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RESEARCH ARTICLE

Pre-oxidative catalytic treatment of toluidine blue with potassium permanganate in acidic solution

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This article describes the potential of $KMnO_4$ for oxidation of the thiazine dye (Toluidine blue TB) in an acidic medium. The effect of different operational parameters like initial concentration of dye, potassium permanganate, pH, ionic strength, catalyst, acids and temperature were investigated spectrophotometrically at λ_{max} = 613 nm. The results showed a complete removal of the TB with mineralization of the dye solution. Smooth and complete decoloration was observed in the presence of monobasic acid (HCl) as compared to the H_2SO_4 where little color removal was observed. Pb was found to be an effective catalyst in oxidation for complete and fast decolorization with mineralization. No significant change at elevated temperatures showed that an intermediate complex degraded with slight change in the temperature. UV/visible spectrophotometry and GC mass analysis showed an intermediate activated complex demethylated sulophooxide of TB which later on degraded into smaller fragments.

Keywords oxidation, TB, potassium permanganate, decoloration, Pb

1 Introduction

Delivery of textile and chemical waste waters and stream or pipe works without an adequate treatment determines undesired consequences. Moreover, most of the dyes used nowadays are refractory compounds. Conventional biologic treatments do not affect most of the synthetic dyes especially due to their poly aromatic structure. That is why advanced oxidation processes (e.g., H_2O_2/Fe^{+2}) for decomposition of non-biodegradable organic contaminants into industrial effluents are attractive alternatives to conventional treatment [1].

Permanganate has the MnO_4^- anion, commonly used as a strong oxidizing agent. Permanganate was a versatile oxidant in organic chemistry including heterogeneous oxidations and diol productions. Permanganate salts have bactericidal, fungicidal, astringent and oxidizing properties. Permanganate destroys dyes and impurities by oxidation [2]. Xu et al. [3] studied effects of reaction conditions on the decolorization efficiency in batch experiments and observed that pH value had a significant effect on the decolorization efficiency. When pH value was < 1.5, the decolorization efficiency was very high. When pH value was > 4.0, the dye solutions were almost not decolorized. Their results on permanganate indicated that the oxidation with potassium permanganate might be used as a pre-treatment process before biologic treatment. Aleboyeh et al. [4] reported that complete removal of the color and partial mineralization for the dye solution under various key operating variables such as initial dye concentration, permanganate amount, pH and temperature were observed. Decolorization reactions were influenced by the acidity and the temperature of the treated solutions and the degradation efficiency of the azo dyes increased with an increase in the potassium permanganate amount [5–9].

The aims and objective of this paper are to discuss the homogenous oxidation of the toluidine blue with the potassium permanganate in an acidic medium in presence and absence of Pb catalyst in order to get the maximum decolorization using spectrophotometric technique, as detailed literature survey revealed that no report was available for the use of potential of $KMnO_4$ as an oxidizing agent for the decoloration of toluidine blue. All kinetic experiments were performed at a room temperature of 30°C–35°C and the reaction scheme was proposed based on kinetics data and product analysis through GC mass spectrometry and UV/visible spectrophotometry.

2 Materials and methods

All reagents were obtained from E-Merck and Fluka, and were used as received. The experiment was divided into different sections like i) preparation of solutions, ii) kinetic measurements, iii) data analysis and iv) investigation of mineralization through GC mass spectrometry.

The solutions were prepared in de-ionized water and diluted

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before used. Kinetics measurements were followed on UV-Visible Schimadzu 180A Spectrophotometer using 1 cm cell [10–12].

2.1 Preparation of sample solutions

TB stock solution of $1 \times 10^{-4}\,\mathrm{mol \cdot L^{-1}}$ and $KMnO_4$ with required concentration were prepared in 250 mL of de-ionized water. Dilutions of these stock solutions were made with de-ionized water to obtain a series of dye solutions with varying concentration of reagents [10]. The absorbance value obtained in each case was plotted against time to obtain rate constant.

