



Decolorization of acid orange 8 from textile effluent using alkaline OsO_4 /Chloramine-B solutions: Optimization and kinetic study

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Abstract

The detoxification of dye effluents produced by the fabric industries is the key challenge in waste water treatment. The oxidation process developed in the present studies shows many benefits viz., simple, low cost, mild experimental conditions, reduced reaction time, and environmental benevolence. Mono azo dye, acid orange 8 (AO 8) was used as model to explore the feasibility of using chloramine-B (CAB) with osmium tetroxide (OsO_4) as a homogeneous catalyst in the practical decolorization of dye in waste water. The influence of process parameters such as dye concentration, CAB concentration, OsO_4 concentration, alkali concentration and temperature was examined. The relative reactivity studies with other platinum group metal ions shows that OsO_4 is an effective catalyst in the present redox system. The suggested oxidation process has appreciably reduced the Chemical Oxygen Demand (COD). The treated dye was less toxic and it was verified by phytotoxicity analysis. Importantly, this method can be expediently scaled up for industrial applications with appropriate adaptations to minimize the toxicity present in industrial effluents.

Keywords: Acid Orange 8, Chloramine-B, OsO_4 catalysis, Oxidation process, Effluents.

Introduction

Synthetic dyes play a crucial role in textile, color, leather, food, pharmaceutical, silk and wool industries due to the presence of most active chromophore functional group. These dyes are extensively used for industrial purposes viz., azo, anthraquinone, sulfur, indigoid, triphenylmethyl and phthalocyanine derivatives. Amongst the above, azo derivatives are widely used¹. Due to extensive application and significant production, these dyes cause considerable pollution in the environment which affects the urban ecosystem. In the quest to protect the environment, there is an obligation, to develop green- tools to reduce harmful effluents produced by these industries. By keeping this in mind, numerous researchers have developed various physical, chemical and biological methods for the removal of dyes from effluents²⁻⁴. All these methods have vices like cost, complexity, time consuming and sludge development.

To address the challenges faced, the proposed technique is simple, easy to handle, efficient and uses eco-friendly reagents. To carry out this study, AO 8 dye is taken as a model sample. AO 8 is chemically known as 4-[(2-Hydroxy-1-naphthalenyl) azo]-3-methylbenzenesulfonic acid sodium salt is one of the important water soluble anionic mono azo dye and its abundantly used for dyeing, leather, wool and paper industries as a coloring agent⁵.

Selections of oxidants are important for the degradation of dyes in effluents. On continuation of our research, we have used N-haloamines as green oxidant due to its diverse behaviour. The adaptable behavior of the oxidant is largely dependent on its ability to perform as bases of nitrogen anions, halonium cations, and hypohalite species⁶⁻⁹. The use of this class of molecules with polarized N-X bond depends on its unique properties and applications in the synthesis of industrial substrates. The studies pertaining to the most significant among them have been enlisted^{9,11}. The important members of N-haloamines are chloramine-T (CAT), chloramine-B (CAB) and the matching bromine similarities are bromamine-T (BAT) and bromamine-B (BAB)⁹. The preliminary oxidation reaction of AO 8 dye with CAT, was sluggish. Under the same set of experimental conditions, the reaction became facile with CAB. . Moreover, literature reports available on oxidation of synthetic dyes with CAB is meagre. Hence, CAB is used as an oxidant in the present study.

Over the last few years, D block metal ions as homogeneous catalysis has attracted numerous researchers in the area of synthetic and redox reactions. Homogeneous catalysis is one of the most fascinating areas of chemistry, specifically for its mechanisms and kinetics¹²⁻¹³. It provides numerous opportunities for the study of molecular causes of reactivity and the path of the reaction. The influence of platinum group metal

ions such as OsO_4 , RuCl_3 , PtCl_4 , PdCl_2 , RhCl_3 and IrCl_3 as catalysts in redox reactions has achieved importance, as these elements have powerful catalytic significance s in many industrial and biological processes¹⁴⁻¹⁸. No literature reports are accessible on the oxidation-kinetics of AO 8 with CAB in presence of platinum group metal ions. The above facts encourage us to optimize the reaction in the presence of platinum group metal ions as a homogeneous catalyst. We believe that this work will give in depth insight about the reactivity and interactions of transition metal ions in these systems.

Under our preliminary experimental conditions, reaction is carried out without catalyst and the rate of the reaction is $3.80 \times 10^{-4} \text{ s}^{-1}$. Consequently, we employed a trace amount of transition metal ions for the decolorization of AO 8 with CAB in aqueous NaOH medium. It was found that the slow reaction became facile with $3.06 \times 10^{-5} \text{ mol dm}^{-3}$ catalyst concentration. Among OsO_4 , RuCl_3 , PtCl_4 , PdCl_2 , RhCl_3 and IrCl_3 transition metal ions, OsO_4 showed five to six fold faster than other catalyst i.e., $16.2 \times 10^{-4} \text{ s}^{-1}$ in the present study. By considering all the above facts, we have opted oxidation of AO 8 with CAB in presence of OsO_4 for removal of the dye in effluents.

