and (6) . Oxidation would be favoured at low concentration of the dye (Azmat R , 2013) .

Effect of the oxidant concentration

The concentration of Potassium dichromate enormously influence the reaction rate, the dye degradation enhances with the concentration of oxidant, but it is also observed that at very high concentration of potassium dichromate rate of reaction decreases Table 4 and 5 , which may be due to the increase in concentration of dichromate ion related to more Cr contents which either involves complex formation or any other side reactions suppressing the activity of ROS free radicals in the reaction (Ackerlay D F ,2006).

$Cr_2O_7^{2-} + 14H^+ + 6e \text{---------}\rightarrow Cr^{3+} + 7H_2O$

The above reaction which shows the formation of Cr^{+3} ion is not accounted because no presence of Cr^{3+} ion observed as indicated by no sea green tinge of the decolorization product mixture was noticed. The oxidation resulted into colorless leuco form of the dye Equation (6) .

Effect of pH and Buffers

The effects of change in pH on the reaction rate were studied using acids and alkalis .pH is very important in controlling coloring behavioral aspect of acidic dyes (Uddin K and Hossain S A , 2013) . The dye degradation took place appreciably between pH 1 - 6 , under high acidic medium as well as moderately under basic medium Tables 6,7,8,9and 12 respectively , which indicates that acid medium favors the production of free ROS radicals and basic atmosphere slightly hinders it. We had monitored the reaction in HCl , H_2SO_4 and HNO_3 and it was observed that although all these acids catalyze the reaction yet HCl has extremely significant effects , which may due to the fact that chloride ions facilitates the reaction and $NO_3^{\,-}$and SO_4^- have the low response ,the reaction is suppressed as evident by their salt effects .

Although more OH^- ions in alkaline medium enhances the chances of hydroxyl free radical formation (Rayaroth , 2015), but due to the presence of more H^+ in the reaction mixture as the dye is an acidic , the neutralization reaction happens and the neutral region disfavours the dye decolorization reaction (Ackerlay D F , 2006).The reaction was also studied under the influence of various buffers in the range from pH 1-6 ,only buffers in the strong acidic medium were effective in successfully carrying out the reaction ,whereas in moderate basic medium the reaction was slow, which follows the similar trend observed earlier and explicated.

Effect of Temperature

Temperature plays a major role in rate acceleration (Okoro H K and Odebunmi E O ,2009), its elevation increases the reaction rate which follows the Arrhenius Theory pretty well, The observed rate constants have been increased with the variations of temperatures in the range (313 – 343K)in acidic medium, Table 10 . Dye was investigated at various temperatures, and activation parameters were determined Table 11 . The values obtained were the energy of activation (E_a=17.068kJ.mol^{-1}), enthalpy change (ΔH=-32.391kJ.mol^{-1}), entropy change (ΔS=0.3327.27kJ.mol^{-1}.K^{-1}), and Gibbs energy change (ΔG = =-32.490 kJ.mol^{-1}) respectively. The activation parameters calculated showed the reaction is exothermic and spontaneous as shown by the negative values of Gibbs free energy of activation and enthalpy of activation and enthalpy is the driving force for the completion of this reaction. The high temperature catalyze this reaction. The moderate value of activation energy shows this reaction to proceed with moderate speed. The influence of temperature from (313-343) was studied in acidic medium.

The Arrhenius equation(1)and linear form of the Eyring-Polanyi equation (2) was used to calculate Activation parameters, Figure 1and 2

$$\ln(k) = \frac{-E_a}{R}\frac{1}{T} + \ln(A) \quad \text{Eq (1)}$$

$$\ln\frac{k}{T} = \frac{-\Delta H^\ddagger}{R}\cdot\frac{1}{T} + \ln\frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} \quad \text{Eq(2)}$$

Mechanism of the Photo catalytic reaction

Rate law

Rate Law gives us a complete insight into the mechanism of the reaction [14] .

Rate of dye decolorization is given as ,

Rate = - d [dye]/dt = k [H^+]^2 [CBB] [K_2Cr_2O7](excess)

Or - d [dye]/dt = k_{obs} [CBB] where k_{obs} = k [K_2Cr_2O7](excess)

K_{obs} , Pseudo first order rate constant of the reaction

Where k , is the specific rate constant or total order of reaction

Therefore Plot of k_{obs} verses concentration of Potassium dichromate determines the value of the rate constant k of the reaction , The value of rate constant from the graph Figure 3 , was found to be, k = 8.0×10^{-3} mole L^{-1} sec^{-1}. Since, value of k is less, the reaction takes place with slow speed.

