= CHEMICAL KINETICS AND CATALYSIS =

Spectrophotometric Oxidative Decolorization of Methyl Red with Chloramine-T and Bromamine-T: Comparative Kinetic Modeling and Mechanistic Study¹

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Abstract—Methyl Red (MR) is a synthetic mono-azo dye which is extensively used as a colorant in textile and paper printing industries. The widespread amount of MR dye in wastewater poses potential threat to ecosystem and human health. In this context, we have developed a simple and expeditious oxidative decolorization technique for the removal of MR dye by organic *N*-haloamines viz., chloramine-T (CAT) and bromamine-T (BAT) present in the wastewater. The reaction was focused to changes in: (i) concentration of *p*-toluenesulfonamide, (ii) ionic strength, (iii) dielectric permittivity, (iv) polymerization study, and (v) halide ions effects. The activation parameters were deduced. Oxidation products of MR dye were identified. The rate of oxidation of MR is about four times faster with BAT than with CAT. The chemical oxygen demand value of the dye was determined. Phytotoxicity and economic analysis were carried out for the proposed decolorization process. A plausible mechanism conforming the kinetic data, reaction stoichiometry and product analysis has been proposed. Further, the present redox system can be adopted for treating MR dye present in industrial effluents with suitable modifications to reduce the toxicity caused by MR dye in wastewater.

Keywords: methyl red, chloramine-T, bromamine-T, oxidative-decolorization, kinetics-mechanism, wastewater

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INTRODUCTION

Azo dyes are the components having the azo group (N=N) and alkyl or anyl group (R-R') and hence the functional group is R-N=N-R'. The color of an azo dye is owing to the interaction between an azo group and two aryl species. These dyes are classified as mono-azo, di-azo, tri-azo dyes etc., depending on the number of azo groups such as one, two, three, etc [1]. Azo dyes are most widely used colorants in textile industries and also in paper printing, color photography and food processing [2–4]. Methyl Red (MR) or C.I. Acid Red 2 (4-dimethylaminoazobenzene-2'-carboxylic acid sodium salt) is a synthetic mono-azo dye which is widely used in textile and paper industries [1, 2]. Wastewater released from these industries in which MR dye used is highly colored and toxic and hence, leads to environmental and health problems. In this context, several physical, chemical, and biological techniques have been developed for the removal of MR dye from wastewater. Amongst all these methods. oxidative decolorization technique has a enormous

potential for the removal of MR dye without introducing any impurities, and also offer several advantages such as its simplicity and cost-effective over the other methods. From these reasons, we carried out the title reaction.

N-Haloarenesulfonamidates, generally known as organic N-haloamines, are mild oxidants containing a strongly polarized N-bonded halogen in its +1 oxidation state. Kinetics and mechanism of oxidation by these reagents have fascinated the alertness of chemists, particularly synthetic chemists and kineticists due to their diverse property to act as halonium cations, hypochlorites and N-anions [5]. They interact with a wide range of functional groups in aqueous and nonaqueous media in the presence of an acid or a base [6-8]. As a result, these reagents have been used as mild and selective oxidizing agents in synthetic and mechanistic chemistry. The prominent member of this group, sodium N-chloro-p-toluenesulfonamide commonly known as chloramine-T (CAT) is a well known analytical reagent. The kinetic and mechanistic aspects of many of its reactions have been well documented [6–9]. Bromamine-T (BAT), the bromine

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Fig. 1. ¹³C FT-NMR spectrum of BAT.

analogue of CAT is giving much importance as a mild oxidant and has been found to be a better oxidizing agent than the chloro compounds [5, 7, 10–13]. This reagent can be easily prepared by the bromination of CAT. A glance of literature indicates that the reports on the oxidation of dyes with these reagents are relatively meager from its kinetic and mechanistic stand point. Further, these oxidants are commercially available, cost-effective, water-tolerant, non-toxic and easy to handle. Therefore, in the present article, we have established the optimum conditions for the facile oxidative decolorization of MR dye with CAT and BAT in acid medium.

