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RESEARCH ARTICLE

ADAPTED MODE OF THE MECHANISM OF THE PHOTOOXIDATION OF COOMASSIE BLUE WITH HYDROGEN PEROXIDE BY pH VARIATIONS IN AQUEOUS MEDIUM

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ABSTRACT

Effects of variation of different parameters on decolorization of the acidic dye Coomassie Brilliant Blue R-250 has been studied in the range λ_{max} = 530nm by UV-Visible spectrophotometry. Effect of change in concentration of Coomassie Brilliant Blue R-250 with Hydrogen peroxide was studied in basic medium (pH = 11) as the decolorization of the dye was catalysed in the presence of NaOH. Effect of pH was studied, variations were(pH =1-11), it was found that high pH had enhanced the % decolorization of the Coomassie Brilliant Blue R-250. Study of Temperature was investigated in the range (313-343K) showed that temperature elevation raised the reaction rate. The activation parameters are Ea 13.33 $KJ.mol^{-1}$, $\Delta S^{\neq}$- 0.19668$KJmol^{-1}$, $\Delta H^{\neq}$+28.53 $KJmol^{-1}$ and $\Delta G^{\neq}$ + 90.0944 $KJmol^{-1}$ revealed the reaction was endothermic, nonspontaneous and strong interactions between dye molecule and oxidant take place under the assistance of NaOH as a catalyst, low value of activation energy exhibits that the reaction was fast, whereas negative entropy of activation shows that the mechanism is an associated one. Rate Law was $-d[CBB]/dt=[OH^-][CBB]^0[H_2O_2]$. Order of the reaction with respect to variation of concentration of CBB dye was zero order and with respect to hydrogen peroxide and hydroxyl ion is found to be first order. Decolorization rates were well in basic medium and unappreciable in acidic medium.

INTRODUCTION

The Coomassie Dyes are disulfonated triphenylmethane dyes. It dissolves in aqueous medium in the form of sodium salt. The hydrogen ions are liberated from two sulfonic acid groups in the dye structure and have therefore low pKa values which are pKa_1 = 1.15and pKa_2 = 1.82, consequently the dye is available in form of negatively ion. The dye is a cation with a charge of +1 in acidic pH, this positive charge is at the the nitrogen atom of the diphenylamine. At neutral pH it has green colour. The blue dye molecule is an anion with a definite charge of -1. In strong alkaline medium the dye looses all its protons and acquires light pink colour which has the pKa_3 = 11.9 (Chial *et al.,* 1993). The initial low pKa_1 and pKa_2 values show high dissociation of the dye protons, whereas the last proton is removed only in high concentration of OH^- ions as evident by the high pKa_3 value. The hydrolyzed dye released as colored effluent in wastewater is the dye that is rejected to get interacted with the fiber, there is high concentration of reactive dye in dyeing effluents together with some of the necessary inorganic ions like NaCl and Na_2CO_3 of Textile industry. Biological treatment (Kannan *et al.,* 2013) appears to be insufficient to remove colour as the dyes usually have stable aromatic rings which resist the micro organisms attack. Electrochemical methods (Bouyakoub *et al.,* 2011) are expansive and exclusive for reactive dyes. Photocatalysis methods using oxides of Mn^{2+}, Ti^{2+}, Zn^{2+} as the catalyst have the problem of the suspension of these catalyst in water as stable hydrocolloid which lacks its separation from water and remains as residue (Daud *et al.,* 2010). Photo assisted methods use photocatalyst which acts via $OH^·$ Radicals generated by the use of H_2O_2 and UV light .the disadvantage is the excessive energy cost of artificial UV light (Adinew, 2012). Chemical Redox methods are less expansive and easy to monitor, which is our method of this study. Oxidation of Coomassie blue is easily carried with hydrogen peroxide in aqueous medium. The working temperature of reaction mixture was 40° C in all runs to maintain the solubility of the dye .Initially the reaction was very slow in aqueous medium, the reaction was further monitored under high pH and found that reaction rate got accelerated as evident by the low value of energy of activation in the presence of OH^- ions rise and high % decolorization of the dye. The reaction kinetics was investigated under the influence of various buffers (pH range 1-11). The reaction rate observed a shift from moderate (low pH) to low (neutral pH) and again high values (high pH). The reactions were performed under excessive exposure of solar light (between 11.0 am - 3.0pm, day time hours).