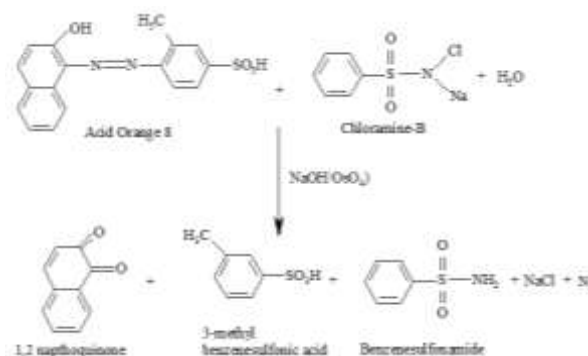
In conclusion, we report that oxidation of AO 8 with CAB in aqueous NaOH medium with efficient OsO_4 catalyst. The key objectives of this study are: i. to build up most favorable environments for the simplistic oxidation of AO 8 with CAB, ii. to observe the impact of reactants on the rate, iii. to deduce the appropriate rate law, iv. to shed light on the plausible mechanism, v. to ascertain the reactive species of CAB, AO 8 and OsO_4 vi. to ascertain the stoichiometry and the products, vii. to find the relative reactivity of platinum group metal ions, viii. to find critical role of catalytic activity of OsO_4 , ix. to validate the formation of complexes, x. to assess the thermodynamic parameters. xi. to determine chemical oxygen demand, xii. to check effect of inorganic additives and xiii. to study phytotoxicity and economic analysis.

Materials and methods

Materials: In the present work, chemicals employed were of analytical grade and their solutions were prepared by dissolving the calculated amount of sample in doubly distilled water. A fresh solution of Acid orange 8 (SD-fine) was prepared by dissolving it in doubly distilled water. Chloramine-B (CAB, Sigma), was purified by Morris *et al* method¹⁹ and prepared afresh as and when required. The stock solutions of the catalyst Viz. OsO_4 (Merck), Ruthenium trichloride (RuCl_3 Merck), Rhodium trichloride (RhCl_3) (Merck), palladium chloride (PdCl_2) (S.D fine chem. Pvt. Ltd) and iridium trichloride (IrCl_3) (S.D fine Chem. Pvt. Ltd) were prepared by dissolving in 0.01 mol dm^{-3} NaOH and 20 mM HCl , respectively¹⁷. The concentration of NaOH / HCl in the catalyst solution was taken into consideration during the kinetic runs¹⁸.

Spectrophotometric kinetic procedure: The pseudo-first-order conditions were followed to perform the kinetic runs by maintaining an excess of CAB over AO 8 in NaOH medium at 303 K. The absorbance measurements were made at 490 nm (λ_{max} of AO 8 dye) in Elico SL 159 UV-visible spectrophotometer. The experimental method followed for the current work was alike to that accounted previously¹⁸.

Stoichiometry and characterization of products: Different ratios of CAB to AO 8 with $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ NaOH and $3.06 \times 10^{-5} \text{ mol dm}^{-3}$ OsO_4 were equilibrated at 303 K for 24 h. Determination of the unreacted CAB, iodometrically showed that one mole of AO 8 consumed one mole of CAB. The stoichiometry of the reaction mentioned below:



The stoichiometric ratio of reaction mixture under stirred condition was left undisturbed for 24 h at 303 K. The reaction was monitored by TLC (Ethyl acetate:Hexane mixture (30:70) is used as eluting solvent) followed by neutralization with HClO_4 and extracted with ethyl acetate organic solvent. Silica gel (60-100 mesh) column chromatography and hexane/ethyl acetate (8:6, v/v) as mobile phase was used for separation of products. The products were found to be 1, 2 naphthoquinone and 3-methyl benzenesulfonic acid and was confirmed by GC-MS analysis with molecular ion peak at 158 (Figure-1) and 172 amu (Figure-2) respectively. No further oxidation was observed. Benzenesulfonamide (BSA or PhSO_2NH_2) was detected by thin layer chromatography²⁰.

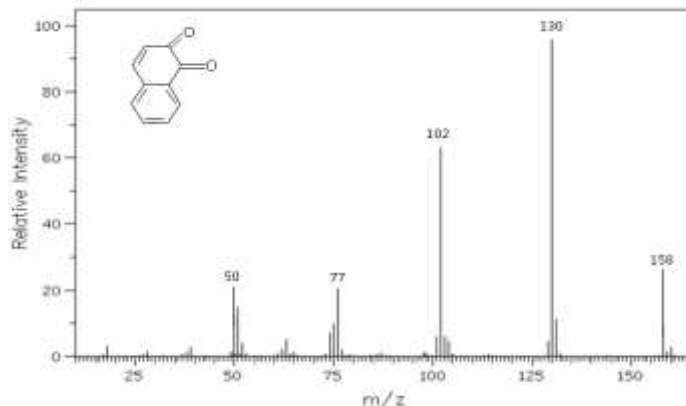


Figure-1: Mass spectrum of 1,2-naphthoquinone with its molecular ion peak at m/z 158 amu.