2.2 Kinetics measurements

Kinetics measurements were made by preparing different sets of reaction mixture in which one species was varied while others were kept constant at given concentration. All contents were mixed together and the progress of the (inlets) reaction was monitored by recording the change in optical density at $\lambda_{\max} = 613$ nm during the reaction on UV/Visible spectrophotometer (Shumadzu 180-A). The order of reaction at different operational parameters and activation parameters were evaluated by measuring the specific reaction rate at various temperature and different ionic strength [10,11]. The pH was adjusted by HCl and NaOH. KCl was used to maintain the ionic strength of the medium. Interference of color of $KMnO_4$ was ignored and no decoloration reagent was added to $KMnO_4$ to avoid further hazards of chemicals and decoloration was assisted through Pb because of its presence in the main stream.

Percent decrease in absorbance was calculated by using the formula [12]

$$\text{Decrease in absorption}(\%) = \left(1 - \frac{A_f}{A_i}\right) \times 100$$

where A_f = Absorbance after 15 min or final absorbance; A_i = Absorbance at 0 min or initial absorbance.

2.3 Stoichiometry

Stoichiometry of redox reaction was determined by mixing 1:1, 2:1, and 1:2 molar ratio of dye and oxidant with an excess of H^+ ion. Fast decoloration obtained with 1:1 and 1:2 molar ratios showed that stoichiometric ratios varied in the above range with the probability of dye degradation [13].

2.4 Product analysis

The reaction mixture was prepared by the combination of 0.32 g of dye in 25 mL of water, 100 mL of HCl and 0.1 mol $\cdot \mathrm{dm^{-3}}$ $KMnO_4$. The mixture was left for 24 h for complete reaction, then the organic component was extracted with ethyl acetate and the solvent was evaporated with the rotary evaporator. Isolated organic compounds were subjected to GC mass chromatography.

3 Results and discussion

This study describes an oxidative properties of potassium permanganate for the de-coloration of the toluidine blue (TB) in an acidic medium through UV/visible spectrophotometry at 613 nm. Potassium permanganate as an oxidizing agent readily oxidizes the C–C double bonds in aromatic and aliphatic unsaturated hydrocarbons, indicating its potential for oxidation of aromatic compounds. The reaction under study was very slow, and was enhanced in the presence of Pb catalyst added in the form of $Pb(NO_3)_2$. The reaction showed that the presence of Pb enhanced the rate but the increasing concentration of Pb showed no significant effect. The oxidation of TB was investigated at various operational parameters and the results were determined by plotting absorbance vs. time graph [10].

3.1 Effect of concentration of dye and permanganate concentration on de-coloration of TB

The effect of initial increase in the dye concentration on the de-colorization of TB by potassium permanganate was studied within a concentration range of $1 \times 10^{-5}\,\mathrm{mol \cdot dm^{-3}}$ to $5 \times 10^{-5}\,\mathrm{mol \cdot dm^{-3}}$, with all the other variables kept constant. The color removal rate constant k was evaluated by the plot of ln absorbance vs. time and reported in Table 1, and a plot of optical density and time was presented in Fig. 1. The log dye vs. log k plot gave a linear line with gradients 2.1 (Corr. Coeff. = 0.7556) with dye, suggesting that the order with respect to dye is bimolecular. The value of R^2 suggesting a complex kinetics with respect to dye and showing more than one oxidizing specie was involved during the collision with dye molecule. The variations in rate of reaction reported in Table 1 also support the complex kinetics with respect to dye concentration. The results in Table 1 showed that the decoloration was enhanced with the dye concentration in the reaction mixture where more than 94% de-colorization efficiency was achieved when the concentration of TB was $5 \times 10^{-5}\,\mathrm{mol \cdot dm^{-3}}$ as reported earlier [4]. This enhancement in the decoloration was probably because of the collision between the dye molecule and permanganate species, due to which the C–C double bonds were degraded, which leads to an increase in the degradation efficiency [5].