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MATERIALS AND METHODS

Preparation of solutions

Stock solution of CBB dye =8.0×10^{-5} $molL^{-1}$, Stock solutions H_2O_2 = 0.1 $molL^{-1}$, HCl = 0.5 $molL^{-1}$, NaOH =0.50 $molL^{-1}$, KOH = 0.1 $molL^{-1}$, NH_4OH = 0.1 $molL^{-1}$, NaCl= 0.60 $molL^{-1}$ in 250 mL were prepared in deionized water. Different Buffers of pH (1-11) were prepared with their standard solutions. All standared were prepared in deionized water by standard procedures (Mendham *et al.,* 2004). Necessary dilutions were made at the time of kinetics measurements.

Decolorization rate and spectral measurements

Kinetic runs were planned under pseudo first order conditions, [H_2O_2] 100 times in excess of [CBB]. All kinetic runs were measured on Spectrophotometer Model No. UVWin 5.0 double beam Spectrophotometer has high performance different spectroscopic use of photomultiplier. Beer Lambert ̀s Law was followed. The spectral measurements were studied at a wavelength of 530 nm (λ_{max}). In all experiments absorbances were noted for 15 min for maximum effects of decolorization. % decolorization was determined by formula (Azmat *et al.,* 2011),

% Decolorization = [A(initial) – A(final)/A(initial)] × 100

Thermostat water bath tank of Model HH-4 was used for controlling temperature of sample solutions.

The molar Absorptivity value of Coomassie Brilliant Blue R-250 is at its λ_{max} was found to be $\epsilon = 2.6950 \times 10^4$ $mol^{-1}.dm^3.cm^{-1}$

RESULTS AND DISCUSSION

The decolorization of CBB R-250 dye by oxidizing agent H_2O_2 was investigated. The effects of parameters such as pH, Temperature, Concentration changes, pH variations of the medium on chemical color removal were determined and compared. The kinetic constants were also determined. In this study infuences of different parameters were measured spectrophotomerically .Spectral measurements were monitored at 530 nm. The decolorization rates were determined from the slope of Absorbance against Time plot. Negligible or zero dye decolorization was recorded in aqueous medium alone without the use of oxidizing agent Table 1,which shows that the chances of auto- oxidization of the dye was not possible.

Table 1. Effect of variation of concentration of coomassie brilliant bluer-250 in aqueous medium

Temperature = 313K

S.No	[CBB]x10^6 ($mol.dm^{-3}$)	(dx/dtx)10^3 ($mol.dm^{-3}s^{-1}$)	K_{obs}x10^3 (s^{-1})	% Decoloration
01	8.0	0.0	0.01	0.251
02	10.0	1.0	1.0	0.312
03	20.0	2.0	1.0	0.323
04	30.0	3.0	1.5	0.335

Effect of the dye concentration on reaction

The oxidation of the dye with H_2O_2 initiates the dye degradation. The results indicate that the decolorization rate was high at low concentration of dye Table 2, which shows that Oxidation would be favoured at low concentration of the dye. The reason could be that maximum photons would be able to strike the H_2O_2 molecule and high OH^- **y**ield takes place comparatively at low concentration of dye. The situation gets reversed at high concentration of dye where the absorption of photons of light by dye itself takes place instead of hydrogen peroxide molecule. Also a significant decolorization decrease resulted at high concentration of dye, could be due to the scarce insolubility of dye in aqueous medium. 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 photoexcited synchronized environment. H_2O_2 molecule irradiated with light photons release hydroxyl free radicals OH^-, these radicals enhance the dye degradation which proceeds on in less than one hour (Rauf *et al.,* 2005). The strong evidence for OH^- attack mechanism is the formation of hydroxylated intermediates which intricate through the addition of hydroxyl group to the aromatic ring of the dye, consequently hydroxylated degraded products are formed Equation (3) (Rayaroth *et al.,* 2015). This follows the detachment of chromophores from dye skeleton and the bleaching is observed.

