Oxidative decolorization of methyl red dye with chloramine-T — Kinetic and mechanistic chemistry

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A simple and expeditious oxidative decolorization technique has been developed for the removal of Methyl Red dye (MR; C.I. Acid Red 2) present in the wastewater. The kinetic and mechanistic aspects of the present redox system have also been investigated. Kinetics and oxidative decolorization of MR dye with sodium N-chloro-p-toluenesulfonamide or chloramine-T (CAT) in HClO₄ medium at 303 K has been investigated spectrophotometrically at λ_max 524 nm. The reaction shows a first-order dependence of rate each on [CAT]₀ and [MR]₀. The reaction is catalyzed by [HClO₄] and the order with respect to [H⁺] is found to be fractional (0.75). Activation parameters have been evaluated. The oxidation products of MR dye are identified as N-(4-dimethylamino-phenyl)-hydroxylamine and 4-nitroso-benzoic acid by GC-MS analysis. The observed results have been explained by a plausible mechanism and the related rate law is deduced. 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.

Keywords: Chloramine-T, Kinetics-mechanistic chemistry, Methyl red dye, Oxidative decolorization

Azo dyes have azo group (N=N) and alkyl or aryl group (R-R'); hence the functional group is R-N=N-R'. These dyes are classified as mono-azo, di-azo and tri-azo dyes depending on the number of azo groups such as one, two and three. Azo dyes, although prohibited for use, are most widely used colorants in textile industries and also in paper printing, color photography and food processing. Methyl Red (MR) or C.I. Acid Red 2 (2-(N,N-dimethyl-4-aminophenyl)azobenzene-carboxylic acid) is a synthetic mono-azo dye, which is widely used in textile and paper industries. Wastewater released from the industries, in which MR dye is used, is highly colored and toxic in nature. Hence, it 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 great potential for the removal of MR dye without introducing any impurities, and also offer several advantages such as its simplicity and cost effectiveness over the other methods. Our preliminary kinetic studies revealed that chloramine-T completely decolorizes MR dye in acid medium.

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 attracted the attention of chemists, particularly synthetic chemists and kineticists due to their diverse property to act as halonium cations, hypochlorites and N-anions. They interact with a wide range of functional groups in aqueous and non-aqueous media in the presence of an acid or a base. As a result, these reagents have been used as mild and selective oxidizing agents in synthetic and mechanistic chemistry. The prominent member of this class of compound is sodium N-chloro-p-toluenesulfonamide commonly known as chloramine-T (CAT), which is a well known analytical reagent and the kinetic and mechanistic aspects of many of its reactions have been well documented. A perusal of literature indicates that the reports on the oxidation of dyes with this reagent are relatively sparse from its kinetic and mechanistic standpoints. Further, chloramine-T is commercially available, cost-effective, water-tolerant, non-toxic and easy to handle. Therefore, in the present study, we have established the optimum conditions for the facile oxidative decolorization of MR dye with CAT in acid medium. The other aim of this study is to unfold the mechanistic chemistry of this redox system.

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kinetically and also to deduce the kinetic modeling for the reaction.

**Experimental Procedure**

**Chemicals**

Chloramine-T (Merck) was purified using the method as reported earlier\(^1\). An aqueous solution of CAT was prepared afresh whenever required, standardized by iodometric method and stored in brown bottles 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.

**Kinetic measurement**

Detailed kinetic runs were performed under pseudo first-order conditions of [CAT]\(_0\) >> [MR]\(_0\) at 303 K in presence of HClO\(_4\). Kinetic measurements were carried out using an UV-visible spectrophotometer (digital spectrophotometer 166, Systronics, India). The experimental procedure followed was identical to that reported earlier\(^1\). Absorbance measurements were made at 524nm (\(\lambda_{\text{max}}\) of the dye) for nearly three half-lives. The absorbance readings at \(t = 0\) and \(t = t\) are \(D_0\) and \(D_t\). Plots of log Do/ D \(t\) versus time were made to evaluate the pseudo first-order rate constants (k/s\(^{-1}\)) which were found reproducible within ±5%. Regression analysis of the experimental data was done on an fx-100 W scientific calculator to evaluate the regression coefficient (R\(^2\)).