Rate with respect to concentration of the dye:

Order of reaction with respect to dye concentration were calculated by plotting lnk verses ln[dye] Figure 4 .The slope of the straight line will show the order of the reaction n with respect to dye concentration.

Order of the reaction with respect to dye concentration was found to be 1 ,which shows first order reaction with respect to CBB concentration .

Rate with respect to concentration of the oxidant :

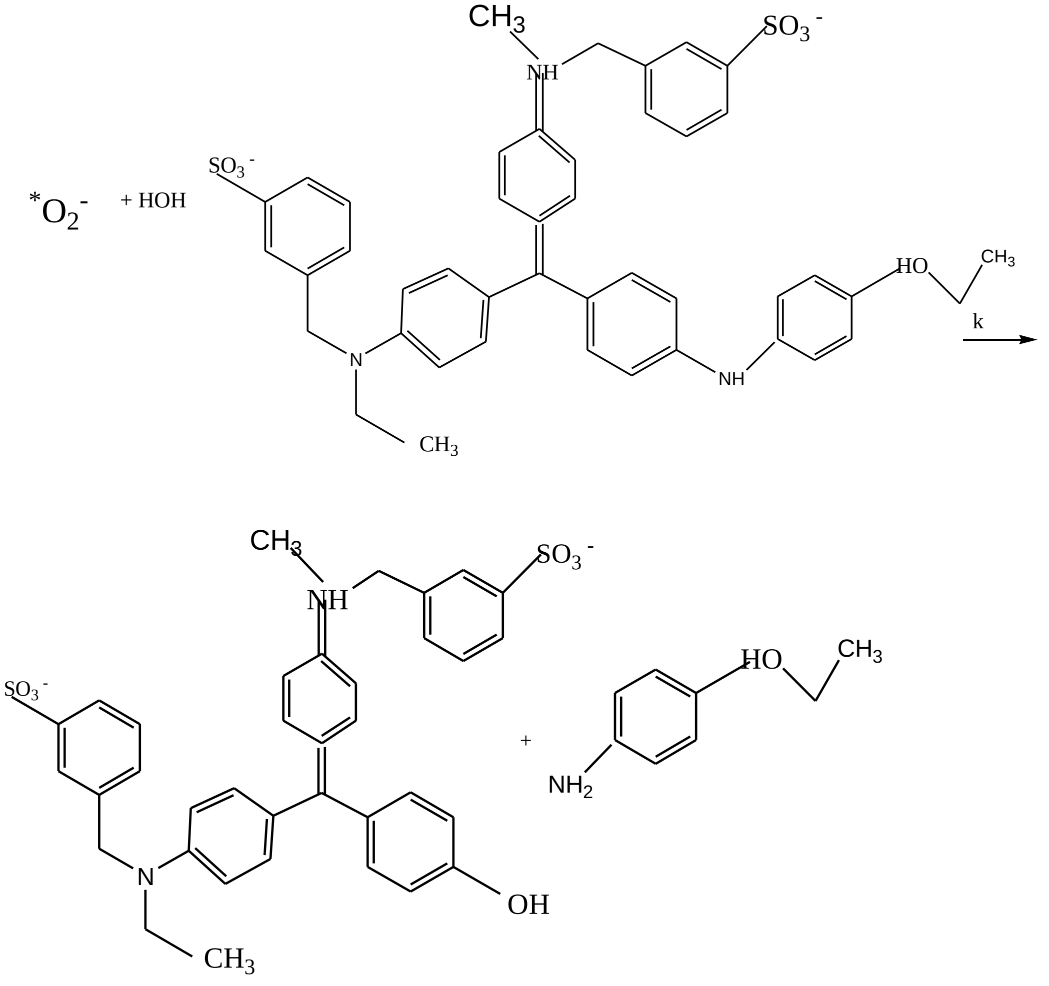
Order of reaction with respect to oxidant concentration were calculated by plotting $\ln k_{obs}$ verses $\ln[K_2Cr_2O_7]$ Figure 5 . The slope of the straight line will show the order of the reaction is 1 with respect to $K_2Cr_2O_7$ concentration.