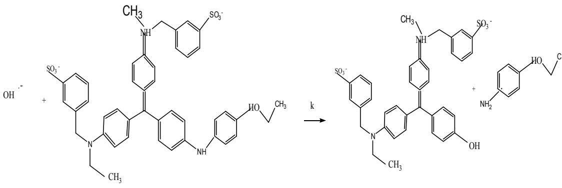
Table 2. Effect of variation of concentration of CBB R-250 dye in the presence of H_2O_2

[H_2O_2]= 0.01 $mol.dm^{-3}$, Temperature = 313K

S.No	[CBB]x10^6 ($mol.dm^{-3}$)	dx/dtx10^3 ($mol.dm^{-3}s^{-1}$)	K_{obs}x10^3 (s^{-1})	% Decoloration
01	8.0	0.008	1.0	15.106
02	10.0	1.00	1.2	4.076
03	20.0	2.00	1.31	3.069
04	30.0	3.00	1.5	1.00

H_2O_2+hυ (LIGHT) ----------→ 2 $OH^{\bullet -}$ Equation (1)

CBB Dye+$O_2^{\bullet -}$+ $OH^{\bullet -}$ -------→Degraded products Equation (2)



Free radical CBB Dye Dye Degraded product

Equation (3) [9 Rayaroth, 2015]

Effect of oxidant concentration on reaction

The concentration of the oxidant hydrogen peroxide enormously influence the reaction rate. The degradation of the dye mainly depends on the concentration of H_2O_2 Table 4. The reaction was enhanced at high concentration of H_2O_2 due to the availability of more hydroxyl radicals. Therefore the degradation reaction favored high concentration of H_2O_2.

Table 3. Effect of variation of concentration of CBB R-250 dye in the presence of H_2O_2 and NaOH

$[H_2O_2]$= 0.01 mol.dm^{-3} , [NaOH]= 0.005 mol.dm^{-3}, Temperature=313K

S.No	[CBB] x10^{6} (mol.dm^{-3})	dx/dtx10^{3} (mol.dm^{-3}s^{-1})	K_{obs}x10^{3} (s^{-1})	% Decoloration
01	8.0	0.03	7.0	95.833
02	10.0	1.5	4.0	91.353
03	20.0	4.0	1.0	75.764
04	30.0	7.0	1.0	58.585

Table 4. Effect of variation of concentration of H_2O_2 in the presence of CBB R-250

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

S.No	$[H_2O_2]$ (mol.dm^{-3})	dx/dtx10^{3} (mol.dm^{-3}s^{-1})	K_{obs}x10^{3} (s^{-1})	% Decoloration
01	0.001	0.01	0.1	0.851
02	0.01	2.00	2.05	1.226
03	0.05	2.00	2.11	0.873
04	0.1	2.21	2.2	1.308
05	0.5	2.0	2.9	1.470

Effect of NaOH concentrations and pH variations in oxidation reaction

The reaction is catalysed by concentration of NaOH. Although reaction was studied under the influence of KOH and NH_4OH but it showed excellent decolorization only in NaOH. The effects of change in pH on the reaction rate were studied using different buffers Table 10. Dye degradation took place brilliantly under high pH medium and moderately under low pH Tables 6 ,7, 8. Which indicates that basic medium favours the production of free hydroxyl radicals and acidic atmosphere hinders it.

Table 5. Effect of variation of concentration OF H_2O_2 in the presence of CBB R-250 and NaOH

[CBB]= 1 x 10^{-5} mol.dm^{-3}, [NaOH] = 0.005 mol.dm^{-3}, Temperature = 313K

S.No	$[H_2O_2]$ (mol.dm^{-3})	dx/dtx10^{3} (mol.dm^{-3}s^{-1})	K_{obs}x10^{3} (s^{-1})	% Decoloration
01	0.001	1.0	1.5	43.087
02	0.01	1.74	2.0	86.283
03	0.05	2.10	8.0	83.957
04	0.1	13.8	20.58	86.127
05	0.5	17.0	33.0	89.783

Table 6. Effect of varation of concentration of NaOH in the presence of CBB R-250 dye and H_2O_2

[CBB]= 1 x 10^{-5}mol.dm^{-3}, $[H_2O_2]$ = 0.01 mol.dm^{-3}, Temperature = 313K

S.No	[NaOH] (mol.dm^{-3})	dx/dtx10^{3} (mol.dm^{-3}s^{-1})	K_{obs}x10^{3} (s^{-1})	% Decoloration
01	0.001	1.0	2.0	71.621
02	0.005	1.0	2.0	75.757
03	0.01	1.0	5.0	83.333
04	0.05	1.0	2.0	87.671
05	0.1	1.0	2.0	88.235

Dye degradation increases in basic medium due to hydrolysis of the dye, also presence of more hydroxyl ions elevate the production of hydroxyl radicals OH^-, under the exposure of light photons. The hydrogen peroxide reacts with sodium hydroxide and form per hydroxyl anion, which later on make a nucleophilic attack on hydrogen peroxide having its excess concentration in the presence of light photons. Highly reactive and oxidizing $OH^{\bullet\,-}$ radical is generated which at pKa 11.9 form highly reactive oxygen free radicals $O_2^{\cdot -}$ Equations (4,5and 6) (Sundara,1998, Tian –Xiang Guo *et al.,* 2013). These radical cause the degradation of CBB.