During oxidative treatment, the process efficiency as a

Table 1 The effect of change in conconcentration of dye on oxidation of TB
[HCl] = 0.2 mol·L^{-1}; [KMnO$_4$] = 1 × 10^{-4} mol·L^{-1}; [Pb(NO$_3$)$_2$] = 1%; [KCl] = 1% ; t = 303 K

TB/(10^{-5} mol·L^{-1})	$\frac{dx}{dt}/(10^{-6}\ \text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1})$	k/(10^{-3} s^{-1})	Decoloration/%
1.0	1.00	0.1	64.440
2.0	5.00	0.6	68.750
3.0	4.00	0.3	78.333
4.0	60.0	1.2	90.476
5.0	40.0	7.1	94.440

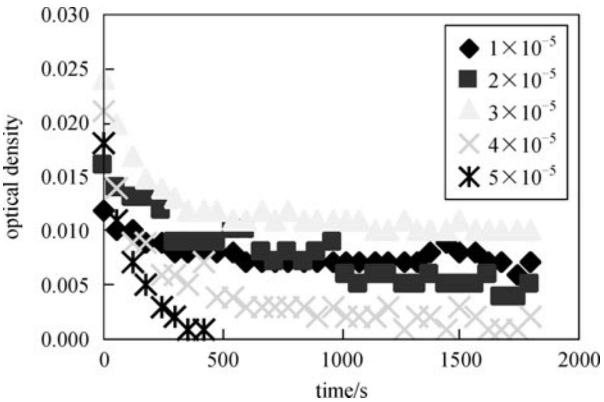


Figure 1 Change in optical density vs. time with variation of concentration of dye

function of the different concentrations of permanganate was investigated. The results were reported in Table 2. As can be observed from Table 2, approximately 88% color removal was achieved by increasing the permanganate concentration to about 1 × 10^{-4} mol·dm^{-3}. The pseudo first order rate coeff. k for different concentrations of permanganate and for the fixed concentration of TB with other parameters was obtained by plotting log absorbance vs. time. The log KMnO$_4$ vs. log k plots gave a line curve with gradient 1.57 with KMnO$_4$, suggesting that the order with respect to KMnO$_4$ was a fractional order as reported earlier by Jonnalagadda and Dumba [13]. A strong significant correlation ($R^2 = 0.954$) was observed in between dye decoloration and concentration of potassium permanganate.

MnO$_4^-$ species of potassium permanganate that is formed during reaction serves as an oxidizing agent. It was observed that at high concentration of KMnO$_4$ the decoloration was decreased, possibly as a result of the scavenging of [O] species or reactive permanganate species [3]. KMnO$_4$ oxidation alone at pH 1.94 showed a satisfactory decrease of UV-Vis absorption peaks, and the maximum percentage of decoloration (78.04%) was achieved (Fig. 2). [14]

3.2 Effect of pH decoloration of TB

The effect of pH on an oxidation of the TB was monitored in the range of 1.7, 1.94, 2.12, 2.36, 6.95, 11.47, 11.59, 11.86 and 12.01 through pH meter (Table 3 and Fig. 3). Maximum decoloration efficiency was obtained at pH 2.12, while a drastic decrease in color removal was obtained at a pH range of 1.94 to 2.36. But at pH 6.95 no decoloration was recorded. Potassium permanganate is a strong oxidizing agent and the role of pH in oxidation by KMnO$_4$ is significant [3] because it strongly influences the redox reaction. We observed the same results as observed by the earlier investigator [3] that the rate of dye decoloration was affected by the pH of colored solution which was adjusted by the change in HCl and NaOH. It is a well known fact that during oxidation by permanganate, Mn(VII) in permanganate is reduced to various states, i.e., Mn(VI), Mn(V), Mn(IV), Mn(III) and Mn(II) in acidic, alkaline and neutral medium. The reactivity of these intermediate states depends on the nature of the reactants and on the pH of the medium. The pH of the reaction mixture determines the rate of reaction and whether oxidation occurs

Table 2 The effect of change in conconcentration of KMNO$_4$ on oxidation of TB
[HCl] = 0.2 mol·dm^{-3}; [TB] = 5 × 10^{-5} mol·dm^{-3}; [Pb(NO$_3$)$_2$] = 1%; [KCl] = 1%; t = 30°C