The first fragmentation pathway for the molecular ion of 1,2 naphthaquinone ($m/z = 158$; $C_{10}H_6O_2$) shown in Figure-1 could be explained with the loss of $-CO$ group to give a fragment ion at m/z 130 (C_9H_6O). The second fragmentations with the loss of another $-CO$ group to give another fragment ion at m/z 102 (C_8H_6). On further fragmentation with a loss of C_2H_2 gives a peak m/z 77 [C_6H_6]⁺. This fragments to another peak at m/z 51 [C_4H_4]⁺.

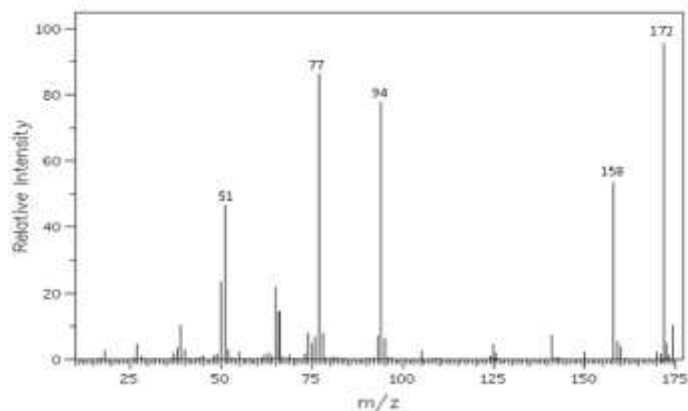


Figure-2: Mass spectrum of 3-methylbenzenesulfonic acid with its molecular ion peak at m/z 172 amu.

The pathway of fragmentation for the molecular ion of 3-methyl benzene sulphonic acid ($C_7H_8O_3S$; $m/z = 172$) in Figure-2 can be explained as follows. The primary fragmentation results in loss of $-OH$ to give a peak at $m/z = 155$ ($C_7H_7O_2S$). The loss of SO_2 gives a peak at $m/z = 91$ [C_7H_7]⁺. This on further fragmentation gives a peak at m/z 77 [C_6H_6]⁺ which gives another fragment peak at $m/z = 51$ [C_4H_4]⁺.

Results and discussion

The kinetics of oxidation of AO 8 with CAB has been examined spectrophotometrically at multiple concentrations of the reactants in the presence of OsO_4 in alkaline medium.

Influence of [AO 8] and [CAB] on the Reaction Rate: With an excess amount of oxidant [CAB], at constant [AO 8]₀, [NaOH] and [OsO_4] and temperature, plots of \log [absorbance] versus time were linear ($R > 0.9833$) indicating a first-order dependence of rate on [AO8]. The calculated pseudo-first-order rate constants (k/s^{-1}) are presented in Table-1. Under the same experimental settings, the rate of the reaction increases with an increase in [CAB] (Table-1) and plot of $k /$ versus \log [CAB] was linear ($R^2 > 0.9950$) with a fractional slope. This establishes that the order of the reaction was fractional with respect to [CAB].

Table-1: Effect of varying [CAB], [AO8], [NaOH] and [OsO_4] on the rate of reaction at 303 K.

10^3 [CAB] ($mol\ dm^{-3}$)	10^4 [AO8] ($mol\ dm^{-3}$)	10^3 [NaOH] ($mol\ dm^{-3}$)	10^5 [OsO_4] ($mol\ dm^{-3}$)	$10^4\ k/ (s^{-1})$	
				Uncatalyzed	OsO_4 Catalyzed
0.39	1.30	5.00	3.06	0.52	2.52
0.78	1.30	5.00	3.06	1.64	5.75
1.56	1.30	5.00	3.06	3.80	16.2
2.34	1.30	5.00	3.06	11.2	32.0
3.12	1.30	5.00	306	16.5	53.3
1.56	0.30	5.00	3.06	3.79	16.2
1.56	0.65	5.00	3.06	3.81	16.1
1.56	1.30	5.00	3.06	3.80	16.2
1.56	2.00	5.00	3.06	3.82	16.3
1.56	2.60	5.00	306	3.81	16.1
1.56	1.30	2.00	3.06	18.6	31.4
1.56	1.30	2.50	3.06	14.8	25.2
1.56	1.30	5.00	3.06	3.80	16.2
1.56	1.30	7.00	3.06	2.43	10.2
1.56	1.30	10.0	306	1.32	7.81
1.56	1.30	2.00	0.76	-	10.4
1.56	1.30	2.50	1.53	-	14.2
1.56	1.30	5.00	3.06	-	16.2
1.56	1.30	7.00	4.59	-	18.6
1.56	1.30	10.0	6.12	-	24.9

Influence of [NaOH] and [OsO₄] on the reaction rate: The rate declines with an increase in [NaOH] (Table-1). A linear ($R^2 = 0.9978$; slope -0.44) graph obtained from a plot of $\log k'$ versus $\log [\text{NaOH}]$, validate that negative fractional-order dependence with respect to [NaOH]. The rate of the reaction was enhanced by increasing [OsO₄] (Table-1) and a linear (Figure-3; $R^2 = 0.9892$) fractional slope of 0.50 was obtained from plot of $\log k'$ versus $\log [\text{OsO}_4]$.