The main objectives of the present investigations are to: (i) develop the optimum conditions for the oxidative decolorization of MR dye by CAT and BAT in acid medium, (ii) accumulate kinetic data, (iii) elucidate suitable mechanisms, (iv) deduce appropriate rate laws, (v) ascertain the various reactive species, (vi) identify the oxidation products, (vii) compute activation parameters, (viii) analysis of phytotoxicity and economic analysis, and (ix) evaluate relative reactivity and kinetic modelings of CAT and BAT toward oxidative decolorization of MR dye in acid medium.

EXPERIMENTAL

Bromamine-T was prepared [14] using chloramine-T. To a solution of CAT (20 g in 400 mL of water), about 4 mL of liquid bromine was added drop wise with constant stirring at room temperature to yield dibromamine-T (DBT). The solid DBT was filtered under suction, washed thoroughly with ice-cold water until all the absorbed bromine had been removed, and then vacuum-dried for 24 h. About 20 g of DBT thus obtained was dissolved in 30 mL of 4 mol dm⁻³ NaOH with constant stirring at room temperature, and the resultant aqueous solution was cooled in ice. The pale yellow crystals of BAT that formed were filtered under suction, washed quickly with the minimum amount of ice-cold water, and dried over P_2O_5 . The compound was recrystallized from hot water (50°C). The purity of BAT was checked iodometrically through its active bromine content and the compound was further characterized [15] by the ¹³C FT-NMR spectrum (Fig. 1) of BAB was obtained in D₂O, using tetramethyl silane (TMS) as the internal standard. (recorded on a Bruker WH 400-MHz nuclear magnetic resonance spectrometer), showed signals ¹³C NMR spectrum (p.p.m. relative to TMS): 145.39 (C-1, carbon attached to S atom), 140.52 (C-4), 131.52 (C-2,6), 129.36 (C-3,5), and 23.0 (methyl carbon). Chloramine-T (Thomas Baker) was purified by the method of Morris et al. [16]. An aqueous solution of these oxidants was prepared afresh whenever required, standardized by iodometric method and stored in brown bottles until further use to prevent its any photochemical deterioration. The concentration of stock solution was periodically determined iodometrically. Methyl Red (Sigma) was used as received and an aqueous solution of the desired strength of the dye was prepared afresh each time. All other chemicals used were of analytical grade. Doubly distilled water was used throughout the experiment.

Detailed kinetic runs were performed under pseudo first-order conditions of $[\text{oxidant}]_o \gg [\text{MR}]_o$ at 303 K in presence of HClO_4 . Kinetic measurements were carried out using an UV–Vis spectrophotometer (Digital spectrophotometer 166, Systronics, India). In the present study, the kinetic experiments were carried out between 293 and 313 K. Raaga ultra cold chamber with digital temperature control (India) was used for kinetic experiments in which a constant desired temperature was maintained with an accuracy of $\pm 0.1^{\circ}$ C. Reactions were carried out in glass stoppered pyrex boiling tubes whose outer surface was coated black to eliminate any photochemical effects. The oxidants as well as requisite amount of MR dye, HClO_4 solutions and water (to keep the total volume constant for all the runs) were taken in separate tubes and were thermostatted for about 30 min at 303 K. The reaction was initiated by the rapid addition of a measured amount of oxidant to the stirred reaction mixture. Immediately, 4 mL aliquot of the solution was pipetted into a cuvette placed in the spectrophotometer. Absorbance measurements were made at 524 nm (λ_{max} of the dye) for nearly three half-lives. The absorbance readings at t = 0 and t are D_0 and D_t . Plots of log D_0/D_t versus time were made to evaluate the pseudo first-order rate constants (k', s^{-1}). All kinetic runs were carried out twice to check reproducibility with $\pm 3\%$ error was found. Regression analysis of the experimental data was carried out on an fx-100 W scientific calculator to evaluate the regression coefficient, R^2 .

The toxicity studies with respect to generation of oxidative stress in plants are yet to get much significant attention. Due to this reason, maize seeds (*Zea Mays* L)

were used as model crop for this study [17]. The germination tests were carried out in three Petri dishes, where 20 maize seeds were sown per dish on a wet filter paper among which one set was treated as control using distilled water. Another two sets of dishes were treated 5 mL each with treated and untreated dye solution at regular intervals. All the three petri plates were incubated at room temperature and observed for radical emergence. The germination was recorded after 7 days.

