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Micelle Catalyzed Oxidative Degradation of Paracetamol by Water Soluble Colloidal MnO_2 in Acidic Medium

The catalytic effect of cationic micelles of cetyltrimethylammonium bromide (CTAB) on the MnO_2-paracetamol (PCM) redox reaction has been examined spectrophotometrically in acidic medium at 298 K. The reaction demonstrates that the stoichiometric ratio of MnO_2 and PCM is 1 : 1. The reaction exhibited first order kinetics with respect to [MnO_2] and [PCM] but a negative fractional order was observed with respect to [H_2SO_4]. Various effects such as ionic strength, dielectric constant, [Mn(II)], [salts] and temperature have been studied. The catalytic effect of CTAB has been treated quantitatively by the well known Menger Portnoy and Piszkiewicz model. The values of binding constant (K_s), rate constant in the micellar phase (k_m), cooperativity index (n) and dissociation constant (K_D) have also been calculated. From the several observations, a reaction mechanism has been proposed and the rate law has been derived. Applying the Arrhenius equation, various thermodynamic activation parameters have also been evaluated.

Key words: Reaction kinetics, Oxidative degradation, Colloidal MnO_2, Paracetamol (PCM), Cetyltrimethylammonium bromide (CTAB)

Mizellare Katalyse des oxidativen Abbaus von Paracetamol mittels wasserlöslichen kolloidalen MnO_2 im sauren Medium. Der katalytische Einfluss von Mizellen des kationischen Cetyltrimethylammoniumbromids (CTAB) auf die MnO_2-Paracetamol-Redoxreaction wurde spektrophotometrisch im sauren Medium bei 298 K untersucht. Das stöchiometrische Verhältnis von MnO_2 und Paracetamol(PCM) beträgt bei dieser Reaktion 1 : 1. Die Reaktionskinetik ist Erster Ordnung hinsichtlich der MnO_2^- und der PCM-Konzentration, sie ist jedoch hinsichtlich der H_2SO_4-Konzentration von negativer gebrochener Ordnung. Es wurden verschiedene Einflüsse wie die Ionenstärke, die dielektrische Konstante, die Mn(II)-Konzentration, die Salzkonzentration und die Temperatur untersucht. Der katalytische Einfluss von CTAB wurde quantitativ mit dem gut bekannten Modell von Menger Portnoy und Piszkiewicz bestimmt. Die Bindungskonstante (K_s), die Geschwindigkeitskonstante in der mizellaren Phase (k_m), der Kooperativitätsindex (n) und die Dissoziationskonstante (K_D) wurden ebenfalls bestimmt. Mit Hilfe der verschiedenen Beobachtungen wird ein Reaktionsmechanismus vorgeschlagen und das Geschwindigkeitsgesetz der Reaktion abgeleitet. Durch Anwendung der Arrhenius Gleichung konnten verschiedene thermodynamische Aktivierungsparameter ebenfalls berechnet werden.

Stichwörter: Reaktionskinetik, oxidativer Abbau, kolloidales MnO_2, Paracetamol (PCM), Cetyltrimethylammoniumbromid (CTAB)

1 Introduction

Surfactant molecules cover small water droplets and are changed into uniformly distributed assemblies of micelles once reaching a critical micellar concentration in an organic bulk solvent [1]. The reaction of a reactive counter ion is generally catalyzed by ionic micelles with hydrophobic substrates which bind to the micelles [2, 3]. Micelle catalyzed reactions which are considered as models for electrostatic and hydrophobic interaction in biological systems will provide information regarding the mechanism of regulation of reactions as micelles are structurally simpler and can easily be modified compared to complex biological interfaces [4]. Investigations of the reaction mechanisms in organized molecular assemblies are being applied more and more due to the fact that a lot of biological processes proceed in a very small heterogeneous system that contains an aqueous and a lipophilic moiety [5]. By the addition of salt or surfactant, a transition of sphere-shaped to larger micelles will occur [6, 7]. The importance of surfactants in environmental impurity control and treatment has long been recognized. In order to change the mobility of contaminants in the aquifer or their availability to bacteria, surfactant enhanced aquifer remediation (SEAR), based on micelle solubilization and interfacial tension (IFT) reduction has been used as a popular technology [8–10]. A lot of works have been carried out on the kinetic degradation of organic compounds by several oxidants in the presence of a micellar system [11–20].

The transparent solutions of manganese dioxide also possess a prominent status due to their wide ranging participation as intermediates [21] as they play a vital role in autocatalytic and oscillating reactions [22, 23]. The colloidal MnO_2 particles can be stabilized in aqueous solutions by attaining a negative electrostatic charge, for e. g., by adsorption of phosphate ions, despite the fact that the stabilizing effect of phosphate is not permanent [24, 25]. Manganese oxides/hydroxides are one of the significant oxides in soils, waters and sediments. One study demonstrated that the levels of manganese oxides in sediments are as high as 205 mol/kg [26]. They are usually more geochemically active due to their high negative surface charge, low point of zero charge, large surface area, and low crystalline and dynamic redox behaviour [27]. Many studies revealed that manganese oxides/hydroxides are capable of degrading various organic pollutants [28–33].

The drug N-acetyl-4-aminophenol usually known as paracetamol (PCM), is an enormously utilized analgesic, antipyretic and anti-inflammatory agent all over the world [34, 35]. It is extensively applied for pain relief, cold, fever and

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non-inflammatory musculoskeletal conditions [36]. Some major sources of water pollution by the PCM is through excretion, from the manufacturing site, direct disposal of expired drugs in households and hospitals, defecated after drug administration to humans and treatments throughout the water in fish farms [37]. A lot of techniques/methods have been reported for the removal or transformation of PCM from marine water like advanced oxidation process: ozonisation [38–41], photo degradation [42–45], photo-Fenton process [46–50] oxidative degradation [51–55], etc. In the present work, we report a new method of oxidative degradation of PCM by colloidal MnO_2 in the presence of a cationic surfactant (CTAB).