Concentration/10^{-4}	$\frac{dx}{dt}/10^{-6}$	k/(10^{-5} s^{-1})	Decoloration/%
1	20.0	90.0	88.16
2	8.00	40.0	76.866
3	10.0	20.0	53.425
4	7.00	8.00	38.372
5	9.00	9.00	41.053

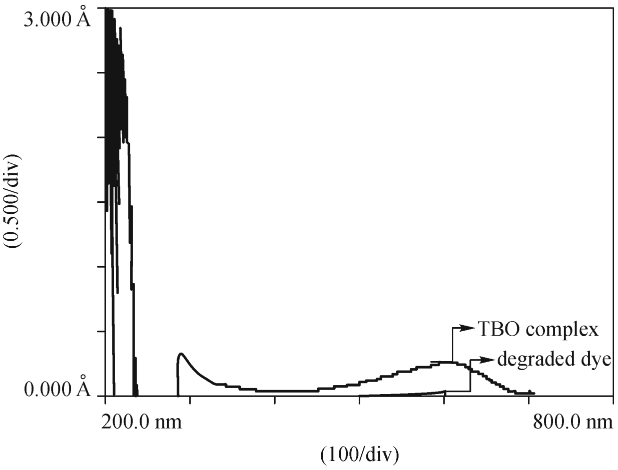
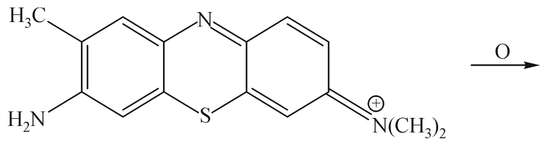


Figure 2 Spectral change of an oxidative intermediate complex of the dye

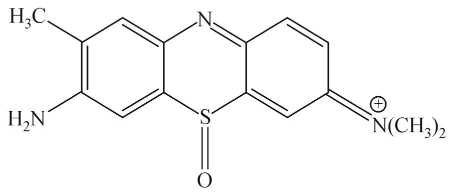
via one, three, or five electron exchanges. Between pH 2.5 and 12 the permanganates undergo a three electron exchange, with reaction in acidic pH conditions and reaction in neutral and alkaline condition. Our results are similar to those got by Xu et al. [3] and Aleboyeh et al. [4] who reported that the overall redox potential of the reaction mixture increases with the decrease of pH. It was concluded that more acidic the solution was, the greater the oxidizing ability of potassium permanganate would be, or the best bleaching was obtained in acidic solution. Chemical compounds which are oxidized by potassium permanganate through several mechanism including electron abstraction, hydrogen abstraction, hydride ion abstraction and oxygen donation. Present investigation suggests that the dye decoration at pH 2.12 was due to the release of MnO_4^- species (Eqs. (1) and (2)) which has predominantly existed in an acidic medium with O* and acts as a strong oxidizing agent for the oxidation of TB (Eq. (3)). It was observed that the potential of oxidation of $KMnO_4$ in acidic medium was much higher than that of in alkaline medium in this work. The value of rate constant at pH 2.12 is $5 \times 10^{-4}\ s^{-1}$ whereas it was $1 \times 10^{-4}\ s^{-1}$ at pH 12.01, which suggests that when a multivalent oxidant oxidies a substrate, the oxidization depends not only on the substrate but also on the medium used in this study.

$$KMnO_4 + H^+ \leftrightarrow MnO_4^- + K^+ \tag{1}$$

$$MnO_4^- \leftrightarrow MnO_3^- + O^{\cdot} \tag{2}$$



TB$^+$



TBO$^+$

(3)

3.3 Effect of catalyst on decoloration of TB

Initially slow kinetics was accelerated by the addition of Pb as a catalyst due to which decoloration time was reduced to exactly half of that of in an absence of catalyst. This mechanism of oxidation of TB may be explained on the basis of the photon of light when it falls on or when the catalyst is exposed to UV/Visible radiation during which an electron hole pair is formed by excitation of electron (Eq. (4))from valence band to conduction band according to the Eqation [14,16].