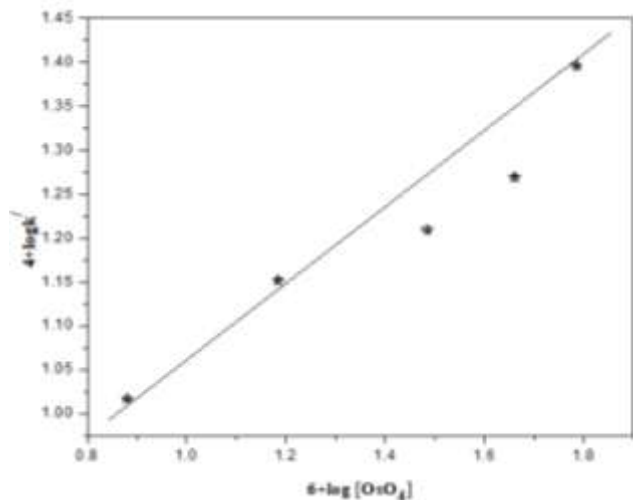


Figure-3: A Plot of $\log k'$ versus $\log [\text{OsO}_4]$.

Influence of [BSA], [NaCl] and methanol on the reaction rate: The reaction rate was not altered by the addition of BSA (PhSO_2NH_2 : $2.5 \times 10^{-3} \text{ mol dm}^{-3}$) and NaCl ($4.0 \times 10^{-3} \text{ mol dm}^{-3}$) to the reaction mixture suggesting its non-involvement in pre-equilibrium with CAB. By varying the percentage of methanol (CH_3OH) (0 - 30% v/v) influence of dielectric constant (D) of

the solvent medium on the reaction rate was studied. The percentage values of D of $\text{CH}_3\text{OH} - \text{H}_2\text{O}$ was reported in earlier literature²¹. With an increase in CH_3OH content in the reaction mixture, rate reaction was found to decrease. The rate constants k' (10^4 s^{-1}), determined at different D values were 16.2, 14.9, 12.8 and 10.6, respectively. Negative slope was obtained in the present case from the plots of $\log k'$ versus $1/D$ (Figure-4; $R^2 > 0.9842$). Blank experiments confirmed that no oxidation of CH_3OH by CAB during the experimental period took place (Table-2).

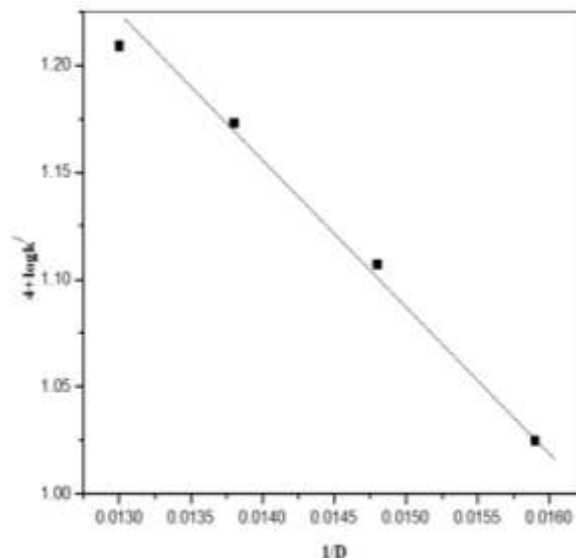


Figure-4: A Plot of $\log k'$ versus $1/D$ for OsO_4 catalyzed reaction.

Table-2: Activation parameters for the decolorization of AO 8 by CAB in alkaline medium with and without OsO_4 catalyst.

Temperature (K)	$10^4 k' (\text{s}^{-1})$		Kc
	Uncatalyzed	OsO_4 -Catalyzed	
293	1.72	8.40	0.22
298	2.60	14.1	0.39
303	3.80	16.2	0.52
308	5.40	24.9	0.82
313	8.30	33.3	1.00
$E_a (\text{kJ mol}^{-1})$	55.1	39.2	47.8
$\Delta H^\ddagger (\text{kJ mol}^{-1})$	54.2	36.7	42.3
$\Delta G^\ddagger (\text{kJ mol}^{-1})$	94.4	88.8	75.9
$\Delta S^\ddagger (\text{JK}^{-1} \text{ mol}^{-1})$	-130	-172	-100
Log A	6.65	11.5	12.6

$[\text{CAB}]_0 = 1.56 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{AO 8}]_0 = 1.3 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{NaOH}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$, and in catalyzed reaction $[\text{OsO}_4] = 3.06 \times 10^{-5} \text{ mol dm}^{-3}$.