2 Experimental

2.1 Reagents

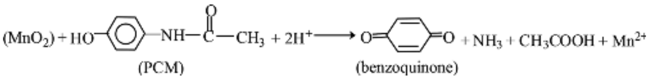
Potassium permanganate (E. Merck, Mumbai, India), sulphuric acid (E. Merck, Mumbai, India), paracetamol (S. D. Fine, India), potassium nitrate (E. Merck, Mumbai, India), acetonitrile (E. Merck, Mumbai, India), manganese(II) chloride (E. Merck, Mumbai, India), sodium thiosulphate (E. Merck, Mumbai, India), cetyltrimethylammonium bromide ((S. D. Fine, India), potassium chloride (CDH, India), potassium bromide (E. Merck, Mumbai, India) and sodium disulphate (E. Merck, Mumbai, India) were used for the present study. All solutions of these chemicals were prepared in triply distilled water for the present work.

2.2 Preparation and characterization of colloidal MnO_2

Water soluble colloidal MnO_2 was synthesized using the method adopted by Perez Benito et al. [56–58]. Required quantities of the standard solution of $KMnO_4$ (1.0×10^{-2} mol dm^{-3}) and of $Na_2S_2O_3$ (1.0×10^{-2} mol dm^{-3}) were mixed together and after addition of water, a new brown colure solution was developed. The obtained solution of colloidal MnO_2 was thoroughly transparent, which was stored in amber bottle for prohibiting the photochemical reaction so that it can remain for several months. Through the scanning graph of MnO_2, the synthesis of colloidal MnO_2 was confirmed by Varian Cary 50 Bio UV-Visible spectrophotometer which showed an absorption spectra at $\lambda_{max} = 375$ nm (Fig. 1). The synthesis of colloidal MnO_2 was further confirmed by the addition of various inorganic salts to the colloidal solution of MnO_2 which makes a precipitation of Mn(IV) [33, 59].

2.3 Stoichiometry and product analysis

Various reaction mixtures with $[MnO_2] >> [PCM]$ were prepared in black coated bottles and kept towards 72 h at room temperature. The stoichiometry of the reaction exhibited that one mole of PCM is oxidized by one mole of MnO_2, as shown in equation (1):



(1)

The completion of the reaction was confirmed by observing the absorbance value. The products were extracted with ether. Benzoquinone was identified as the main oxidation product of PCM [60], along with ammonia which has also been confirmed by the spot test [61–62].

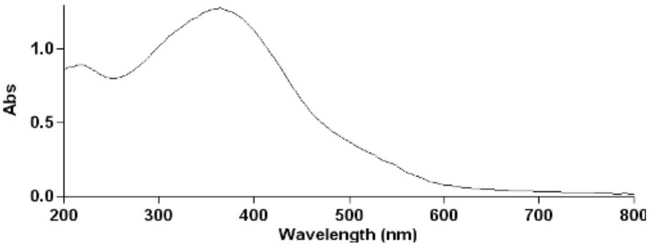


Figure 1 Absorption spectrum of water soluble colloidal MnO_2 (0.6×10^{-4} mol dm^{-3}) which is the reaction product of the $KMnO_4$ (1.0×10^{-2} mol dm^{-3}) and $Na_2S_2O_3$ (1.0×10^{-2} mol dm^{-3}) solution

2.4 Test for free radicals

During the course of the reaction, the production of free radicals could be confirmed by using monomeric acrylonitrile. In the reaction mixture containing MnO_2, PCM, H_2SO_4 and CTAB, an appropriate quantity of acrylonitrile was added. The development of a precipitation indicated that free radicals were generated during the reaction.

3 Result and Discussion

3.1 Kinetic measurements

All the kinetic measurements were carried out by taking an appropriate quantity of aqueous solutions of PCM, H_2SO_4 and CTAB in the beaker at 298 K. The reaction started with the addition of the colloidal MnO_2 solution containing reaction mixture. During the progress of the reaction, the absorbance of the disappearing colloidal MnO_2 was recorded spectrophotometrically at fixed wavelength of 375 nm and known various time intervals. The spectral changes obtained in the presence of the cationic surfactant (CTAB) are depicted in Fig. 2. The pseudo first order rate constant was appraised by plotting log (absorbance) versus time (Fig. 3).

3.2 Effect of $[MnO_2]$ on the rate of reaction

The oxidation of PCM by water soluble colloidal MnO_2 was carried out as a function of $[MnO_2]$ at fixed [PCM] (1.2×10^{-3} mol dm^{-3}), $[H_2SO_4]$ (1.0×10^{-4} mol dm^{-3}) and [CTAB] (10.0×10^{-4} mol dm^{-3}) at 298 K. The rate of reaction was

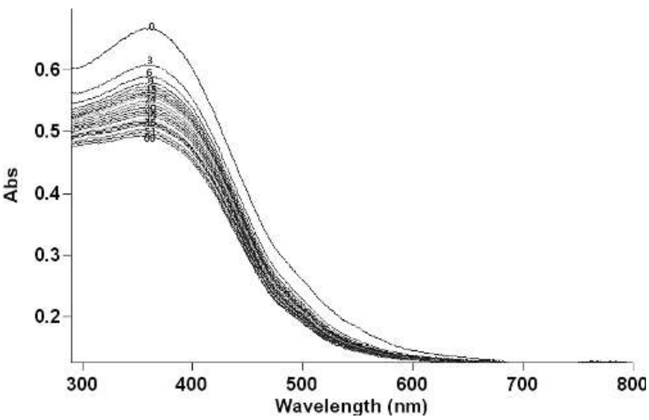


Figure 2 UV-visible spectral changes during the oxidation of paracetamol by colloidal MnO_2 in the presence of the cationic surfactant (CTAB) in acidic medium at 298 K; conditions: [PCM] = 1.2×10^{-5} mol dm^{-3}, $[MnO_2] = 0.6 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 1.0 \times 10^{-4}$ mol dm^{-3} and [CTAB] = 10.0×10^{-4} mol dm^{-3}; time scanning interval: 3 min

found to be decreased with increasing [MnO_2] (Fig. 3 and Table S1 in the supporting documents), which may be due to the flocculation of the colloidal particles of MnO_2 [33, 63–65].