Dye Hydrolysis in the presence of oxygen free Radicals :

Cr^{+6} + H^{+} (reductant)+ hυ (LIGHT) ----------→ Cr^{+5} Eq(3)

Cr^{+5} + HOH (hydrolysis) + hυ (LIGHT) ---------→ Cr^{+6} + $^{*}O_2^{-}$ **(**ROS) +H^{+} Eq (4)

Dye +$^{*}O_2^{-}$ (ROS) +HOH ---------→Degraded products Eq (5)



DYE HYDROLYSIS IN PRESENCE OF OXYGEN FREE RADICAL

Eq (6)

The possible degradation product [8]demonstrates that most of the products obtained by the ROS free radical $^{*}O_2^{-}$ **,** attack in aqueous medium(hydrolysis) Equation (6).

TABLE 1: EFFECT OF VARIATION OF CONCENTRATION OF COOMASSIE BRILLIANT BLUE R-250 IN AQUEOUS MEDIUM

Temperature = 313K

S.No	[CBB]x10^{-6} (mol.dm^{-3})	(dx/dt) x 10^{-3} mol.dm^{-3}s^{-1}	K_{obs} x 10^{-3} (s^{-1})	% Decoloration
01	8.0	0.00	0.00	-0.568
02	10.0	0.0	0.00	-0.207
03	20.0	0.0	0.00	-0.390
04	30.0	0.0	0.00	-0.00

TABLE 2: EFFECT OF VARIATION OF CONCENTRATION OF CBB R-250 DYE IN THE PRESENCE OF $K_2Cr_2O_7$

[$K_2Cr_2O_7$]= 0.01 mol.dm^{-3} , Temperature = 313K

S.No	[CBB] x10^{-6} (mol.dm^{-3})	(dx/dt)x10^{-3} (mol.dm^{-3}s^{-1})	K_{obs} x 10^{-5} (s^{-1})	% Decoloration
01	8.0	0.001	0.70	1.825
02	10.0	0.001	8.00	1.972
03	20.0	0.002	20.0	1.990
04	30.0	0.001	7.51	1.121

TABLE 3: EFFECT OF VARIATION OF CONCENTRATION OF CBB R-250 DYE IN THE PRESENCE OF $K_2Cr_2O_7$ AND *HCl*

[$K_2Cr_2O_7$]= 0.01 mol.dm^{-3}, [HCl] = 0.1 mol.dm^{-3}, Temperature = 313K

S.No	[CBB] x10^{-6} mol.dm^{-3}	(dx/dt)x10^{-3} (mol.dm^{-3}s^{-1})	K_{obs} x 10^{-3} (s^{-1})	% Decoloration
01	8.0	0.01	1.0	52.94
02	10.0	0.045	2.0	78.37
03	20.0	0.052	2.2	84.31
04	30.0	0.040	2.0	79.54

TABLE 4: EFFECT OF VARIATION OF CONCENTRATION OF $K_2Cr_2O_7$ IN THE PRESENCE OF AQUEOUS MEDIUM

[CBB]= 1x10^{-5} mol.dm^{-3} , Temperature = 313K

S. No.	$[K_2Cr_2O_7]$ (mol.dm^{-3})	(dx/dt)x10^{-5} (mol.dm^{-3}.s^{-1})	K_{obs} x 10^{-5} (s^{-1})	% Decoloration
01	0.001	1.0	7.0	0.200
02	0.005	2.0	8.0	0.249
03	0.01	2.0	10	0.850
04	0.05	3.0	15	1.362
05	0.1	1.0	9.0	0.893

TABLE 5: EFFECT OF VARIATION OF CONCENTRATION OF $K_2Cr_2O_7$ IN THE PRESENCE OF CBB R-250 AND HC*l*

[CBB]= 1 x 10^{-5} mol.dm^{-3} , [HCl] = 0.1 mol.dm^{-3} ,Temperature = 313K

S.No	$[K_2Cr_2O_7]$ (mol.dm^{-3})	(dx/dt)x10^{-3} (mol.dm^{-3}s^{-1})	K_{obs} x 10^{-3} (s^{-1})	% Decoloration
01	0.001	0.07	0.09	33.93
02	0.005	1.0	2.0	85.20
03	0.01	1.0	2.06	86.27
04	0.05	1.0	2.02	86.49
05	0.1	1.5	2.0	87.48