RESULTS AND DISCUSSION

Varying ratios of oxidant to MR dye in the presence of 4.0×10^{-3} mol dm⁻³ HClO₄ were equilibrated at 303 K for 48 h. The iodometric titration of unreacted oxidant in the reaction mixture showed that one mole of oxidant was consumed per mole of the dye according to the Eq. (1):



Here $Ts = CH_3C_6H_4SO_2$ for CAT and BAT, with X = Cl or Br.

The reaction mixture in the stoichiometric ratio under stirred condition was allowed to progress for 48 h at 303 K. After completion of the reaction (monitored by TLC), the reaction products were neutralized with NaOH and products were extracted twice with diethyl ether. The organic products were subjected to spot tests and chromatographic analysis (TLC technique), which revealed the formation of oxidation products, namely 4-dimethylaminophenylhydroxylamine and 2-nitrosobenzoic acid. These oxidation products were separated by column chromatography and confirmed by GC-MS. The GC-MS data were obtained on a 17A shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer. The mass spectra showed a molecular ion peak at 153 and 151 amu, clearly conforming 4-dimethylaminophenylhydroxylamine and 2-nitrosobenzoic acid, respectively (Figs. 2 and 3). All other peaks observed in GC-MS can be interpreted in accordance with the observed structure. Further, it was noticed that there was no reaction between 4-dimethylaminophenylhydroxylamine and 2-nitrosobenzoic acid with CAT and BAT under the present set of experimental conditions. Further, these compounds are largely used in textile and tannery industries, and also in water treatment and dye making plants [18]. The reduction product of oxidant, *p*-toluenesulfonamide (PTS or TsNH₂), was extracted with ethyl acetate and detected by paper chromatography [19]. Benzyl alcohol saturated with water was used as the solvent with 0.5% vanillin in 1% HCl solution in ethanol as spray reagent ($R_f = 0.905$).

Preliminary kinetic runs revealed that CAT and BAT (henceforth abbreviated as oxidant) decolorizes MR dye completely within 45 and 20 min, respectively under the present set of experimental conditions. The kinetics of oxidative decolorization of MR dye with oxidant was investigated at several initial concentrations of the reactants in HClO₄ medium at 303 K. Under pseudo first-order conditions of [oxidant]₀ \gg



Fig. 2. Mass spectrum of 4-dimethylaminophenylhydroxylamine with its parent molecular ion peak at 153 amu.



Fig. 3. Mass spectrum of 4-nitrosobenzoic acid with its parent molecular ion peak 151 amu.

 $[MR]_o$ at constant $[oxidant]_{o,}$ $[HClO_4]$ and temperature, plots of log (absorbance) versus time were linear $(R^2 > 0.9910)$, indicating a first-order dependence of rate on $[MR]_o$. The values of pseudo first-order rate constants (k', s^{-1}) are reported in Table 1. The values of k' remain unaffected with a change in $[MR]_{o,}$ confirming the first-order dependence of rate on $[MR]_o$. Under the same experimental conditions, an increase in [oxidant]_o increased the rate (Table 1). A plots of log k' versus [oxidant] was linear ($R^2 > 0.9930$) having a slope equal to unity, indicating a first-order dependence of the reaction rate on [oxidant]_o. Further, a plots of k' versus [oxidant], was linear ($R^2 > 0.9930$) passing through the origin, confirming the first-order dependence of rate on $[oxidant]_o$ and also showing that the MR dye-oxidant complex has only transient existence.

At constant [oxidant]_o, [MR]_o, and the temperature, the reaction rate enhanced with increase in $[HClO_4]$ (Table 1). A plots of log k' versus log $[HClO_4]$ was linear ($R^2 > 0.9891$) with a slopes of 0.75 and 0.27 for CAT and BAT, indicating a fractional-order dependence of rate on [HClO₄]. Addition of *p*-toluenesulfonamide (PTS or TsNH₂), to the reaction mixture in the concentration range of 2.0×10^{-3} to $8.0 \times$ 10^{-3} mol dm⁻³ did not influence the rate significantly. It indicates that PTS is not involved in any step prior to the rate-determining step (rds) in the proposed reaction scheme. Similarly, addition of Cl⁻ or Br⁻ ions in the form of their sodium salts in the concentration range of 2.0×10^{-3} to 8.0×10^{-3} mol dm⁻³ had no substantial effect on the rate of reaction indicates that the halide ions are not participate in the reaction sequence.