3.3 Effect of [PCM] on the rate of reaction

In order to find out the reaction order as a function of [PCM], the k_{obs} value was determined with variable concentrations of PCM (0.6×10^{-3} to 2.4×10^{-3} mol dm^{-3}) keeping the concentrations of MnO_2, H_2SO_4 and CTAB constant at 298 K. The first order reaction was obtained with respect to [PCM] and it was confirmed by the linearity obtained from the plot of $\log k_{obs}$ vs. $\log$ [PCM] with a slope of 0.995 ($R^2 = 0.973$) (Fig. 4, Table S1).

3.4 Effect of [H_2SO_4] on the rate of reaction

Table S1 (see Appendix) contains the relevant data related to the reaction performed as a function of [H_2SO_4] in the concentration rage from 0.2×10^{-4} to 2.0×10^{-4} mol dm^{-3}. The decrease in the reaction rate has been observed with increasing the H_2SO_4 concentration. A negative fractional order was obtained by plotting $\log k_{obs}$ vs. $\log$ [H_2SO_4]. The slope is equal to –0.452 ($R^2 = 0.938$) (Fig. 5).

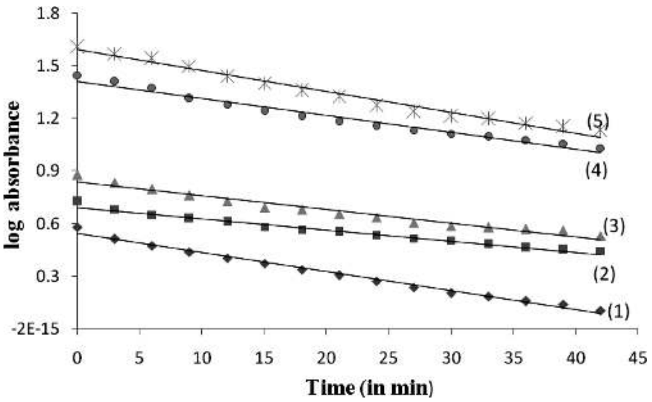


Figure 3 First order plots for the oxidation of paracetamol by colloidal MnO_2 in the presence of CTAB at 298 K; conditions: [PCM] = 1.2×10^{-3} mol dm^{-3}, [H_2SO_4] = 1.0×10^{-4} mol dm^{-3}, [CTAB] = 10.0×10^{-4} mol dm^{-3} and [MnO_2] = (1) 0.4×10^{-4}, (2) 0.6×10^{-4}, (3) 0.9×10^{-4}, (4) 1.2×10^{-4}, (5) 1.5×10^{-4} and (6) 1.8×10^{-4} mol dm^{-3}

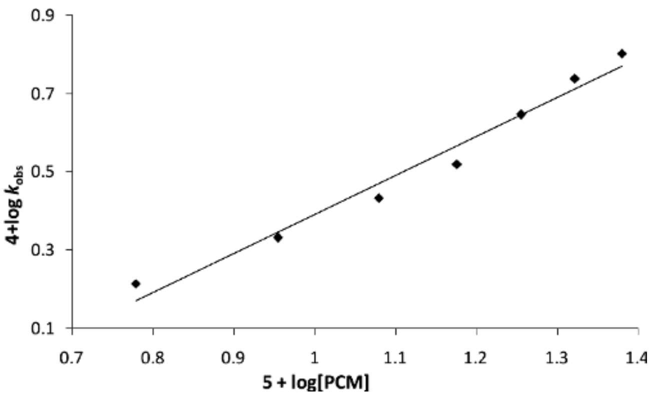


Figure 4 Effect of [PCM] on k_{obs} for the oxidation of paracetamol by colloidal MnO_2 in the presence of CTAB at 298 K. (Conditions: [MnO_2] = 1.2×10^{-4} mol dm^{-3}, [H_2SO_4] = 1.0×10^{-4} mol dm^{-3}, [CTAB] = 10.0×10^{-4} mol dm^{-3}, [PCM] = (1) 0.6×10^{-3}, (2) 0.9×10^{-3}, (3) 1.2×10^{-3}, (4) 1.5×10^{-3}, (5) 1.8×10^{-3}, (6) 2.1×10^{-3} and (7) 2.4×10^{-3} mol dm^{-3})

3.5 Effect of ionic strength on the rate of reaction

The effect of ionic strength (I) was determined according to the theory of Bronsted and Bjerrum [46, 47, 66], where the effect of ionic strength on the rate can be expressed as:

$$\log k_1 = \log k_0 + 1.02\, Z_A Z_B I^{1/2} \tag{2}$$

where Z_A and Z_B indicate the valence of the ions A and B, I is ionic strength and k_1 and k_0 refer as the rate constants in the presence and absence of the added electrolyte respectively. A linear slope of 1.02 $Z_A Z_B$ will be obtained from a plot of $\log k_1$ vs. $I^{1/2}$. If Z_A and Z_B ions have similar signs, $Z_A Z_B$ will exhibit a positive slope as the rate increases proportionally with the ionic strength. On the other hand, if these ions have dissimilar signs, a negative slope would have been obtained. With the varying concentrations of [KNO_3] (3.0×10^{-3} to 9.0×10^{-3} mol dm^{-3}), no change in rate constant was noticeable which indicated that a neutral molecule is involved in rate determining step.