Table 7. Effect of variation of concentration of KOH in the presence of CBB R-250 dye and H_2O_2

[CBB]= 1x10^{-5} mol.dm^{-3}, $[H_2O_2]$ = 0.01 mol.dm^{-3},Temperature = 313K

S.No	[KOH] (mol.dm^{-3})	dx/dtx10^{3} (mol.dm^{-3}s^{-1})	K_{obs}x10^{3} (s^{-1})	% Decoloration
01	0.001	1.0	0.04	10.990
02	0.005	1.0	0.07	13.743
03	0.01	1.0	0.04	16.962
04	0.05	1.0	0.00	23.713
05	0.1	1.0	0.00	29.541

Table 8. Effect of variation of concentration of NH_4OH in the presence of CBB R-250 dye and H_2O_2

[CBB]= 1x10^{-5} mol.dm^{-3}, $[H_2O_2]$ = 0.01 mol.dm^{-3}, Temperature = 313K

S.No	$[NH_4OH]$ (mol.dm^{-3})	dx/dtx10^{3} (mol.dm^{-3}s^{-1})	K_{obs}x10^{3} (s^{-1})	% Decoloration
01	0.001	1.0	0.0	1.671
02	0.005	1.0	0.0	4.359
03	0.01	1.0	0.0	5.081
04	0.05	1.0	0.0	2.622
05	0.1	1.0	0.0	2.053

Table 9. Effect of variation of concentration of HCl in the presence of CBB R-250 dye and H_2O_2

[CBB]= 1x10^{-5} mol.dm^{-3}, $[H_2O_2]$ = 0.01 mol.dm^{-3}, Temperature = 313K

S.No	[HCl] (mol.dm^{-3})	dx/dtx10^{3} (mol.dm^{-3}s^{-1})	K_{obs}x10^{3} (s^{-1})	% Decoloration
01	0.005	2.0	0.0	1.9772
02	0.01	2.0	0.0	2.792
03	0.05	2.0	0.0	3.900
04	0.1	2.0	0.0	2.285
05	0.5	2.0	0.0	4.643
06	1.0	1.0	0.0	16.457

Table 10. Effect of variation in pH using buffers in the presence of CBB R-250 dye and H_2O_2

[CBB]= 1x10^{-5} mol.dm^{-3}, $[H_2O_2]$ = 0.01 mol.dm^{-3}, Temperature = 313K

Buffers	pH	dx/dtx10^{3} (mol.dm^{-3}s^{-1})	K_{obs}x10^{3} (s^{-1})	% Decolorization
KCl/HCl	1.0	1.0	1.0	5.422
KCl/HCl	2.0	1.0	0.05	4.277
$NaCH_3COO/CH_3COOH$	3.0	2.0	1.6	2.805
$NaCH_3COO/CH_3COOH$	4.0	1.0	1.0	2.484
$NaCH_3COO/CH_3COOH$	5.0	1.0	2.0	2.213
KH_2PO_4/NaOH	6.0	1.0	2.0	0.0001
KH_2PO_4/NaOH	7.0	2.0	2.0	0.0001
$Na_2B_4O_7$/HCl	8.0	2.01	2.04	6.22
$Na_2B_4O_7$/HCl	9.0	2.5	2.0	6.90
$NaHCO_3$/NaOH	10.0	3.11	1.89	8.41
$NaHCO_3$/NaOH	11.0	3.16	1.5	8.4

H_2O_2 + NaOH $\dashrightarrow$ HO_2^- (per hydroxyl anion) + H_2O Equation (4)

HO_2^- + H_2O_2 + hʋ (Light) $\dashrightarrow$ $OH^{\bullet -}$ + OH^- + $HO_2^{\cdot}$ Equation (5)

$OH^{\bullet -} \xrightleftharpoons{pKa = 11.9} O^{\cdot -} + HO_2^- \dashrightarrow O_2^{\cdot -} + OH^-$ Equation(6)

At low pH of the medium (acidic), the protons trap the hydroxyl radicals and $H_2O^{\cdot}$ radical is generated which is less powerful oxidizing agent and the reaction gets slower Table 9.