**Stoichiometry**

Reaction mixtures containing varying ratio of CAT to MR, under the experimental conditions of [CAT] >> [MR], in presence of 4.0 \(\times 10^{-3}\) mol dm\(^{-3}\) HClO\(_4\) were equilibrated at 303 K for 48 h. The iodometric titration of unreacted CAT in the reaction mixture showed that one mole of CAT was consumed per mole of the dye, as shown by the following equation:

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{N} & \quad \text{(MR dye)} \\
\text{(CH}_3\text{)}_2\text{N} & \quad \text{(N-(4-dimethylamino-phenyl)-hydroxylamine)}
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{(4-nitroso-benzoic acid)}
\end{align*}
\]

\[
\text{(Ts= CH}_3\text{C}_6\text{H}_4\text{SO}_3^-) \\
\text{Stoichiometry \ldots (1)}
\]

**Product analysis**

The reaction mixture in the stoichiometric ratio ([CAT] >> [MR]) 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 N-(4-Dimethylamino-phenyl)-hydroxylamine and 4-Nitroso-benzoic acid. These oxidation products were separated by column chromatography on silica gel (60-120 mesh) using hexane and ethyl acetate (1:1 v/v) as the mobile phase and were 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 N-(4-dimethylamino-phenyl)-hydroxylamine and 4-nitroso-benzoic acid respectively (Figs 1 a and b). All other peaks observed in GC-MS can be interpreted in accordance

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**Fig. 1**—Characterization of N-(4-dimethylamino-phenyl)-hydroxylamine and 4-nitroso-benzoic acid (a) mass spectrum of N-(4-dimethylamino-phenyl)-hydroxylamine with its parent molecular ion peak at 153 amu (b) mass spectrum of 4-nitroso-benzoic acid with its parent molecular ion peak 151 amu.
with the observed structure. Further, no reaction was noticed between $N$- (4-dimethylamino-phenyl)-hydroxylamine and 4-nitroso-benzoic acid with CAT under the present set of experimental conditions. Additionally, these compounds are largely used in textile and tanning industries, and also in water treatment and dye making plants. The reduction product of CAT, $p$-toluenesulfonamide (PTS or TsNH$_2$), was extracted with ethyl acetate and detected by paper chromatography$^{12}$. 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).

**Results and Discussion**

Preliminary kinetic runs reveal that CAT decolorizes MR dye completely within 45 min under the present set of experimental conditions. The kinetics of oxidative decolorization of MR dye with CAT was investigated at several initial concentrations of the reactants in HClO$_4$ medium at 303 K. Under pseudo first-order conditions of $[\text{CAT}]_0$, > > $[\text{MR}]_0$ at constant $[\text{CAT}]_0$, HClO$_4$ and temperature, plots of log (absorbance) versus time are found to be linear ($R^2 > 0.9910$), indicating a first-order dependence of rate on $[\text{MR}]_0$. 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 $[\text{MR}]_0$, confirming the first-order dependence of rate on $[\text{MR}]_0$. Under the same experimental conditions, an increase in $[\text{CAT}]_0$ increases the rate (Table 1). A plot of log $k'$ versus $[\text{CAT}]_0$ is linear ($R^2 = 0.9960$) having a slope equal to unity, indicating a first-order dependence of the reaction rate on $[\text{CAT}]_0$. Further, a plot of $k'$ versus $[\text{CAT}]_0$ is linear ($R^2 = 0.9960$) passing through the origin, confirming the first-order dependence of rate on $[\text{CAT}]_0$, and also showing that the MR dye-CAT complex has only transient existence. Furthermore, second-order rate constants $k'' = k'/[\text{MR}]$ are almost constant, establishing the first-order dependence of rate on $[\text{MR}]_0$. The calculated $k''$ values are reported in Table 1.