3.6 Effect of dielectric constant on the rate of reaction

In order to find out the effect of dielectric constant of the medium on the reaction rate in the reaction mixture, the experiments were performed in micellar media with varying the concentration of acetonitrile from 5% to 25%. It can be shown by well the known eq. (3)

$$\log k_1 = \log k_0' = \frac{Z_A Z_B e^2 N}{2.303\,(4\pi\varepsilon_0) d_{AB} RT} \times \frac{1}{D} \tag{3}$$

where Z_A and Z_B are the charges of reacting ions, d_{AB} is known as size of activated complex, k_0' refers the rate constant in a medium of infinite dielectric constant, D is dielectric constant and T is absolute temperature. It was clearly seen that the k_{obs} value decreased with decreasing dielectric constant of the medium (Table S2). The obtained plot $\log k_1$ vs. $1/D$ is based on eq. 3 (Fig. 6); a line with a negative slope was obtained indicating that an interaction between negative ions and dipole molecules or between two dipoles is possible [14, 46, 47].

3.7 Effect of [Mn(II)] on the rate of reaction

With increasing [Mn(II)] and keeping all the concentrations of reactants constant at fixed temperature, the observed

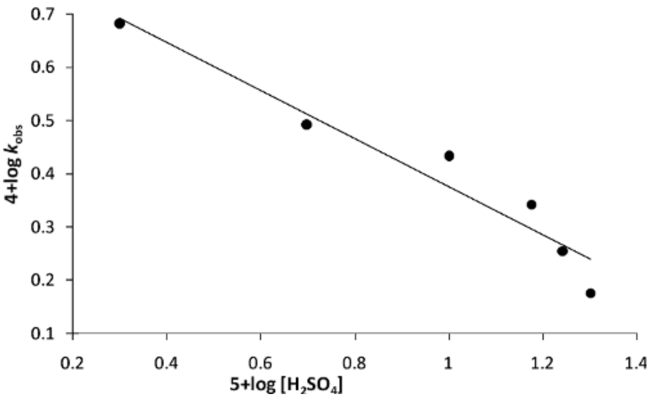


Figure 5 Effect of [H_2SO_4] on k_{obs} for the oxidation of paracetamol by colloidal MnO_2 in the presence of CTAB at 298 K. (Conditions: [MnO_2] = 1.2×10^{-4} mol dm^{-3}, [PCM] = 1.2×10^{-3} mol dm^{-3}, [CTAB] = 10.0×10^{-4} mol dm^{-3} and [H_2SO_4] = (1) 0.2×10^{-4}, (2) 0.5×10^{-4}, (3) 1.0×10^{-4}, (4) 1.5×10^{-4}, (5) 1.75×10^{-4} and (6) 2.0×10^{-4} mol dm^{-3})

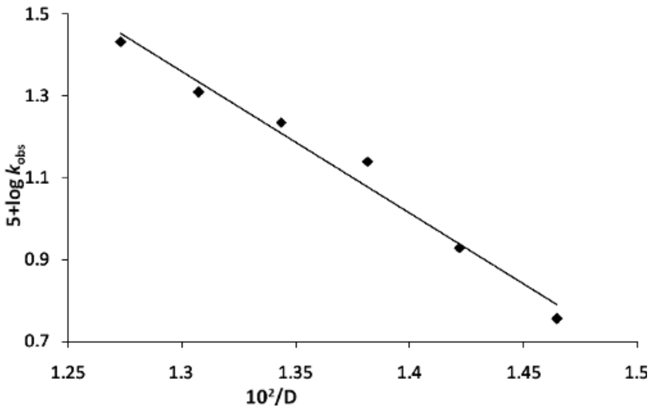


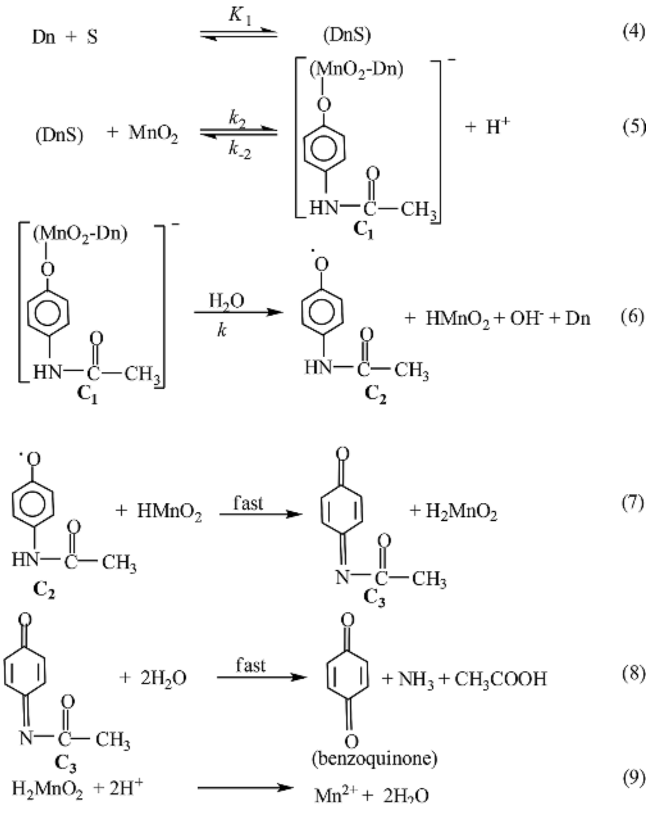
Figure 6 Effect of dielectric constant on k_{obs} for the oxidation of paracetamol by colloidal MnO_2 in the presence of CTAB at 298 K. (Conditions: $[MnO_2] = 1.2 \times 10^{-4}$ mol dm^{-3}, $[PCM] = 1.2 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0 \times 10^{-4}$ and $[CTAB] = 10.0 \times 10^{-4}$ mol dm^{-3})

reaction rate was almost constant (Table 1) indicating that Mn(II) ions were not involved before the rate limiting step.

3.8 Effect of [salt] on the rate of reaction

At fixed [PCM], [MnO_2] and [H_2SO_4] in the presence of the micellar system CTAB, the effect of added salts like KCl, KBr and Na_2SO_4 did not significantly influence the reaction rate (Table 1).