$H^+ + OH^{\cdot -} \dashrightarrow H_2O^{\cdot}$ Equation (7)

Effect of temperature on reaction

Temperature elevation increases the reaction rate which follows the Arrhenius Theory well, Table 11. The activation parameters were determined and the negative value of entropy of activation, $\Delta S^{\neq}$ = - 196.68Jmol $^{-1}$ shows that this reaction has associated mechanism (Flourence *et al.,* 2014), the dye and oxidizing agent forms an activated unstable complex, which resembles a single species. Activated complex is highly structural and organised. The positive value of enthalpy of activation $\Delta H^{\neq}$ = + 28.53 KJmol^{-1} shows that this reaction is endothermic and photocatalytic i.e. acquires energy, occurs under assistance of high temperature (100% decolorization recorded), the positive value of free energy of activation $\Delta G^{\neq}$ = + 90.0944 KJmol^{-1} shows that the reaction is nonspontaneous, and indicates it requires involvement of Catalyst and depends on its concentration (Wilkins, 2002). The activation energy, Ea = 13.33 KJ.mol^{-1}, the moderate value of activation energy shows this reaction to proceed with moderate speed.

Table 11. Effect of variation in temperature in the presence of H_2O_2, CBB R-250 and NaOH

[CBB]= 1x10^{-5} mol.dm^{-3}, [H_2O_2] = 0.01 mol.dm^{-3}, [NaOH]=0.005 mol.dm^{-3}

S.No	Temperature (K)	dx/dtx10^3 (mol.dm^{-3}s^{-1})	K_{obs}x10^3 (s^{-1})	% Decoloration
01	313	0.00	5.0	100
02	323	0.00	6.0	100
03	333	0.00	7.0	100
04	343	0.08	8.0	100

KINETIC ORDER OF THE REACTION

RATE LAW

Rate of dye decolorization is given as,

Rate = - d [CBB]/dt = k [OH^-] [CBB]^0 [H_2O_2](excess)
Or - d [CBB]/dt = k_{obs} [CBB] where k_{obs} = k [H_2O_2]

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

Where k is the rate constant of reaction.

Therefore the slope of the Plot of k_{obs} verses concentrations of H_2O_2, determines the value of rate constant k of the reaction is, k= 6.0x10^{-3} s^{-1} (with out NaOH), that shows this reaction is slow and k$^{'}$ =6.5x10^{-2}M^{-1}s^{-1} (with NaOH) ,which has moderate rate, Figure 1.

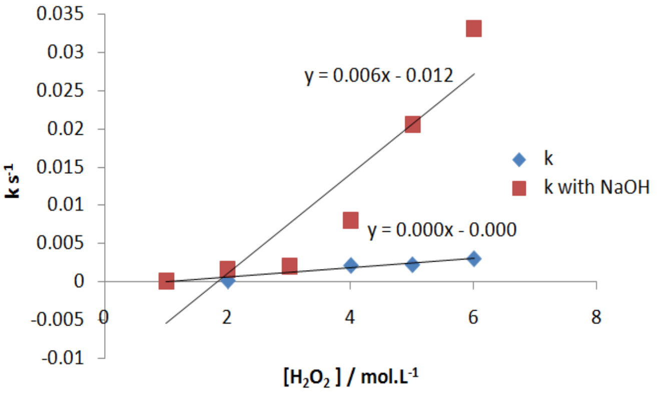


Figure 1. Plotting k $_{obs}$ values verses concentrations of hydrogen peroxide with NaOH and without NaOH

Therefore Rate Law of the decolorization of CBB without NaOH is given as

- d [CBB]/dt = k [CBB]^0 [H_2O_2]$^{0.5}$

and rate Law of the decolorization of CBB with NaOH is given as

- d [CBB]/dt = k [OH^-] [CBB]^0 [H_2O_2]$^{0.5}$

The fractional order dependence of the oxidizing agent indicates H_2O_2 gets involved in the formation of a complex configuration (Jana *et al.,* 2000) with the dye before the degradations of the dye happened. Whereas the zero order dependence of the dye shows that reaction remains unaffected with the change in dye concentration.