Effect of ionic strength of the reaction system on the rate of the reaction was studied by adding 0.2 mol dm⁻³ NaClO₄ solution to the reaction mixture. It was noticed that there was no notable change on the rate of the reaction signifies the involvement of at least one neutral molecule in the rate-determining step. Hence, no attempt was made to keep the ionic strength of the system constant for kinetic runs. The dielectric constant (D) of the medium was varied by adding MeOH (0-30 vol %) to the reaction mixture, all other experimental conditions being held constant. The rate increased with increase in MeOH content (Table 2) and plots of $\log k'$ versus 1/D were linear (Fig. 4; $R^2 > 0.9905$) with positive slopes. It was further noticed that no reaction of dielectric with the oxidant occurred under the experimental conditions employed. Values of D of MeOH-H₂O mixtures were taken from the literature [20] were employed.

The reaction was studied at different temperatures (293, 298, 303, 308, and 313 K), keeping other experimental conditions constant. From the linear Arrhenius plots of log k' versus 1/T (Fig. 5; $R^2 > 0.9907$), activation parameters (E_a , ΔH^{\neq} , ΔS^{\neq} , ΔG^{\neq} , and log A) for the overall reaction were computed and these results are summarized in Table 3. Addition of acrylamide to the reaction mixture did not initiate polymerization, showing the absence of free radical species in the reaction sequence. The control experiments were also performed under similar reaction conditions without the oxidant.

CAT and BAT (TsNXNa) are acts as a mild oxidant in both acidic and alkaline media. In general, oxidant undergoes a two electron change in its reactions forming the reduction products, PTS and NaCl [21]. The oxidation potential of CAT-PTS redox couple is pH dependent [22] and decreases with increase in pH of the medium (the redox potential E_{redox} of CAT-PTS

Table 1. Effect of variation of [oxidant], [MR], and $[HClO_4]$ on the reaction rate at 303 K

$10^{4} [MR]_{o}$	10 ³	10 ³	$10^4 k' (s^{-1})$	
(mol dm^{-3})	$[\text{oxidant}]_{\text{o}}$ (mol dm ⁻³)	$[HClO_4]$ (mol dm ⁻³)	CAT	BAT
0.5	4.0	4.0	5.90	26.45
2.0	4.0	4.0	5.97	26.47
4.0	4.0	4.0	5.92	26.42
6.0	4.0	4.0	6.02	26.50
8.0	4.0	4.0	5.96	26.48
2.0	1.0	4.0	1.50	7.38
2.0	2.0	4.0	2.92	12.79
2.0	4.0	4.0	5.97	26.47
2.0	8.0	4.0	12.0	51.17
2.0	12.0	4.0	15.8	55.76
2.0	4.0	2.0	3.37	21.54
2.0	4.0	4.0	5.97	26.47
2.0	4.0	6.0	7.48	28.11
2.0	4.0	8.0	7.68	30.56
2.0	4.0	10.0	11.0	33.37

Table 2. Effect of varying dielectric constant of the medium on the rate of reaction at 303 K

MeOH	D	$10^4 k' (s^{-1})$		
(vol %)		CAT	BAT	
0	76.73	5.97	26.47	
10	72.37	6.42	27.24	
20	67.48	6.99	27.94	
30	62.71	7.24	28.31	