3.9 Reaction mechanism and rate law



Scheme 1 Reaction mechanism in the presence of CTAB

Considering Scheme 1 and eq. (6) the rate law may be derived as follows:

$$\text{rate} = k[C_1] \tag{10}$$

where C_1 is complex of (DnS-MnO_2).

From eq. (4), we have

$$[DnS] = K_1[Dn][S] \tag{11}$$

where S represents paracetamol [PCM].

From eq. (5), we get

$$K_2 = \frac{[C_1][H^+]}{[DnS][MnO_2]} \tag{12}$$

Applying a steady state approximation method for the complex C_1, we have the following equations

$$\frac{d[C_1]}{dt} = 0 = k_2[DnS][MnO_2] - k_{-2}[C_1][H^+] - k[C_1] \tag{13}$$

$$[C_1] = \frac{k_2[DnS][MnO_2]}{k + k_{-2}[H^+]} \tag{14}$$

Inserting the value of [DnS] from eq. (11) in eq. (14)

$$[C_1] = \frac{K_1\,k_2[Dn][S][MnO_2]}{k + k_{-2}[H^+]} \tag{15}$$

Inserting the value of [C_1] from eq. (15) in eq. (10), we get eq. (16):

$$\text{rate} = \frac{k\,k_2 K_1[Dn][S][MnO_2]}{k + k_{-2}[H^+]} \tag{16}$$

Eq. (16) is the final rate law based on the observed kinetic orders with respect to each reactant which involved in the reaction.

By reversing eq. (16), eq. (17) can be written as

$$\frac{[MnO_2]}{\text{rate}} = \frac{[H^+]}{k\,k_2\,K_1[Dn][S]} + \frac{1}{k_2\,K_1[Dn][S]} \tag{17}$$

Eq. (17) indicates that if a plot is made between $1/k_{obs}$ and 1/[PCM], a straight line will be obtained which passes through the origin and if a plot is made between $1/k_{obs}$ and [H^+], a straight line will be obtained with positive intercept on y-axis (Fig. 7 and 8). The proposed scheme supports the rate law represented in eq. (16).

In the reaction mechanism displayed in Scheme 1, reactions between surfactant CTAB i.e. Dn and substrate (S) i.e. PCM to form (DnS) is shown (eq. (4)). The species DnS again reacts with MnO_2 giving rise to H^+ and C_1 anionic complex in the initial equilibrium step but break down in the subsequent rates producing step produce C_2 complex (free radical), $HMnO_2$ along with hydroxide ion (eq.6). This C_2 radical complex further combines with $HMnO_2$ giving rise to C_3 complex and H_2MnO_2. Consequently, H_2MnO_2 reacts with a hydroxide ion giving rise to Mn(II) and further the C_3 complex hydrolyzed giving rise to the final products (benzoquinone and ammonia) (eq. 8).

3.10 Effect of temperature on the rate of reaction

In order to evaluate the value of thermodynamic activation parameters, the reaction rate was performed at five various temperatures, viz., 293, 298, 303, 308 and 313 K at constant concentration of PCM, MnO_2, H_2SO_4 and CTAB. The rate constant was found to be increased with increasing temperature (Fig. 9, Table S3). Linear plot was observed in log k_{obs} vs. 1/T. The Arrhenius equation was applied for calculating the activation energy and other thermodynamic activation parameters (Table 2).

4 Determination of CMC

The critical micelle concentration (CMC) is one of the most practical quantities for characterizing surfactant. This parameter captures most of the surface activity of the molecule. The conductometrically measurement of the CMC val-

$[KCl]/10^3$ mol dm^{-3}	$[KBr]/10^3$ mol dm^{-3}	$[Na_2SO_4]/10^3$ mol dm^{-3}	$[MnCl_2]/10^5$ mol dm^{-3}	CTAB/$k_{obs}10^4$ s^{-1}
0.0				2.71
0.2				2.69
0.4				2.71
0.6				2.70
0.8				2.71
1.0				2.71
	0.0			2.71
	0.2			2.70
	0.4			2.72
	0.6			2.71
	0.8			2.71
	1.0			2.70
		0.0		2.71
		0.2		2.71
		0.4		2.69
		0.6		2.68
		0.8		2.69
		1.0		2.70
			0.0	2.71
			1.0	2.70
			2.0	2.71
			3.0	2.69
			4.0	2.70
			40.0	2.71

Table 1 Effect of [KCl], [KBr], $[Na_2SO_4]$ and $[MnCl_2]$ for the oxidation of paracetamol in the presence of CTAB at 298 K, experimental conditions [PCM] = 1.2×10^{-3} mol dm^{-3}, $[MnO_2] = 1.2 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 1.0 \times 10^{-4}$ mol dm^{-3} and [CTAB] = 10.0×10^{-4} mol dm^{-3}

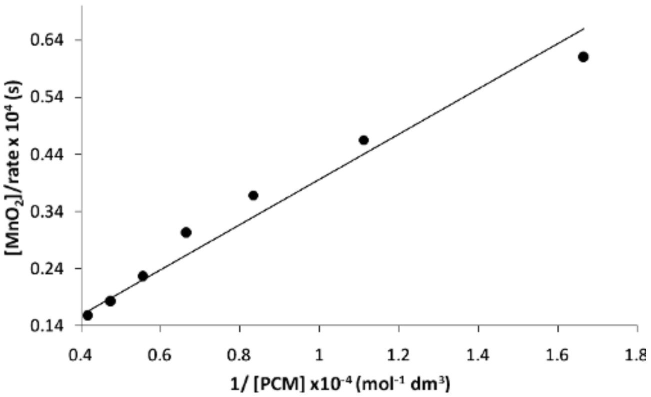


Figure 7 Verification of rate law for 1/[PCM] of oxidation of paracetamol by colloidal MnO_2 in the presence of CTAB at 298 K. (Conditions: $[MnO_2] = 1.2 \times 10^{-4}$ mol dm^{-3} and $[H_2SO_4] = 1.0 \times 10^{-4}$ mol dm^{-3})