Rate with respect to dye concentration

Order of reaction with respect to dye concentration were calculated by plotting lnk_{obs} verses ln[CBB] Figure 2. The slope of the straight line shows the order of the reaction with respect to dye concentration. Order of the reaction is found to be zero with respect to CBB concentration.

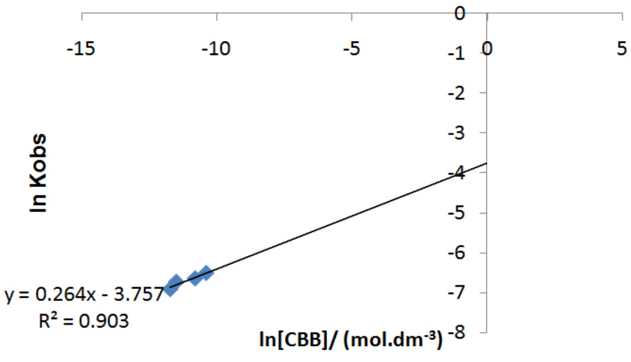


Figure 2. Plotting lnk $_{obs}$ values verses ln concentrations of the dye

Rate with respect to oxidant concentration

Order of reaction with respect to oxidant concentration were calculated by plotting lnk_{obs} verses ln [H_2O_2] Figure 3. The slope of the straight line shows the order of the reaction with respect to H_2O_2 concentration. Order of the reaction is found to fractional order (0.5 order).

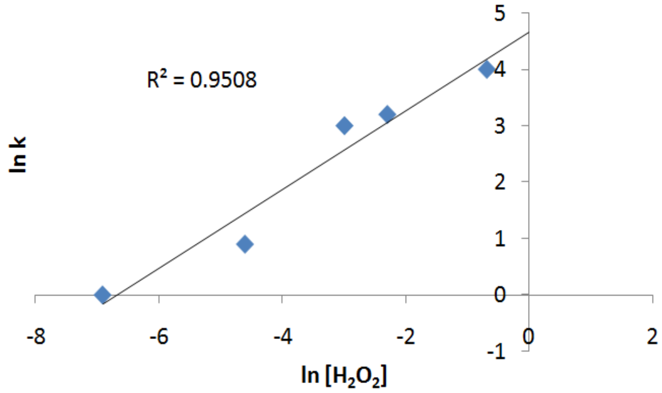


Figure 3. Plotting lnk_{obs} values verses ln concentrations of the hydrogen peroxide

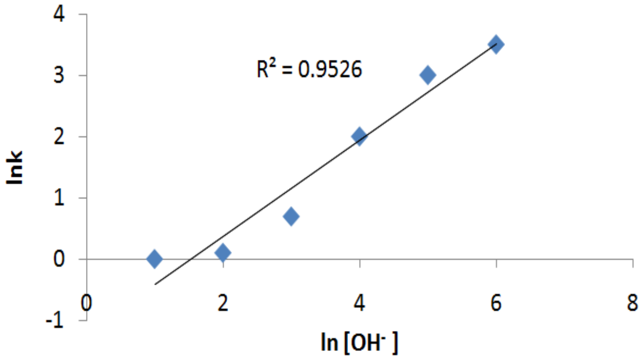


Figure 4. Plotting lnk_{obs} values verses ln concentrations of the hydroxyl ions

Rate with respect to hydroxyl ion concentration

Order of reaction with respect to hydroxyl ion concentration were calculated by plotting lnk_{obs}verses ln[OH^-] Figure 4. The slope of the straight line will show the order of the reaction with respect to OH^- concentration. Order of reaction is found to be first.

Conclusion

The current research describes a chemical oxidation method to minimize the color of an acidic dye CBB and proposes its interaction with the different inorganic compounds. It was investigated that the decolorization of the dye with the oxidant could be carried out tremendously only by the photocatalysis with NaOH. Although slight reduction of the colour intensity of the dye was observed in acidic medium but it was unappreciable. Metallic catalytic redox methods (Flourence *et al.,* 2014) are currently in profound investigations. Metallic catalyst residue in dyes structure and could also contribute to the metal ions presence in the wastewater effluent. It is difficult to judge how current trace metal removal technologies could reduce the concentrations of these metal ions to the prescribed standards. Source chemical oxidation appears to be the only solution in achieving the intoxication of untreated dyes by degradations in the textile effluents.

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