Influence of [NaClO₄] on the Reaction Rate: The influence of ionic strength on the rate of reaction gives appreciable evidence about the type of the species intricate in the rate-determining step, i.e. whether they are ionic or non-ionic in nature. In the present case, the addition of 0.2–0.4 mol dm⁻³ of NaClO₄ solution to the reaction mixture has not altered the reaction rate. Hence there was no need to maintain the volume of NaClO₄ constant for the kinetic runs.

Influence of temperature on the reaction rate: Under different temperatures (293 - 313 K) all the five transition metal ions (Os, Ru, Pd, Rh and Ir) catalyzed reaction were studied under similar set of experimental conditions. It was found that reaction rate increased with an increase in temperature. Activation parameters for the composite reactions were calculated (Table-2) using Arrhenius plots of log *k'* versus 1/T (Figure 5; *R*² > 0.9941).

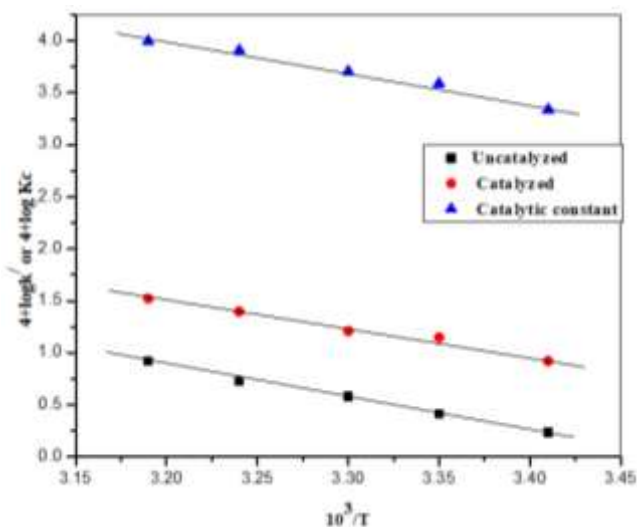


Figure-5: Plots of (a) log *k'* versus 1/T and (b) log Kc versus 1/T.

Influence of free radicals: Addition of aqueous solutions of acrylamide to the reaction mixture did not cause polymerization. This suggests the absence of free radical species involvement during the reaction sequence.

Reactive species of CAB: In aqueous solutions, both CAT and CAB show similar equilibria due to their identical properties²²⁻²⁴. The redox potential of CAB/BSA couple is pH dependant and falls with rise in pH of the medium²⁵⁻²⁸. Predominantly, PhSO₂NHCl, PhSO₂NCl⁻, HOCl and OCl⁻ are reactive oxidizing species existed in the alkaline solutions. Many researchers have observed the hindered effect of OH⁻ ions on the reaction rate [29,30] and it was due to the formation of the conjugate acid from an anion in the OH⁻ retarding step. The pH-dependant relative concentrations study by Hardy and Johnston²⁶ and also the observed kinetic results points out that PhSO₂NHCl is the active species in the current reaction scheme.

Reactive species of OsO₄: OsO₄ is found to be a proficient catalyst in the oxidation of many organic substrates by diverse oxidants in NaOH medium³¹⁻³³. OsO₄ is stable in its +8 oxidation state and in alkaline solutions, in the following equilibria:



The complexes in Equation (2) and (3) can be further reduced to octahedral species, [OsO₂(OH)₄]²⁻ which may not be involved with the oxidant/substrate. Hence, it is more appropriate to assume that OsO₄^{33,34} as the dynamic catalyst species due to its geometry^{16,18}.

Reaction scheme and kinetic investigation: The complex intermediate species are X^I and X^{II} as shown in Scheme-1. In the fast basic retarding step (step(i)), the anion PhSO₂NCl⁻ undergoes to give conjugate acid PhSO₂NHCl. In the subsequent succeeding fast step (step(ii)), PhSO₂NHCl combines with OsO₄ catalyst to provide the co-ordinate complex X^I. Further, the anionic complex interacts with the AO 8 to form additional transition complex X^{II} in the slow and rds (step(iii)). Lastly, the complex X^{II} undertakes decomposition via numerous fast steps in the presence of H₂O and OH⁻ ions to give the products with an elimination of PhSO₂NH₂ and N₂ and regeneration of OsO₄.

Complex Establishment between CAB and OsO₄: CAB and OsO₄ complex was evidenced by using UV-Vis spectrophotometry as an analytical tool. Spectral data shows that CAB and OsO₄ solutions and the mixture of both showed absorption bands at 235, 326 and 309 nm respectively (Figure-6). A hypsochromic shift of 17nm of the OsO₄ suggested that the complexation occurred between CAB and OsO₄.