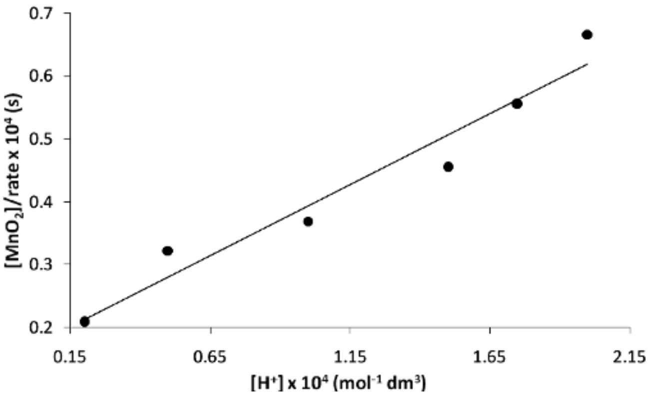


Figure 8 Verification of rate law for $[H^+]$ of oxidation of paracetamol by colloidal MnO_2 in the presence of CTAB at 298 K. (Conditions: $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3} and $[MnO_2] = 1.2 \times 10^{-4}$ mol dm^{-3})

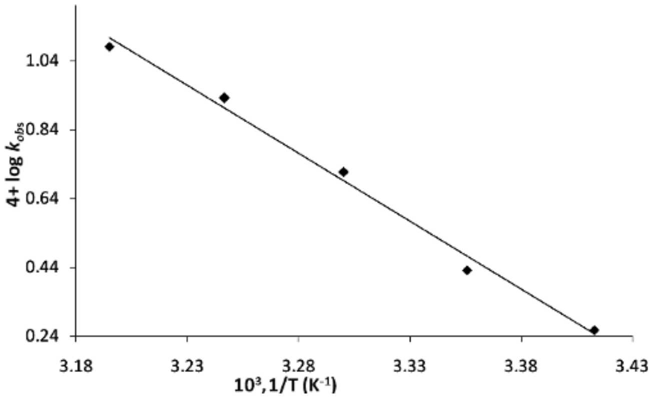


Figure 9 Effect of temperature on the pseudo-first-order rate constant for the oxidation of paracetamol by colloidal MnO_2 (Conditions: $[MnO_2] = 1.2 \times 10^{-4}$ mol dm^{-3}, $[PCM] = 1.2 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[CTAB] = 10.0 \times 10^{-4}$ mol dm^{-3} and temperature = 293 K, 298 K, 303 K, 308 K, 313 K and 318 K)

Parameter	CTAB$k_{obs}/10^4$ s^{-1}
E_a/kJ mol^{-1}	75.40
$\Delta H^{\#}$/kJ mol^{-1}	72.92
$\Delta S^{\#}$ /J K^{-1} mol^1	−60.20
$\Delta G^{\#}$/kJ mol^{-1}	90.86
logPz^c	9.65

Table 2 Thermodynamic activation parameters in the presence of CTAB

ue of CTAB was determined at 298 K using a Systronic digital conductivity meter 304. In the absence and presence of the reactants PCM and MnO_2, the CMC value of surfactant was calculated from the breaking point of the two straight line of the plot of specific conductivity versus [surfactant] (Table S4).

5 Influence of CTAB

An uncommon medium provided by micelles may affect the reaction rate. Due to the electrical charge on their head groups micelles can either attract or repel the reactive ions [15]. The effect of CTAB was investigated on the rate of reaction by performing the reaction on varying the amount of CTAB at fixed concentration of other reactants at 298 K. The value of k_{obs} increases from 1.94×10^{-4} to 7.30×10^{-4} s^{-1} with increasing [CTAB] while keeping the concentration of the other reactants constant at 298 K (Table 3).

6 Menger and Portnoy model

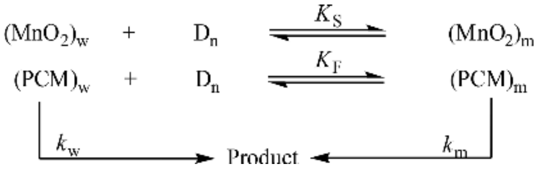
The rate of micellar catalysis in the presence of CTAB has been explained by the pseudo phase model proposed by Menger and Portnoy. The variation of the reaction rate with surfactant is usually carried out on the assumption that the substrate is distributed between the aqueous and micellar phases as exhibited in Scheme 2.

The rate law according to Scheme 2 is:

$$k_{obs} = \frac{k_w + k_m K_s[D_n]}{1 + K_s[D_n]} \qquad (18)$$

10^4 [CTAB]/mol dm^{-3}	$k_{obs}/10^4$ s^{-1}
0.0	1.94
2.0	2.29
4.0	2.36
6.0	2.45
8.0	2.52
10.0	2.71
12.0	2.81
14.0	3.06
16.0	3.25
18.0	3.70
20.0	3.84
22.0	4.34
25.0	6.28
30.0	7.30

Table 3 Effect of [CTAB] on the oxidation of paracetamol by colloidal MnO_2 at 298 K; experimental conditions: $[PCM] = 1.2 \times 10^{-3}$ mol dm^{-3}, $[MnO_2] = 1.2 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 1.0 \times 10^{-4}$ mol dm^{-3} and $[CTAB] = 10.0 \times 10^{-4}$ mol dm^{-3}



Scheme 2 Menger and Portnoy model

In the case of micellar catalysis this model leads to the following relationship:

$$\frac{1}{(k_w - k_{obs})} = \frac{1}{(k_w - k_m)} + \frac{1}{(k_w - k_m)K_s[D_n]} \qquad (19)$$

where $[D_n]$ is the surfactant in the micellar phase (i.e., $[D_n]$ = [CTAB]-CMC), k_w represents the rate constant in the absence of surfactant, the rate constant in the micellar phase (k_m) and K_S and K_F are the binding constant. Linearity should be obtained by the plots of $1/k_w$-k_{obs} versus $1/[D_n]$ (Fig. 10), which shows the applicability of the model. Under the experimental conditions, the value of k_m and K_S were calculated using the slope and intercept. The value of k_m and K_S of PCM in CTAB were found to be 50.69×10^{-4} and 20.20 respectively.