Experimental conditions: $[oxidant]_{o} = 4.0 \times 10^{-3} \text{ mol } dm^{-3};$ $[MR]_{o} = 2.0 \times 10^{-4} \text{ mol } dm^{-3};$ $[HClO_{4}] = 4.0 \times 10^{-3} \text{ mol } dm^{-3}.$

couple is 1.138, 0.778, 0.614, and 0.50 V at pH 0.65, 7.0, 9.7, and 12, respectively). In view of the homogeneity in properties of CAT and BAT, similar redox potential behavior can be expected for BAT as well. The nature of the active oxidizing species and mechanism depends on the nature of halogen atom, the groups attached to the nitrogen, and the reaction condition. The species responsible for such oxidizing character may be different depending on the pH of the medium. Aqueous solutions of CAT and BAT behave as a strong electrolyte and depending on the pH of the medium, it furnishes [15, 21–24] following equilibria in solutions:

$$\Gamma sNXNa \rightleftharpoons TsNX^{-} + Na^{+}, \qquad (2)$$

$$\Gamma sNX^{-} + Na^{+} \rightleftharpoons TsNHX,$$
 (3)





$$2T_{s}NHX \rightleftharpoons T_{s}NH_{2} + T_{s}NX_{2},$$
 (4)

$$TsNHX + H_2O \rightleftharpoons TsNH_2 + HOX,$$
 (5)

$$TsNX_2 + H_2O \rightleftharpoons TsNHX + HOX,$$
 (6)

 $HOX \rightleftharpoons H^+ + XO^-,$ (7)

$$HOX + H^+ \rightleftharpoons H_2O^+X.$$
 (8)

Therefore, the possible oxidizing species in acidified CAT and BAT solutions are TsNHX, TsNX₂, HOX, and possibly H_2O^+X . If di-haloamine (TsNX₂) were to be the reactive species, then according to Eq. (4) the rate law predicts a second-order dependence of rate on [oxidant]_o, which is converse to the experimental

 Table 3. Temperature dependence and activation parameters for the oxidative decolorization of MR by oxidant in acid medium

	$10^4 k' (s^{-1})$		
	CAT	BAT	
Temperature (K)			
293	2.60	12.9	
298	4.43	18.4	
303	5.97	26.4	
308	7.93	37.3	
313	9.03	51.3	
$E_{\rm a}$ (kJ mol ⁻¹)	45.6	40.2	
ΔH^{\neq} (kJ mol ⁻¹)	43.0	37.7	
ΔG^{\neq} (kJ mol ⁻¹)	88.7	90.5	
$\Delta S^{\neq} (\mathrm{J} \mathrm{K}^{-1} \mathrm{mol}^{-1})$	-174	-170	
log A	9.01	8.70	

Experimental conditions: $[\text{oxidant}]_0 = 4.0 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, $[\text{MR}]_0 = 2.0 \times 10^{-4} \text{ mol } \text{dm}^{-3}$, $[\text{HClO}_4] = 4.0 \times 10^{-3} \text{ mol } \text{dm}^{-3}$.



Fig. 5. Plots of $\log k'$ versus 1/T.

observations. If HOX is primarily involved, a firstorder retardation of rate by added *p*-toluenesulfonamide is expected (Eq. (5)). However, no such effect was noticed and hence HOX can be feint out as the oxidizing species. Hardy and Johnston [23] were made detailed calculations on the concentration dependence of various oxidizing species of CAT and BAT on pH in aqueous oxidant solution and have shown that TsNHX is the predominant oxidizing species in acid medium.

In the present case, the fractional-order dependence of rate on [H⁺] suggests that the protonation of TsNHX results in the formation of TsN⁺H₂X which is likely to be the active oxidizing species in the oxidation of MR dye in acid medium. In view of the foregoing discussion and the experimental results, Scheme 1 is formulated for the MR-oxidant redox system in acid medium. In Scheme 1, an initial equilibrium H⁺ ion accelerating step (step (i)) involves protonation of the conjugate acid TsNHX forming the active oxidizing species TsN⁺H₂X. In the next slow and rate-determining step (step (ii)), a lone pair of electrons on the nitrogen atom of the dye attacks the positive chlorine of the protonated oxidant species to form an intermediate complex (X) with the elimination of $T_{s}NH_{2}$. In the next subsequent fast steps, this complex undergoes hydrolysis followed by cleavage of N-N bond to yield the ultimate products viz. 4-dimethylaminophenylhydroxylamine and 4-nitrosobenzoic acid. Based on Scheme 1, the rate law can be formulated as shown below.