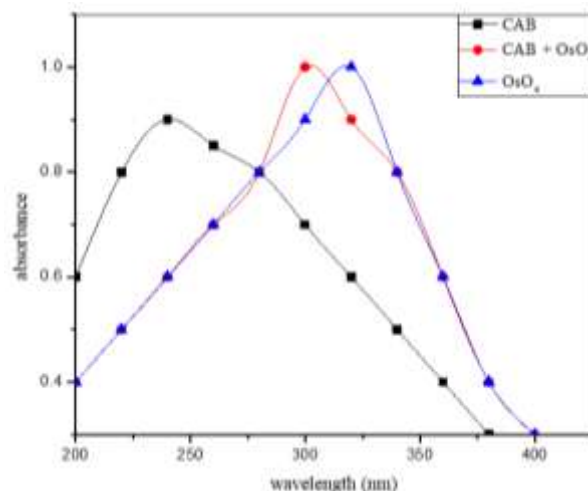
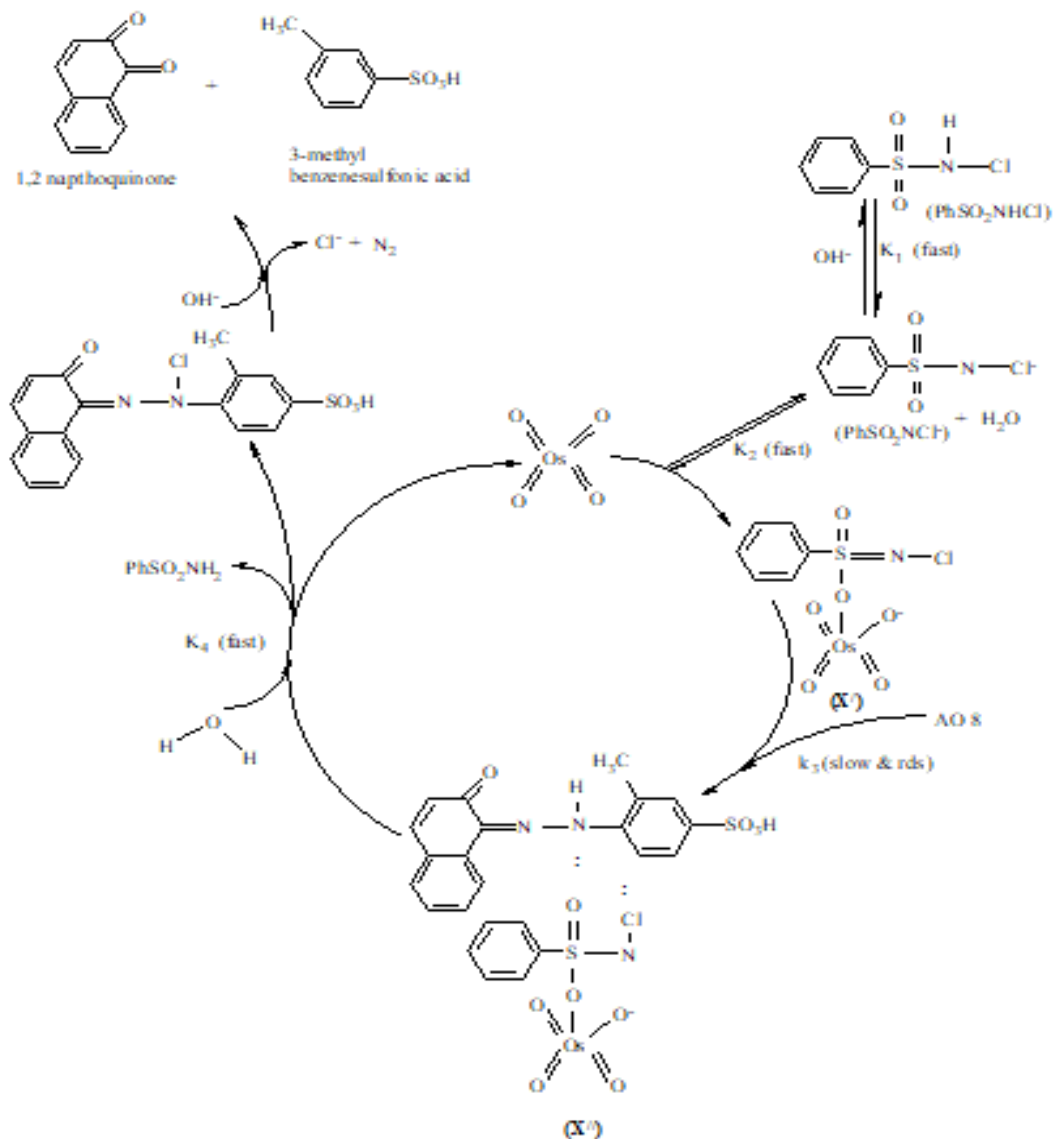


Figure-6: UV-Visible spectra of CAB, CAB+OsO₄ and OsO₄.



Scheme-1: A detailed plausible mechanism for the oxidation of AO 8 with CAB in presence of OsO₄.