<table>
<thead>
<tr>
<th>$[\text{MR}]_0 \times 10^4$ mol dm$^{-3}$</th>
<th>$[\text{CAT}]_0 \times 10^3$ mol dm$^{-3}$</th>
<th>$[\text{HClO}_4] \times 10^3$ mol dm$^{-3}$</th>
<th>$k' \times 10^4$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>4.0</td>
<td>4.0</td>
<td>5.90</td>
</tr>
<tr>
<td>2.0</td>
<td>4.0</td>
<td>4.0</td>
<td>5.97</td>
</tr>
<tr>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>5.92</td>
</tr>
<tr>
<td>6.0</td>
<td>4.0</td>
<td>4.0</td>
<td>6.02</td>
</tr>
<tr>
<td>8.0</td>
<td>4.0</td>
<td>4.0</td>
<td>5.96</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>4.0</td>
<td>1.50 (0.15)</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>4.0</td>
<td>2.92 (0.14)</td>
</tr>
<tr>
<td>2.0</td>
<td>4.0</td>
<td>4.0</td>
<td>5.97 (0.15)</td>
</tr>
<tr>
<td>2.0</td>
<td>8.0</td>
<td>4.0</td>
<td>12.0 (0.15)</td>
</tr>
<tr>
<td>2.0</td>
<td>12.0</td>
<td>4.0</td>
<td>15.8 (0.13)</td>
</tr>
<tr>
<td>2.0</td>
<td>4.0</td>
<td>2.0</td>
<td>3.37</td>
</tr>
<tr>
<td>2.0</td>
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<td>4.0</td>
<td>5.97</td>
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<td>2.0</td>
<td>4.0</td>
<td>6.0</td>
<td>7.48</td>
</tr>
<tr>
<td>2.0</td>
<td>4.0</td>
<td>8.0</td>
<td>7.68</td>
</tr>
<tr>
<td>2.0</td>
<td>4.0</td>
<td>10.0</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Values in parentheses refer to second-order rate constants $k''$/s$^{-1}$.

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 $2.0 \times 10^{-3}$ to $8.0 \times 10^{-3}$ mol dm$^{-3}$ has no significant effect on the rate of reaction, indicating that the halide ions play no role 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$^{-3}$ NaClO$_4$ solution to the reaction mixture. It is noticed that there is no remarkable change on the rate of reaction and this signifies the involvement of at least one neutral molecule in the rate-determining step. Hence, no attempt has been made to keep the ionic strength of the system constant for kinetic runs.

The dielectric constant (D) of the medium has been varied by adding MeOH (0-30%v/v) to the reaction mixture, keeping all other experimental conditions constant. The rate increases with increase in MeOH content. The reaction rates ($10^4 k'$/s$^{-1}$) at 76.73, 72.37, 67.48 and 62.71 of D are found to be 5.97, 6.42, 6.99 and 7.24 respectively. A plot of log $k'$ versus 1/D is found to be linear ($R^2 = 0.9905$) with a positive slope. It is further noticed that no reaction of dielectric with the oxidant occurs under the experimental conditions employed. Values of D of MeOH-H$_2$O mixtures are taken from the literature.$^{16}$ As the dependence of the rate on H$^+$ ion concentration is observed, solvent isotope studies are made in D$_2$O medium. For the standard run (Table 1), values of $k'(\text{H}_2\text{O})$ and $k'(\text{D}_2\text{O})$ are $5.97 \times 10^4$ and $7.30 \times 10^4$ s$^{-1}$.
respectively, giving a solvent isotope effect $k'(H_2O)/k'(D_2O) = 0.80$. The reaction is studied at different temperatures (293, 298, 303, 308 and 313 K), keeping other experimental conditions constant. From the linear Arrhenius plot of log $k'$ versus $1/T$ ($R^2 = 0.9907$), activation parameters ($E_a$, $\Delta H^\circ$, $\Delta S^\circ$, $\Delta G^\circ$ and log $A$) for the overall reaction have been computed and these results are summarized in Table 2. Addition of acrylamide to the reaction mixture does not initiate polymerization, showing the absence of free radical-species in the reaction sequence. Proper control experiments were also performed under similar reaction conditions without the oxidant.