7 Piszkiewicz model

Several analogies have been proposed to describe the micellar phase reaction. Reactions influenced by surfactants have been viewed as models of enzyme catalyzed reactions. A kinetic model analogous to the Hill model was used by Piszkiewicz to explain the catalysis of molecular reactions by surfactants. This model is applicable especially at lower surfactant concentrations and the data may be treated without reference to CMC. According to this model a substrate (S) and a number n of detergent molecules (D), combined to form an active micelle (D_nS) that may react to produce product as shown in Scheme 3.

Where K_D is the dissociation constant of micelle back to its free components, n and D represent the index of cooperativity and total surfactant respectively.

As per this model, the observed rate constant is shown as a function of detergent given by following equation.

$$k_{obs} = \frac{k_m[D]^n + k_w K_D}{K_D - [D]^n} \tag{20}$$

After rearrangement of eq. (20), we have

$$\log = \frac{k_{obs} - k_w}{k_m - k_{obs}} = n \log[D] - \log K_D \tag{21}$$

From the linear plot obtained between log $\{(k_{obs}-k_w)/(k_m-k_{obs})\}$ and log [D], the values of n and K_D were found to be 1.32 and 1.11 respectively from the slope and intercept of the plot for CTAB (Fig. 11). Our observations for the value of n (between 1 to 3) are in good agreement with the earlier observations of Piszkiewicz [73] and is viewed as indices of a positive cooperativity that induced interaction of the additional substrate molecule due to the interaction of micelle with the first substrate molecule. These values are far less than the number of surfactant molecules found in the micelle and have previously been interpreted as indicative of the pre-micellar aggregates [74].

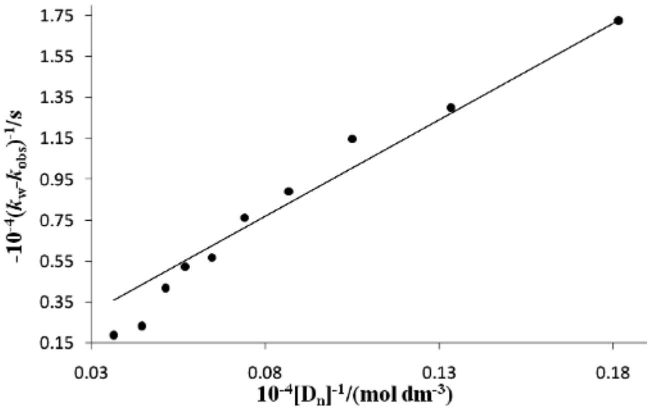
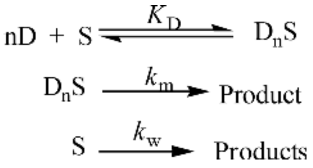


Figure 10 Plot of $1/(k_w - k_{obs})$ versus $1/[D_n]$ for the oxidation of paracetamol by colloidal MnO_2 at 298 K



Scheme 3 Piszkiewicz Model

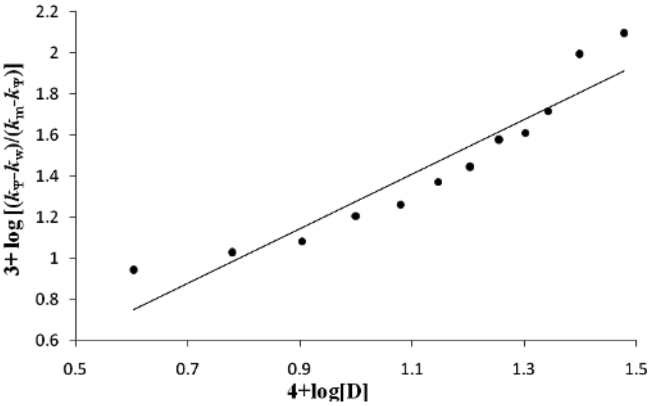


Figure 11 Piszkewicz model for CTAB mediated reaction. (conditions: $[PCM] = 1.2 \times 10^{-3}$ mol dm^{-3}, $[MnO_2] = 1.2 \times 10^{-4}$ mol dm^{-3} and $[H_2SO_4] = 1.0 \times 10^{-4}$ mol dm^{-3} at 298 K)

8 Probable reaction site

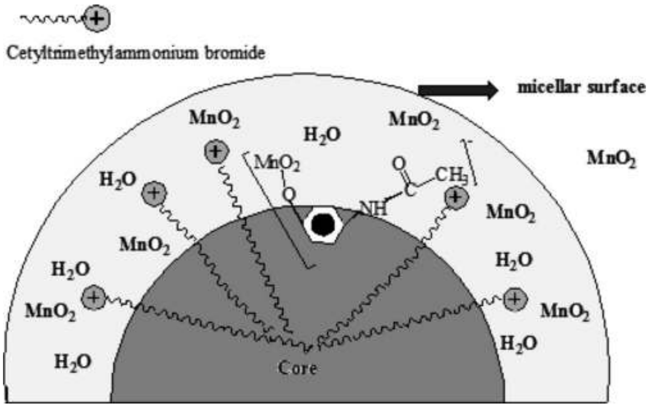
Owing to the diverse properties of the micellar pseudophase, the exact site of the reaction is not possible to locate precisely, but to some extent, location of reactants can be reasoned. The results demonstrated that the catalytic effect of CTAB on the reaction rate increased not only in post-micellar catalysis but also in pre-micellar catalysis. The catalysis of the reaction in CTAB surfactant solution is mainly because of the association/incorporation of the substrate into the micelle. One of the three factors like electrostatic/hydrophobic and hydrogen bonding interactions between the PCM and MnO_2 might have been responsible for the enhanced reaction rate. The probable reaction site occurs in the palisade-Stern layer's junctural region of micelles, which is clearly seen in the Scheme 4.