If $[oxidant]_t$ is the total effective concentration of [oxidant], then

$$[oxidant] = [TsNHX] + [TsN^{+}H_{2}X].$$
(9)

From step (i) of Scheme 1

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4-Dimethylaminophenylhydroxylamine

Scheme 1. A detailed mechanistic interpretation for the oxidative decolorization of MR dye with oxidant in $HClO_4$ medium.

$$[TsNHX] = \frac{[TsN^{+}H_{2}X]}{K_{1}[H^{+}]}.$$
 (10)

By substituting for [TsNHX] from Eq. (11) into Eq. (10), we get

$$[T_{s}N^{+}H_{2}X] = \frac{K_{1}[oxidant]_{l}[H^{+}]}{1 + K_{1}[H^{+}]}.$$
 (11)

From slow and rds (step (ii)) of Scheme 1

$$Rate = k_2[TsN^{\dagger}H_2X][MR].$$
(12)

By substituting for $[TsN^+H_2X]$ from Eq. (12) into Eq. (13), we obtain

Rate =
$$\frac{K_1 k_2 [\text{oxidant}]_{t} [\text{MR}] [\text{H}^+]}{1 + K_1 [\text{H}^+]}$$
. (13)

The rate law (13) is in complete agreement with the experimentally observed results, wherein a first-order dependence of rate each on $[oxidant]_o$ and $[MR]_o$, and fractional-order on $[H^+]$ was observed.

Most of the organic reactions are carried out in solution, and it is therefore important to realize the effect of solvent on the course and rate of the reactions. A change in solvent composition by varying methanol content affects the reaction rate. Several approaches [25-30] have been made to explain quantitatively the effect of the dielectric constant of the medium on the rates of reactions in solutions. For the limiting case of zero angle of approach between two dipoles or an ion-dipole system, Amis [30] has shown that a plot of $\log k'$ versus. 1/D gives a straight line with a negative slope for the reaction between a negative ion and a dipole or between two dipoles, while a positive slope indicates a reaction between a positive ion and a dipole. The positive dielectric effect observed in the present studies (Table 2) clearly supports the involvement of a positive ion and a dipole in the rate-determining step (step (ii)) of Scheme 1.

The rate constant of ionic reactions depends upon the charges of reacting ions and also upon the ionic strength of the solution. The study of the influence of

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ionic strength on the rate of the reaction gives a valuable information about the type of the species involved in the rate-determining step, i.e., whether ionic or non-ionic species are involved in the reaction. The effect of primary salt on the rate of the reaction is explained by Bronsted and Bjerrum equation [28] $\log k' = \log k_0 + 1.018 Z_A Z_B \sqrt{I}$. Here *I* is the ionic strength of the reaction medium. *k*' and k_0 are the specific rate constants in the bulk of the reaction and at infinite dilution; and Z_A and Z_B are the ionic charges of the reactants A and B. The variation of k' with ionic strength should depend on the sign of Z_A and Z_B . From the above equation, a plot of log k' versus \sqrt{I} would be linear yielding the slope equal to 1.018 $Z_A Z_B$ and an intercept log k_{0} . This equation predicts that: (i) if both ions have same charges then, $Z_A Z_B$ is positive and so k' increases with I; (ii) if Z_A and Z_B have opposite signs, then $Z_A Z_B$ is negative and so k' decreases with I; and (iii) if either Z_A or Z_B have neutral valence, then $Z_A Z_B$ is zero, so k' is independent of the ionic strength of the solution. In the present investigations, variation of ionic strength of the medium by adding NaClO₄ solution (0.20 mol dm^{-3}) does not alter the rate indicates that one of the reacting species i.e., MR dye has neutral valence in the rds as shown in Scheme 1 (step (ii)). Therefore, the observed ionic strength effect is in accordance with the Bronsted-Bjerrum concept and proposed scheme.

The proposed mechanism is also supported by the moderate values of energy of activation and other activation parameters. The positive values of ΔG^{\neq} and ΔH^{\neq} indicate that the transition state is highly solvated. The negative values of $\Delta S^{\#}$ suggest the formation of a rigid associative transition state with a few degrees of freedom in both cases. Further, the comparable value of $\Delta G^{\#}$ signifies the same type of the reaction mechanism could be operative for the oxidation of MR by CAT and BAT in acid medium. The values of frequency factor (A) specify the frequency of collisions and the orientation of reacting molecules. The ineffectiveness of the additions of p-toluenesulfonamide and halide ions on the rate of reactions is in also agreement with the proposed mechanism and the derived rate law.