Chloramine-T (TsNCINa) acts as a mild oxidant in both acidic and alkaline media. In general, CAT undergoes a two electron change in its reactions, forming the reduction products PTS and NaCl. If di-chloramine-T (TsNCl$_2$) is the reactive species, then the rate law predicts a second-order dependence on the oxidant. Hardy and Johnston have made detailed calculations on the concentration dependence of various oxidizing species of CAT on $p$H in aqueous CAT solution and have shown that TsNHCl is the predominant oxidizing species in acid medium. Further, formation of species of the type TsN$^\circ$H$_2$Cl has been reported with CAT and the protonation constant for the reaction, is found to be $1.02 \times 10^2$ at 298 K, as shown below:

$$\text{TSNHCl} + \text{H}^+ \rightleftharpoons \text{TSN}^\circ \text{H}_2\text{Cl}$$

(2)

**Reaction mechanism**

In the present case, the fractional-order dependence of rate on [H$^+$] suggests that the protonation of TsNHCl results in the formation of TsN$^\circ$H$_2$Cl, which is likely to be the active oxidizing species in the oxidation of MR dye in acid medium. Scheme 1 shows the MR-CAT redox system in acid medium. In Scheme 1, an initial equilibrium H$^+$ ion accelerating step [step (i)] involves protonation of the conjugate acid TsNHCl forming the active oxidizing species TsN$^\circ$H$_2$Cl. 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 TsNH$_2$. In the next subsequent fast steps, this complex undergoes hydrolysis followed by cleavage of N-N bond to yield the ultimate products viz. N-(4-dimethylamino-phenyl)-hydroxylamine and 4-nitroso-benzoic acid. Based on Scheme 1, the rate law can be formulated as shown below:

If [CAT]$_i$ is the total effective concentration of [CAT], then

$$[\text{CAT}]_i = [\text{TsNHCl}] + [\text{TsN}^\circ \text{H}_2\text{Cl}]$$

(3)

From [step (i)] of Scheme 1

$$[\text{TsNHCl}] = \frac{[\text{TsN}^\circ \text{H}_2\text{Cl}]}{K[H^+]}$$

(4)

By substituting for [TsNHCl] from Eq. (4) into Eq. (3), we get

$$[\text{TsN}^\circ \text{H}_2\text{Cl}] = \frac{K([\text{CAT}]_i[H^+])}{1 + K[H^+]}$$

(5)

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

$$\text{Rate} = k_2[\text{TsN}^\circ \text{H}_2\text{Cl}][\text{MR}]$$

(6)

**Table 2**—Effect of varying temperature on the rate of reaction and activation parameters for the oxidation of MR dye by CAT in acid medium

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$k'/10^8$, s$^{-1}$</th>
<th>Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$, kJ mol$^{-1}$</td>
<td>45.6</td>
<td>293</td>
</tr>
<tr>
<td>$\Delta H^\circ$, kJ mol$^{-1}$</td>
<td>43.0 ± 0.01</td>
<td>298</td>
</tr>
<tr>
<td>$\Delta G^\circ$, kJ mol$^{-1}$</td>
<td>88.7 ± 0.35</td>
<td>303</td>
</tr>
<tr>
<td>$\Delta S^\circ$, JK$^{-1}$ mol$^{-1}$</td>
<td>-174 ± 0.07</td>
<td>308</td>
</tr>
<tr>
<td>Log A</td>
<td>9.01 ± 0.01</td>
<td>313</td>
</tr>
</tbody>
</table>

From different equilibria in the medium, it furnishes couple is 1.138, 0.778, 0.614 & 0.50 V at pH 0.65, 7.0, 9.7 & 12 respectively. Aqueous solutions of CAT-PTS undergoes a two electron change in its reactions, both acidic and alkaline media. In general, CAT behaves as a strong electrolyte and depending on $p$H of the medium, it furnishes different equilibria in solutions. The possible oxidizing species in acidified CAT solutions are TsNHCl, TsNCl$_2$, HOCl and possibly H$_2$O$^\circ$Cl. If di-chloramine-T (TsNCl$_2$) is the reactive species, then the rate law predicts a second-order dependence of rate on [CAT]$_i$, which is contrary to the experimental observations. If HOCl is primarily involved, a first-order retardation of rate by added $p$-toluenesulphonamide is expected. However, no such effect is noticed and hence HOCl can be ruled out as the oxidizing species.
By substituting for $[\text{TsNH}_2\text{Cl}]^+$ from Eq. (5) into Eq. (6), we obtain

$$\text{Rate} = \frac{K_1 k_2 [\text{CAT}][\text{MR}][H^+]}{1 + K[H^+]} \quad \cdots (7)$$

The rate law [Eq. (7)] is in complete agreement with the experimentally observed results, wherein a first-order dependence of rate each on $[\text{CAT}]_o$ and $[\text{MR}]_o$, and fractional-order on $[H^+]$ has been observed.