TABLE 6: EFFECT OF VARIATION OF CONCENTRATION OF N*a*OH IN THE PRESENCE OF CBB R-250 DYE AND $K_2Cr_2O_7$

[CBB]= 1 x 10^{-5} mol.dm^{-3} , $[K_2Cr_2O_7]$ = 0.01 mol.dm^{-3}, Temperature = 313K

S.No	[NaOH] (mol.dm^{-3})	(dx/dt)x10^{-5} (mol.dm^{-3}s^{-1})	K_{obs}x10^{-5} (s^{-1})	% Decoloration
01	0.001	2.0	1.0	0.237
02	0.005	2.0	1.0	0.648
03	0.01	2.0	1.0	0.122
04	0.05	2.0	1.10	19.13
05	0.1	3.0	2.33	26.05

TABLE 7:EFFECT OF VARIATION OF CONCENTRATION OF HC*l* IN THE PRESENCE OF CBB R-250 DYE AND $K_2Cr_2O_7$

[CBB]= 1 x 10^{-5} mol.dm^{-3} $[K_2Cr_2O_7]$ = 0.01 mol.dm^{-3} ,Temperature = 313K

S.No	[HCl] (mol.dm^{-3})	(dx/dt)x10^{-3} (mol.dm^{-3}s^{-1})	K_{obs} x 10^{-3} (s^{-1})	% Decoloration
01	0.005	1.0	0.001	16.52
02	0.01	1.0	0.05	21.44
03	0.05	2.00	1.0	78.07

04	0.1	2.00	2.0	81.36
05	0.5	1.5	2.0	58.72

TABLE 8 :EFFECT OF VARIATION OF CONCENTRATION OF H_2SO_4 IN THE PRESENCE OF CBB R-250 DYE AND $K_2Cr_2O_7$

[CBB]= 1 x 10^{-5} mol.dm^{-3} , [$K_2Cr_2O_7$] = 0.01 mol.dm^{-3} , Temperature = 313K

S.No	[H_2SO_4] (mol.dm^{-3})	(dx/dt)x10^{-3} (mol.$dm^{-3}s^{-1}$	K_{obs} x 10^{-3} (s^{-1})	% Decoloration
01	0.005	1.0	0.004	18.01
02	0.01	1.0	0.00	30.15
03	0.05	2.00	2.0	67.23
04	0.1	2.00	2.0	69.01
05	0.5	0.07	1.0	57.52

TABLE 9: EFFECT OF VARIATION OF CONCENTRATION OF HNO_3 IN THE PRESENCE OF CBB R-250 DYE AND $K_2Cr_2O_7$

[CBB]= 1 x 10^{-5} mol.dm^{-3} ,[$K_2Cr_2O_7$] = 0.01 mol.dm^{-3},Temperature = 313K

S.No	[HNO_3] (mol.dm^{-3})	(dx/dt)x10^{-3} (mol.$dm^{-3}s^{-1}$	K_{obs} x 10^{-3} (s^{-1})	% Decoloration
01	0.005	1.0	0.06	16.17
02	0.01	1.0	0.07	21.5
03	0.05	1.00	1.0	68.5
04	0.1	1.00	2.0	70.21
05	0.5	0.00	3.0	45.21

TABLE 10: EFFECT OF VARIATION IN TEMPERATURE IN THE PRESENCE OF $K_2Cr_2O_7$, CBB R-250 and HC*l*

[CBB]= 1 x 10^{-5} mol.dm^{-3} , [$K_2Cr_2O_7$] = 0.01 mol.dm^{-3} ,[HCl] = 0.1M

S.No	Temperature (K)	dx/dt (mol.$dm^{-3}s^{-1}$)	K_{obs} x 10^{-3} (s^{-1})	% Decoloration
01	313	2.0	4.0	61.66
02	323	2.0	4.0	65.44
03	333	2.7	4.11	78.56
04	343	3.1	4.6	78.76

TABLE 11: VARIATION OF ACTIVATION PARAMETERS AT DIFFERENT TEMPERATURES OF THE DECOLORIZATION OF CBB R-250 USING POTASSIUM DICHROMATE AS OXIDANT