9 Comparative study

It is interesting to discuss the reactivity of PCM oxidized by MnO_2 as compared to an other oxidant Cr(VI) [59]. In the present investigation, a fractional order kinetics was observed with respect to $[H^+]$ where as a first order kinetics with respect to $[H^+]$ was observed in the presence of Cr(VI). Reaction was proceeded in the presence of the anionic surfactant SDS in case of Cr(VI) and in the present study, it was found that cationic surfactant CTAB also enhanced the reaction rate. The catalytic effect was explained by various

	Parameter
k_m	5.07×10^3
Ks	20.20
n	1.324
K_D	1.114

Table 4 Other parameters for the oxidation of paracetamol by colloidal MnO_2 at 298 K in the presence of CTAB



Scheme 4 Schematic representation of the probable reaction site for the oxidation of paracetamol by colloidal MnO2 in the presence of CTAB micelles

models. Mn(II) was not affected on the rate of reaction in the present work but it showed a catalytic effect in the presence of Cr(VI) [59].

10 Conclusion

The main aim of the present investigation is to study the effect of a cationic micelle (CTAB) on the oxidation of the analgesic drug PCM by colloidal MnO_2. The catalytic role of CTAB, owing to the incorporation/association of colloidal MnO_2 and PCM into the micelle, has been discussed by the models of Menger Portnoy and Piszkiewicz. All the experimental evidences, the rate law and various parameters are evaluated. Under the experimental conditions, the degraded product of PCM was identified as benzoquinone.

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Abbreviations

Z_A and Z_B = Charges of reacting ions
d_{AB} = Size of activated complex
T = Absolute temperature
$\Delta S^{\#}$ = Entropy of activation
$\Delta H^{\#}$ = Enthalpy of activation
$\Delta G^{\#}$ = Gibb's free energy
k_w = The pseudo-first order rate constant in the aqueous
k_m = The pseudo-first order rate constant in the micellar
K_s and K_F = Binding constants
CMC = Critical micelle concentration
CTAB = Cetyltrimethylammonium bromide
MnO_2 = Manganese dioxide
PCM = Paracetamol
D = Dielectric constant
I = Ionic strength
D_nS = active micelle
S = substrate (Paracetamol)
K_D = dissociation constant
n = index of cooperativity
D = total surfactant
$[D_n]$ = [CTAB]-CMC)

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APPENDIX

$[MnO_2]/ 10^4$ mol dm^{-3}	[PCM] $10^3/$ mol dm^{-3}	$[H_2SO_4]/ 10^4/$mol dm^{-3}	CTAB $k_{obs}/ 10^4$ s^{-1}
0.4	1.2	1.0	23.30
0.6	1.2	1.0	10.36
0.9	1.2	1.0	4.14
1.2	1.2	1.0	2.71
1.5	1.2	1.0	1.15
1.8	1.2	1.0	1.11
1.2	0.6	1.0	1.64
1.2	0.9	1.0	2.15
1.2	1.2	1.0	2.71
1.2	1.5	1.0	3.31
1.2	1.8	1.0	4.43
1.2	2.1	1.0	5.49
1.2	2.4	1.0	6.35
1.2	1.2	0.2	4.80
1.2	1.2	0.5	3.10
1.2	1.2	1.0	2.71
1.2	1.2	1.5	2.20
1.2	1.2	1.75	1.80
1.2	1.2	2.0	1.50

Table S1 Effect of $[MnO_2]$, [PCM] and $[H_2SO_4]$ for the oxidation of paracetamol by colloidal MnO_2 in the presence of CTAB at 298 K; experimental conditions: [PCM] = 1.2×10^{-3} mol dm^{-3}, $[MnO_2] = 1.2 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 1.0 \times 10^{-4}$ mol dm^{-3} and [CTAB] = 10.0×10^{-4} mol dm^{-3}

$[CH_3CN]$/% (v/v)	D	CTAB $k_{obs}/10^4$ s^{-1}
0.0	78.2	2.71
5.0	76.16	2.04
10.0	74.13	1.72
15.0	72.10	1.38
20.0	70.06	0.85
25.0	68.02	0.57

Table S2 Effect of dielectric constant for the oxidation of paracetamol by colloidal MnO_2 in presence of CTAB at 298 K; experimental conditions: [PCM] = 1.2×10^{-3} mol dm^{-3}, $[MnO_2] = 1.2 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 1.0 \times 10^{-4}$ mol dm^{-3} and [CTAB] = 10.0×10^{-4} mol dm^{-3}

T/K	CTAB $k_{obs}/10^4$ s^{-1}
293	1.81
298	2.71
303	5.22
308	8.55
313	12.05

Table S3 Effect of temperature for the oxidation of paracetamol by colloidal MnO_2 in the presence of CTAB at 298 K; experimental conditions: [PCM] = 1.2×10^{-3} mol dm^{-3}, $[MnO_2] = 1.2 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 1.0 \times 10^{-4}$ mol dm^{-3} and [CTAB] = 10.0×10^{-4} mol dm^{-3}

Solution	$CMC_{(CTAB)}/10^{-4}$ mol dm^{-3}
Water	10.1
Water + MnO_2	6.4
Water + PCM	5.0
Water + H_2SO_4	2.6
Water + PCM + MnO_2 + H_2SO_4	3.1

Table S4 CMC values of CTAB in different solutions at T = 298 K (conductivity measurements); literature value of CTAB in water at T = 298 K: 10.0×10^{-4} mol dm^{-3} [15]