According to Scheme-1 the total effective concentration of CAB is,
 $[CAB]_T = [PHSO_2NHCl] + [TsNC'] + [X']$ (6)

From steps (i) and (ii) of Scheme-1, solving for we get,

$$[X'] = \frac{K_4 K_5 [CAB]_T [OH^-] [OsO_4]}{[H_2O] + K_4 [OH^-] + K_4 K_5 [OH^-] [OsO_4]} \quad (7)$$

From the slow step of Scheme-1,

$$\text{Rate} = [X] [AO\ 8] \quad (8)$$

Upon substituting [X'] from Equation (7) into Equation (8), the following rate law can be derived.

$$\text{Rate} = \frac{K_4 K_5 [CAB]_T [AO8][OH^-][OsO_4]}{[H_2O] + K_4 [OH^-] + K_4 K_5 [OH^-][OsO_4]} \quad (9)$$

The above rate law (9) fits well to all the experimental data. The proposed mechanisms and derived rate laws were also validates the experimental results discussed below:

A negative methanol effect is in conformity with the proposed mechanism. An alter in the solvent ratio by varying the methanol content in CH₃OH-H₂O affects the reaction rate. The result of changing solvent composition on the rate of reaction has been described in detail in various well known monographs³⁵⁻³⁷. For the limiting case of zero angle of approach within two dipoles or an ion dipole system, Amis³⁷ has shown that plots of log *k'* versus 1/D gives a straight line, with a

negative slope for a reaction between a negative ion and a dipole or between two dipoles, while a positive slope results for a positive ion-dipole interaction. In the current studies, such plots were linear with negative slopes, thus supportive to the involvement of negative ion and dipole species in the rds Scheme-1.

Polar solvents are the best media for studying the ionic reactions.

Bronsted and Bjerrum theory³⁸ have explained the primary salt effect on the reaction rates.

$$\text{Log } k' = \text{log } k_0 + 1.018 Z_A Z_B \mu^{1/2} \quad (10)$$

Here, k' and k_0 are the rate constants in the presence and absence of electrolyte and Z_A and Z_B are the charges of the ions A and B, respectively. A plot of $\text{log } k'$ versus $\mu^{1/2}$ should be a straight line with a slope equal to $1.018 Z_A Z_B$ as per the above equation. The sign of $Z_A Z_B$ determines the direction of slope. When the ions A and B are of same charge, then $Z_A Z_B$ will be positive and the rate constant k' increases with $\sqrt{\mu}$. If A and B have unlike charges, then $Z_A Z_B$ will be negative and the rate constant k' decreases with $\sqrt{\mu}$. For the reactions that involve uncharged reactants, $Z_A Z_B$ is equal to zero and then independent of the ionic strength of the solution is k' . In the current examination, adjustment of the ionic strength does not modify the reaction rate which endorses that the uncharged species are involved in the rds of Scheme-1.

Catalytic Activity of OsO₄: The catalyzed and uncatalyzed reactions proceed parallelly and the relationship is narrated by Moelwyn – Hughes³⁹:

$$K_1 = k_0 + k_c [\text{catalyst}]^x \quad (11)$$

Here k_1 is the observed pseudo-first-order rate constant attained with OsO₄ catalyst and uncatalyzed reaction is denoted by k_0 . K_C is the catalytic constant and x is the order of the reaction with respect to OsO₄, which is found to be 0.66 in the current study. Then the value of K_C is calculated using the relationship:

$$K_C = (k_1 - k_0) / [\text{OsO}_4]^{0.66} \quad (12)$$

At different temperatures (293, 298, 303, 308 and 313 K) the values of K_C have been evaluated, and the values were found to vary with the temperature. A plot of $\text{log } K_C$ versus $1/T$ was linear (Figure-5; $R^2 = 0.9896$) and with respect to OsO₄ catalyst, values of activation parameters were determined and tabulated in Table-2.

Comparison of platinum group metal ion catalyzed and uncatalyzed reaction: Under an indistinguishable set of experimental settings, to understand the influence of other transition metal ions on the decolorization of AO dye in waste water, we have attempted to carry out the reaction compared the reaction rates of various transition metal ions such as Os, Rh, Ru, Ir, and Pd catalyzed reactions with uncatalyzed reaction at different temperatures (293-313K). The witnessed rates of oxidation of AO 8 in the presence of these metal ion catalysts are 3 to 10 fold quicker than without the catalyst (Table-3 as evidenced), the formation of the transient complex (X') between OsO₄ and CAB lowers the activation energy and enhances the decolourization rate¹⁸.

Table-3: Effect of varying temperature on the reaction rate and activation parameters for the oxidative decolorization of AO8 dye by CAB in the presence of OsO₄, RuCl₃, IrCl₃, RhCl₃ and PdCl₂ catalysts.

Temperature (K)	$10^4 k' s^{-1}$				
	OsO ₄	RuCl ₃	IrCl ₃	RhCl ₃	PdCl ₂
293	8.40	5.90	4.29	4.19	2.51
298	14.1	7.31	6.41	6.80	3.48
303	16.2	10.8	8.01	8.41	4.91
308	24.9	16.4	11.8	11.7	7.32
313	33.3	21.3	15.9	16.1	10.4
E_a (kJ mol ⁻¹)	39.2	42.3	49.8	49.6	52.4
ΔH^\ddagger (kJmol ⁻¹)	36.7	39.8	47.2	47.0	49.9
ΔG^\ddagger (kJ mol ⁻¹)	88.8	89.6	90.6	90.7	91.6
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-172	-164	-143	-144	-137
Log A	8.9	9.3	10.4	10.4	10.7

Experimental conditions as mentioned in Table-2.