An evaluation of the rates of reaction of CAT and BAT shows that the oxidation of MR is about fourfold faster in BAT compared with that of CAT, under identical set of experimental conditions. This is legitimate by the relative magnitudes of activation energies (Table 3). This trend may be due to the difference in elctrophilicities of the halocations, Cl^+ and Br^+ ions, involved in the oxidation processes and is also related to the ease with which these species are generated in reactions. In these oxidation reactions, the electronegativity values of Br^+ and Cl^+ play a crucial role. Bromine has the electronegativity of 2.7, whereas chlorine has a higher value of 2.8. As the electronegativity increases, the electropositive nature decreases. Because the halo cations are the reactive species in these oxidation reactions, the electropositive nature is in the order Br > Cl. Therefore, the reactivity of BAT is more, when compared with CAT. This tendency may also be due to the moderate difference in the van der Waals's radii of bromine and chlorine. A similar behavior has been noted [7, 10–13, 31–33] in the oxidation of several other substrates using CAT and BAT. The details furnished in this research and the literature reports, led to conclude that BAT is a stronger oxidant compared with CAT.

COD is a measure of oxidizable matter in dve stuff. In the present research, an effort has been made to determine the chemical oxygen demand (COD) for MR dye. The COD of MR dye was determined using the standard dichromate method. The procedure followed to determine COD value was according to a literature procedure [34]. Under the prevailing experimental conditions, COD of MR dye sample was found to be 483.2 mg/L. Phytotoxicological analysis is used for the discharge of treated industrial wastewater before discharged into water bodies. They can be used to estimate the function capability of aquatic biotops and as an early warning system for the monitoring and screening of surface water. The toxicity studies with respect to generation of oxidative stress in plants are yet to get much significant attention. Due to this reason, maize seeds (Zea Mays L) were used as model crop for this study [17]. The result of phytotoxicity study showed that there is a significant effect on the percentage germination of maize seeds: 38% germination was observed for untreated dve solution, 74% germination for treated dye solution, and 88% germination for control. The plumule and radicle lengths also decreased in the case of untreated textile dye MR, effluent and dye mixture samples. It shows that the untreated dye solution is more toxic than treated solution which concludes that the decolorization of the dye in wastewater is necessary.

Cost plays an important role in any wastewater remediation techniques. In this analysis, cost of the materials were taken into account [35]. The operating cost was calculated using an expression:

USD,
$$m^3 = aC + bC$$
,

where a is cost of CAT/BAT, B is cost of perchloric acid.

For treating 1 m³ of the synthesized aqueous dye solution under present experimental conditions consumed 0.18 kg of CAT (4.97 USD) and 1.4 L of perchloric acid (39.4 USD) which gives a total cost of 44.37 USD. This justifies the proposed decolorization technique is an expeditious technique for the removal of methyl red in wastewater effluents.

Optimum conditions for the facile oxidative decolorization of MR dye with CAT and BAT have been developed. Under comparable experimental conditions, reactions with both the oxidants follow identical kinetics with a first-order dependence of rate each on $[oxidant]_{o}$ and $[MR]_{o}$, a fractional-order dependence on [HClO₄]. 4-Dimethylaminophenylhydroxylamine and 2-nitrosobenzoic acid have been identified as the oxidation products of MR dye. Thermodynamic parameters were evaluated. TsNHX is the assumed to be reactive oxidizing species in the present redox system. Suitable mechanism and relevant rate law have been worked out. COD of MR dye sample was found to be 483.2 mg/L. Phytotoxicity and economic analysis determined for the proposed decolorization process. The rate of oxidation of MR is about four-fold faster with bromamine-T when compared with chloramine-T. This may be due to the van der Waal's radii of chlorine and bromine and also difference in electrophilicites of Cl⁺ and Br⁺ ions. A plausible mechanism conforming to kinetic data, reaction stoichiometry and product analysis has been proposed. Accordingly, this method will be a valuable addition to the existing methods with more advantages.

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