$$\text{Catalyst} + hv \rightarrow e_{cb} + h_{vb}^+ \tag{4}$$

where e_{cb} and h_{vb} are the electrons in the conduction band and the electron vacancy in the valance band respectively [14]. Both these species can penetrate in a redox reaction with specie present on the surface. Most probably h_{vb}^+ can easily react with surface bound H_2O molecule to produce OH* radical and e_{cb} can react with O_2 to produce super oxide radical anion of oxygen (Eqs. (5) and (6)) [15].

$$H_2O + h_{vb} \rightarrow OH^* + H^+ \tag{5}$$

$$O_2 + e_{cb} \rightarrow O_2^{*-} \tag{6}$$

The above reactions present the combination of electron and hole formed in the first steps. Rauf et al. [14] reported the oxidation mechanism of these dyes on surface catalyst as follows (Eqs. (7)–(9)).

$$2H + O_2 \rightarrow H_2O_2 + O_2 \tag{7}$$

$$H_2O_2 + hv \rightarrow 2OH \tag{8}$$

$$OH + \text{dye} \rightarrow \text{intermediate} \rightarrow \text{product} \tag{9}$$

$$KMnO_4 + H^+ \rightarrow MnO_3^- + O^* \tag{10}$$

$$TB + O^* \rightarrow TBO \tag{11}$$

The rapid decoloration of dye in the presence of catalyst supports the above mechanism in this work (Eqs. (10) and (11)).

Table 3 The effect of pH change in oxidation of TB
[HCl] = 0.2 $\mathrm{mol \cdot dm^{-3}}$; [TB] = 5×10^{-5} $\mathrm{mol \cdot dm^{-3}}$; [$Pb(NO_3)_2$] = 1%; t = 30°C; [$KMnO_4$] = 1×10^{-4} $\mathrm{mol \cdot dm^{-3}}$

pH	$\frac{dx}{dt}/10^{-5}$	$k/(10^{-4}\ s^{-1})$	Decoloration/%
12.01	3.00	1.0	34.980
11.86	4.00	1.0	30.847
11.59	20.0	5.0	62.132
11.47	20.0	4.0	60.115
6.95	10.0	2.0	33.920
2.36	1.00	3.0	53.880
2.12	1.00	2.0	67.836
1.94	2.00	1.0	78.049
1.7	2.00	1.0	77.703

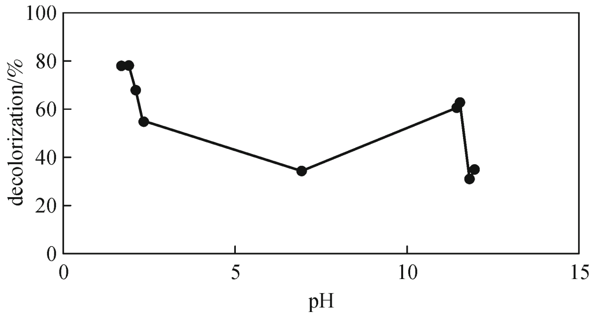


Figure 3 Percentage decoloration of dye with respect to pH

3.4 Effect of ionic strength, H^+ ion and temperature on decoloration of TB

The effect of salt electrolyte was studied on decoloration kinetics of TB by Potassium permanganate via varying amount of KCl keeping all other factors constant. The results reported in Table 4 showed that the rate is affected by the addition of salt electrolyte. The observed positive salt effect suggests that the rate determining step may be permanganate or protonated TB that have oppositely charged species [17,18]. The addition of salt electrolyte decreases the decolorization time, which showed that dye degradation increases with the increase in concentration of Cl ion, possibly due to the formation of hypochlorous acid according to Eq. (12)

$$\mathrm{H} + \mathrm{Cl} + \mathrm{O} \rightarrow \mathrm{HClO} \tag{12}$$

The H^+ ion concentration in the reaction mixture showed a significant effect on the rate of reaction. An increase in H ion concentration increases the rate of reaction and decreases the time of decoloration with an increase in percentage of decoloration (Table 5). The order of reaction with respect to H^+ ions was uni-molecular.