Relative reactivities of platinum group metal ions: d^0 electronic pattern of OsO_4 has shown larger catalytic effect amongst the other metal ions shown in the contemporary studies. d^5 electronic pattern of RuCl_3 displays second highest reactivity in the series. PdCl_2 having d^8 electronic configuration was anticipated to have the minimum catalytic efficiency. d^6 electronic configurations of RhCl_3 and IrCl_3 shows in-between catalytic effectiveness with almost similar reaction rates¹⁸. Hence, based on the d electron configuration of the metal ions, the rate of reactivity decreases as the number of electrons increases in the d orbital as d^0 (OsO_4) > d^5 (RuCl_3) > d^6 (IrCl_3) $\geq d^6$ (RhCl_3) > d^8 (PdCl_2). The orders of reactivities of the metal ions under investigation are: $\text{OsO}_4 > \text{RuCl}_3 > \text{IrCl}_3 \geq \text{RhCl}_3 \geq \text{PdCl}_2$, which are in conformity with the activation energies (Table-3). This may be due to the d-electronic configuration of the metal ions. Similar performance has been noticed in our earlier works¹⁸. It is probable that through the progression of the reaction, the metal ion transitorily undergoes change in the valence state when the CAB is attached to the metal ion and later the metal ion gets back to its original valance state as shown in Scheme-1. Hence, it can be concluded that OsO_4 is the most proficient to catalyze AO 8-CAB redox system in alkaline medium.

Chemical oxygen demand (COD) analysis: COD is essential a significant parameter to identify chemical impurities present in wastewater¹⁷. Determination of COD for treated and untreated dyes was determined by the potassium dichromate method⁴⁰. The untreated dyes solution showed high COD values (1109.10 mg /L) under the similar set of experimental conditions, which indicates that it has high oxygen demanding waste which affects marine ecosystem. It was found that COD value for AO 8 dye after decolorization process is 309.2 mg/L.

Effect of inorganic additives in dyeing process: Addition of organic and inorganic additives to dye stuff may have an influence in the decolourization process. The additives used in the studies are sodium salts of carbonate, sulfate, nitrate, and chloride ions (0.04 M). The decolorization rate constant k' (10^4 s^{-1}) acquired at 0.04 M of Cl^- , NO_3^{2-} , SO_4^{2-} , and CO_3^{2-} is 16.1, 15.6, 15.4 and 6.3 for AO 8 dye. $16.2 \times 10^{-4} \text{ s}^{-1}$ rates constant is obtained for OsO_4 catalysed oxidation process under standard experimental conditions at 303 K. This clearly confirms that, rate of decolorization decreases with increase in concentration of nitrate and sulphate ions. Whilst, there is no significant change in rate of addition of chloride and carbonate ions.

Phytotoxicity analysis: The phytotoxicity analysis in vitro was studied on Vigna radiate, commonly known as green gram which is commonly used in Indian cuisine. A sample concentration (300mg/L) of treated and untreated reaction mixture was carried out for analysis. Twenty seeds each were placed separately in sterilized glass petri plate covered with filter paper. The filter paper was wetted with 5ml. of untreated and treated dye solutions respectively. Control set was carried out using distilled water simultaneously¹⁷. At regular intervals,

the plates were moistened with treated and untreated dye solutions. Petri dishes were covered and incubated at room temperatures. After 5 to 7 days, the % germination was recorded. 85% germination was recorded for control, 71% for treated dye solution and 45% was recorded with untreated dye solution⁴¹. This indicates that the untreated dye solution has hindered the crop growth which further proves that this method of decolorizing the dye is crucial to prevent the toxicity on plant growth.

Conclusion

Developed oxidation process offers numerous benefits such as simplicity, efficiency, cost-effectiveness, short reaction times, mild experimental conditions and are environmentally benign. The derived rate law is:

$$\text{Rate} = \frac{K_1 K_5 [\text{CAB}] [\text{AO8}] [\text{OH}^-] [\text{OsO}_4]}{[\text{H}_2\text{O}] + K_4 [\text{OH}^-] + K_1 K_5 [\text{OH}^-] [\text{OsO}_4]}$$

it is clearly confirm with the experimental findings.

1, 2 naphthoquinone and 3-methyl benzenesulfonic acid are oxidation products of AO 8 dye. Activation parameters were computed. Catalyzed reactions with different platinum group metal ions are 3-10 folds faster than without catalysts. The relative orders of catalysts under investigation are: $\text{OsO}_4 > \text{RuCl}_3 > \text{IrCl}_3 \geq \text{RhCl}_3 \geq \text{PdCl}_2$. It proves that OsO_4 is the efficient catalyst and the same has been used throughout the experiment. Phytotoxicity and economic analysis substantiates that this method is suitable in removing the toxic pollutants from waste water. Based on the above analysis, we can conclude that this method could be a valuable addition to the existing methods in the waste water treatment.

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