Since Rate $= k' [\text{CAT}]_i$, then

$$k' = \frac{K_1 k_2 [\text{MR}][H^+]}{1 + K[H^+]} \quad \cdots (8)$$

$$\frac{1}{k'} = \frac{K_1 k_2 [\text{MR}][H^+]}{1} + \frac{1}{k_2 [\text{MR}]} \quad \cdots (9)$$

From the double reciprocal linear plot of $1/k'$ versus $1/[H^+]$ ($R^2 = 0.9910$), the slope = 5.07 and intercept = 400. Using these values, protonation constant ($K_1$) and decomposition constants ($k_2$) are found to be 79.4 dm$^3$ mol$^{-1}$ and 1.25 s$^{-1}$ respectively. The deprotonation constant for step (i) of Scheme 1 is found to be $1.26 \times 10^{-2}$ mol dm$^{-3}$. Scheme 1 and rate law [Eq. (7)] can explain the following observed experimental results.

Most of the oxidation reactions of organic compounds involve the cleavage of C-H bond. Deuterium isotope effect on such reactions provide information about the nature of the rate determining step. As expected for a $H^+$ catalyzed reaction, in the present study the rate of the reaction increases in D$_2$O medium and the solvent isotope effect $k'/k$ (D$_2$O) is 0.80. For a reaction involving a fast equilibrium $H^+$ or OH$^-$ ion transfer, the rate increases in D$_2$O medium since D$_3$O$^+$ or OD$^-$ are stronger acid and a stronger base respectively, than H$_2$O$^+$ or OH$^-$ ions$^{21,22,28}$. In the present case, the observed solvent isotope effect is less than unity, which is due to the greater acidity of D$_3$O$^+$ ion compared to H$_3$O$^+$. 

Scheme 1—A mechanistic interpretation of MR – CAT redox system in acid medium
However, the extent of acceleration in D₂O medium is small compared to the expected value which is 2-3 times greater. This can be attributed to the fractional-order dependence of rate on [H⁺].

Most of the organic reactions are carried out in solution. 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 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 has shown that a plot of log k' versus 1/I 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 clearly supports the involvement of a positive ion and a dipole in the rate determining step [step (ii)] of Scheme 1.

The rate constants of ionic reactions depend upon the charges in reacting ions and also upon the ionic strength of the solution. The study of the influence of ionic strength on the rates of reactions in solutions is 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:

\[ \log k' = \log k_o + 1.018 Z_A Z_B \sqrt{I} \]

Here \( I \) is the ionic strength of the reaction medium; \( k_o \), the specific rate constants in the bulk of the reaction and at infinite dilution; and, \( Z_A \) and \( Z_B \), the ionic charges of the reactants A and B. The variation in \( k' \) 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 a slope equal to 1.018 \( Z_A Z_B \) and an intercept \( \log k_o \). 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 investigation, variation in ionic strength of the medium by adding NaClO₂ solution (0.20 mol dm⁻³) does not alter the rate, indicating 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 \( \Delta G^0 \) and \( \Delta H^o \) indicate that the transition state is highly solvated. The large negative entropy of activation suggests the formation of the compact activated complex with fewer degrees of freedom. The ineffectiveness of the addition of p-toluenesulfonamide and halide ions on the rate of reactions is also in agreement with the proposed mechanism and the derived rate law.

Conclusion

In the present research, optimum conditions for the facile oxidative decolorization of MR dye with CAT in acid medium have been obtained. Chloramine-T decolorizes MR dye completely within 45 min in acidic conditions. Oxidative decolorization of MR dye with CAT in acid medium obeys the experimental rate law: \(-d[CAT]/dt = k [CAT][MR][H^+][O_2]^{0.57}\).

Hence, this method is a simple and efficient method including a number of benefits such as cost effectiveness, short reaction time, use of relatively non-toxic reagent and environmentally benign process. Therefore, this method can be scaled up to industrial operation to remove MR dye present in wastewater after suitable modifications. Accordingly, this method will be a valuable addition to the existing methods with more advantages. In addition to this, the kinetic and mechanistic picture of MR dye–CAT redox system in acid medium has also been clarified.

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References