The reaction was studied at different temperatures and the

Table 4 The effect of change in conconcentration of KCl on oxidation of TB
[HCl] = 0.2 $\mathrm{mol \cdot dm^{-3}}$; [TB] = 5×10^{-5} $\mathrm{mol \cdot dm^{-3}}$; [$Pb(NO_3)_2$] = 1%; t = 30°C; [$KMnO_4$] = 1×10^{-4} $\mathrm{mol \cdot dm^{-3}}$

Concentration/10^{-1}	$\frac{dx}{dt}/10^{-5}$	$k/(10^{-5}\ s^{-1})$	Decoloration/%
1.0	1.0	4.00	48.850
2.0	0.4	5.00	54.900
3.0	4.0	70.0	87.350
4.0	5.0	80.0	88.350
5.0	5.0	80.0	88.660

Table 5 The effect of change in conconcentration of HCl in oxidation of TB
[TB] = 5×10^{-5} $\mathrm{mol \cdot dm^{-3}}$; [$Pb(NO_3)_2$] = 1%; [KCl] = 1%; t = 30°C; [$KMnO_4$] = 1×10^{-4} $\mathrm{mol \cdot dm^{-3}}$

Concentration/10^{-1}	$\frac{dx}{dt}/10^{-5}$	$k/(10^{-4}\ s^{-1})$	Decoloration/%
2.0	1.0	1.00	50.000
1.5	2.0	5.00	60.000
1.0	0.9	8.00	70.500
0.5	1.0	11.00	71.900
0.1	4.0	21.00	85.000

Table 6 The effect of change in temperature on oxidation of TB
[HCl] = 0.2 mol·dm^{-3}; [TB] = 5 × 10^{-5} mol·dm^{-3}; [Pb(NO$_3$)$_2$] = 1%; [KCl] = 1%; t = 30°C; [KMnO$_4$] = 1 × 10^{-4} mol·dm^{-3}

Temperature/K	$\frac{1}{T}/10^{-3}$	$\frac{dx}{dt}/10^{-4}$	$k/(10^{-4}\ \mathrm{s}^{-1})$	Decoloration/%
298	3.35	1.0	2.0	42.100
303	3.30	1.0	2.0	33.836
308	3.25	1.0	2.0	30.000
313	3.19	2.0	3.0	41.630
318	3.14	5.0	6.0	64.820

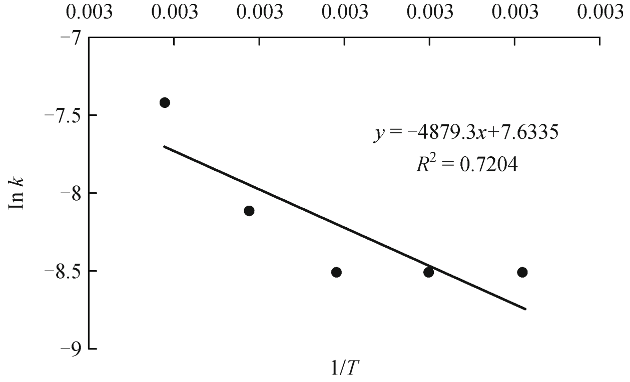


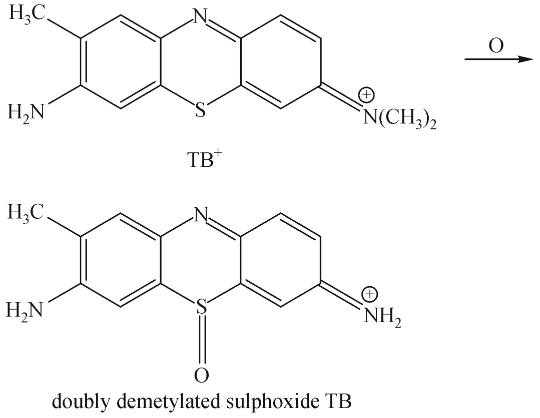
Figure 4 Effect of temperature on reaction rate of TB

results are reported in Table 6 and showed in Fig. 4. It was observed that an increase in the temperature has no significant effect on dye decoloration except at 45°C where 64.82% of the dye is removed. These results suggest that although the increase of the temperature benefits the de-colorization efficiency, both the investment and operational costs are higher in the actual treatment of the waste water. Thus it is recommended that the optimum temperature for the dye decolorization is room temperature. Chemical compounds are oxidized by the potassium permanganate through several mechanisms including increasing electron abstraction, hydrogen atom abstraction, hydride ion abstraction and oxidation donation. The present investigation has suggested that the dye decolorization at pH 2.12 results from the release of MnO$_3$ species which is a pre-dominant species in acidic mediums and act as a strong oxidizing agent with the release of reactive O* for the oxidation of TB. Here it was noticed that TBO was degraded to some extent as the temperature increased and mineralization was observed.