Temp. (K)	**Ea (activation energy) $kJmol^{-1}$**	**-ΔH (enthalpy) $kJmol^{-1}$**	**ΔS (entropy) JK^{-1}**	**-ΔG (Gibb's free energy) $kJ.mol^{-1}$**
313	17.068	32.391	327.27	32.490
323	17.068	32.391	290.708	32.493
333	17.068	32.391	289.506	32.497
343	17.068	32.391	288.837	32.500

TABLE 12: EFFECT OF VARIATION IN pH USING BUFFERS IN THE PRESENCE OF CBB R-250 DYE AND $K_2Cr_2O_7$

[CBB]= 1 x 10^{-5} $mol.dm^{-3}$ $[K_2Cr_2O_7]$ = 0.01 $mol.dm^{-3}$,Temperature = 313K

S.No	**pH**	**(dx/dt)x10^{-3} ($mol.dm^{-3}s^{-1}$)**	**K_{obs}x10^{-3} s^{-1}**	**% Decoloration**
01	1	0.00	0.003	63.97
02	2	1.0	0.00	19.74
03	3.48	1.0	0.00	6.710
04	4.16	1.0	0.00	3.605
05	5.13	1.0	0.00	0.530
06	6	1.0	0.00	0.271

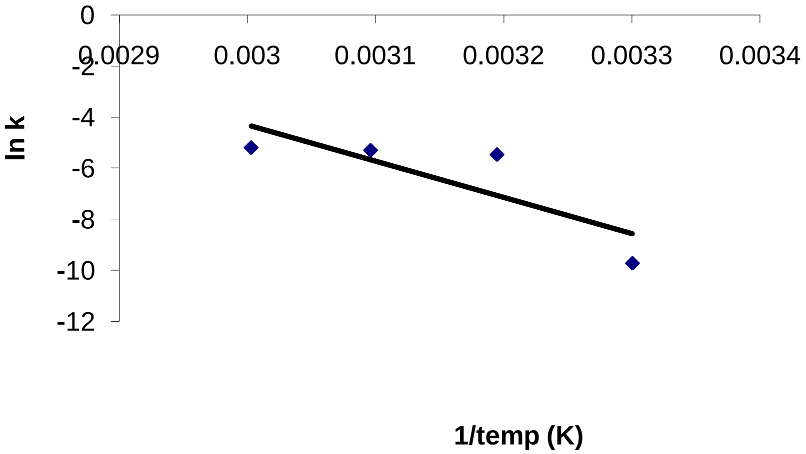


Figure1 :A plot of ln k vs 1/temp in presence of dye and oxidant

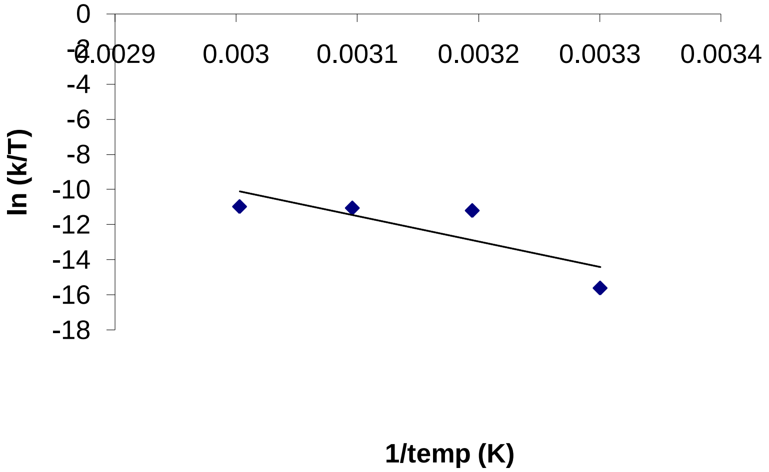


Figure 2 : A plot of ln(k/T) and 1/T in presence of dye and oxidant

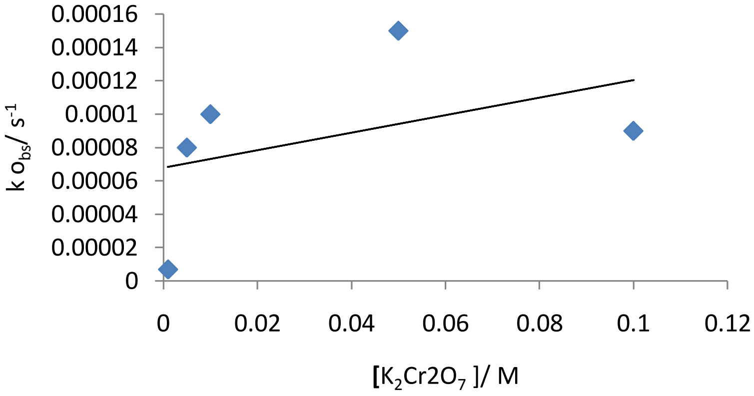


Figure 3: Plotting k $_{obs}$ values verses concentrations of potassium dichromate