3.5 GC mass analysis of reaction mixture

The GC mass analysis of ethyl acetate extracted samples of dye and oxidant showed peaks of m/e 1070(45), 1261(52), 1331(56) and 1496(62), indicating four compounds. They are likely demethylated or doubly demethylated complexes of initial materials (Eqs. (13) and (14)). The presence of sulfooxides and doubly methylated sulfooxides was confirmed by further mass spectrometry which showed m/z at 279.3, 396.3, 394.2, 398.3, and 432.2. These molecular ions peaks suggest that the dye degraded into smaller fragments through complex formation in the activated state (Eqs. (15) and (16)). The complex formation is also supported by UV/visible spectrum during oxidation (Figs. 2 and 5).

Scheme of oxidation leading to degradation of dye



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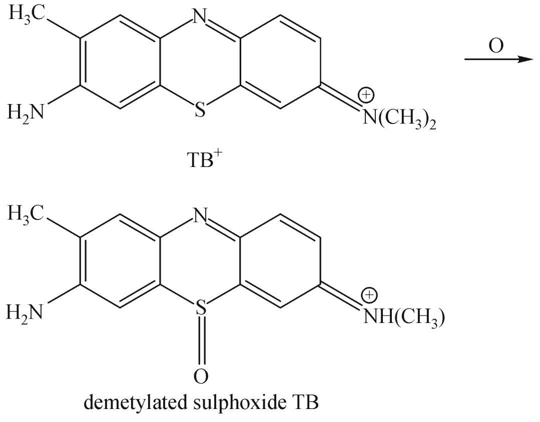

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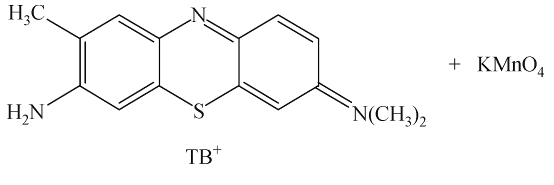
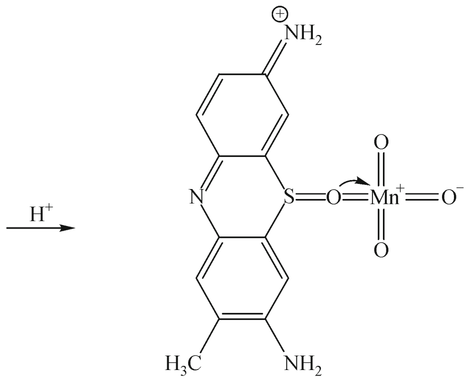
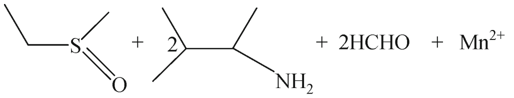




(15)

activated intermediate complex



(16)

degraded product

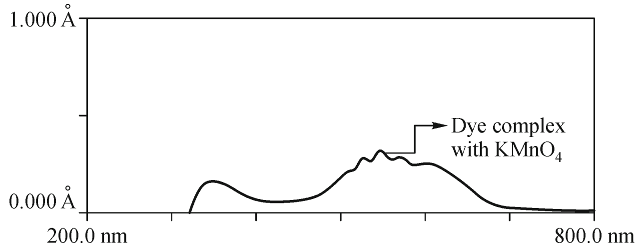


Figure 5 Spectral change of complex of dye with potassium permanganate

3.6 Reaction pathway

The molecular ion peaks suggest that the first intermediate complex formed initially with the demethylation and decoloration of substrate upon oxidation may be resulted from the non planner structure of the product at sulfer upon oxidation to sulphooxide [13].

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