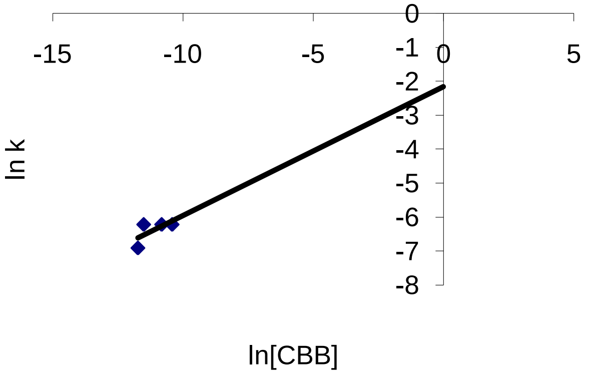


Figure 4: Plotting lnk $_{obs}$ values verses ln[dye]

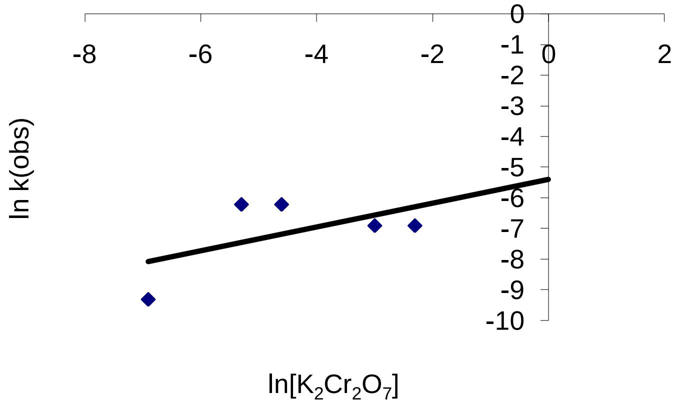


Figure 5: Plotting lnk $_{obs}$ values verses ln[$K_2Cr_2O_7$]

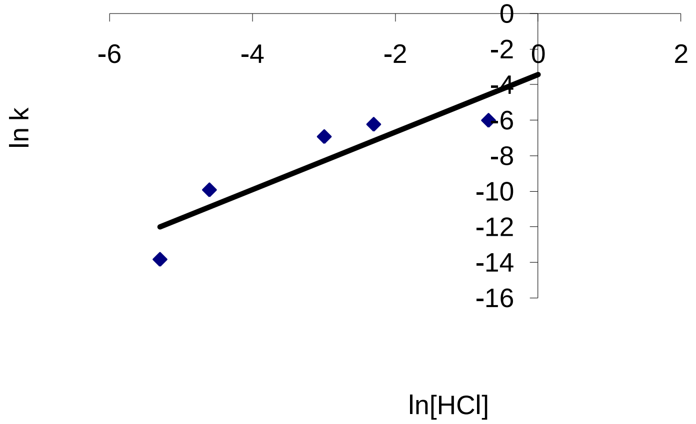


Figure 6: Plotting lnk $_{obs}$ values verses ln[HCl]

Conclusion

The above observations, results ,reaction mechanism and facts of the discussion clearly establish that hydrolytic degradation of Coomassie blue with dichromate ion $Cr_2O_7{}^{2-}$is possible only under catalytic surveillance of hydrogen ion. This process occurs in the presence of extreme exposure to sun light, due to which the highly reactive transient free radicals (ROS) are discharged . These radicals during the hydrolysis in aqueous medium oxidize the dye molecule , consequently degradation of the dye happens .The oxidation mainly occurs at the chromophores rather the dye molecular skeleton as evident by the decolorization .

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