# Oxidative degradation of norfloxacin by water soluble colloidal MnO$_2$ in the presence of cationic surfactant

Ajaya Kumar Singh[a,*], Neelam Sen[a] & Som Kumar Chatterjee[b]

[a]Department of Chemistry, Government Vishwanath Yadav Tamaskar Post Graduate Autonomous College Durg, Chhattisgarh, 491 001, India

Email: ajayaksingh_au@yahoo.co.in

[b]Department of Chemistry, Government Narayan Rao Meghawale Girls College, Dhamtari Chhattisgarh 493 773, India

The oxidative degradation of norfloxacin (NOR) by water soluble colloidal MnO$_2$ in alkaline medium has been studied spectrophotometrically in the absence and presence of cationic surfactant, cetyltrimethylammonium bromide (CTAB) at 298 K. The rate of reaction has been followed under pseudo-first order condition with respect to [MnO$_2$]. Positive fractional order and negative fractional order are observed with respect to [NOR] and [NaOH] respectively in both aqueous and micellar media. The rate constant increases with decreasing dielectric constant of the medium in both the systems. The retardation effect observed by CTAB is discussed by well known Berezin's model and from this model micelle binding constant has been computed. Using the Arrhenius equation, thermodynamic activation parameters have also been evaluated in both the media. On the basis of experimental results suitable mechanism and rate law are proposed.

**Keywords:** Kinetics, Reaction mechanisms, Degradation, Oxidative degradation, Surfactants, Cationic surfactants, Colloidal MnO$_2$, Norfloxacin, Cetyltrimethylammonium bromide

In a bulky solution of water, above a certain concentration of monomers, micelles are stable aggregates of amphiphilic monomers, which can influence reaction rate because of dissimilar phase properties between a micelle and the bulk solvent[1, 2]. Micelle catalyzed reactions become a region of highly increasing interest[3]. The self-aggregation or micellization of amphiphilic molecules (drugs, surfactants, polymer etc.) in solution could be an accepted phenomenon that depends on the amphiphilic species and on the conditions of the system within which they are dissolved[4]. This tends to enhance the solubility of organic compounds in water owing to the involvement of organic compounds in the micelle[5] and catalyze many reactions due to the concentration effect in the micellar pseudo-phase, sometimes even change the reaction pathways[6]. Micelles can dissolve partially soluble drugs in their hydrophobic core, thus improving their biological presence which protects drugs from destructive factors upon parenteral administration[7-9]. The study of electron transfer processes in organized molecular assemblies has brought a drastic change in biochemical analysis which is multidisciplinary in nature[10,11]. The salient properties of the surfactants that affect electron transfer reactions include localization, pre-orientational polarity, counter ion effects and the influence of charged interfaces[12]. There are several reports in the literature on the kinetic oxidative degradation of organic compounds by various oxidants in the presence of micellar[13-22].

In the past few decades, there has been great concern on pharmaceuticals waste which is a key source of impurities in the aquatic ecosystem, ground water and soil, and which leads to the bacterial resistance against antibiotics even at their low concentrations[23]. Fluoroquinolones (FQs) are anthropogenic contaminants which are comprehensively used as pharmaceuticals for both human and veterinary purposes[24, 25]. The most widely used fluoroquinolone antibacterial agent is NOR [{1-ethyl-6-fluoro-1, 4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid}][26], a common antibiotic in pharmaceuticals effluents[27-29]. It is a synthetic expanded spectrum chemotherapeutic antibacterial agent, which is widely used for treatment of urinary tract infection, gastrointestinal and skin infections, due to its potency and broad spectrum of activity against many gram-positive and gram-negative bacteria[30-34]. Due to its applications in such wide areas including human, veterinary treatment and

aquaculture, it is used in large amounts extensively. However, a major part of NOR remains un-metabolized and is ultimately discharged into the aquatic environment, contaminating the surface water as well as finally the ground water level[35-37]. Removal of NOR residue from aquatic environment is therefore considered as a priority and serves as an important study. Various technologies/methods available for this purposes include adsorption, photo-degradation, chlorine oxidation, ozonation, UV, $ClO_2$, $KMnO_4$, chloramine-T, $UV/O_3$ and $UV/TiO_2$[38-47].

Of the oxides of manganese, Mn(III and IV) oxides are insoluble and Mn(II) ions are soluble in natural waters[48]. $MnO_2$ acts as catalyst in the $pH$ range 9–10. The colloidal $MnO_2$ solution is negatively charged in aqueous solution[49]. In the present work, the oxidative behaviour of NOR by colloidal $MnO_2$ was explored and the kinetic and mechanistic aspects of the micellar catalyzed reaction in a basic medium have been studied.

## Materials and Methods

All chemicals used were of analytical grade and all the solutions were prepared with doubly distilled deionised water at room temperature (298 K). The stock solution of NOR (USP powder, plasma, m. p. 99.9%) was prepared in 10% acetic acid without any further purification, and was further diluted with doubly distilled water. Cetyltrimethylammonium bromide (SD Fine, India), potassium nitrate (E. Merck, Mumbai, India), potassium permanganate (98.5%, E. Merck, Mumbai, India), sodium thiosulphate (99%, E. Merck, Mumbai, India) and sodium hydroxide (E. Merck, Mumbai, India) solutions were prepared in doubly distilled water. Sodium hydroxide was standardized against a standard solution of oxalic acid.

### Preparation and characterization of colloidal $MnO_2$

Water-soluble colloidal $MnO_2$ was prepared in laboratory as per the procedure given by Perez-Benito *et al*.[50-52] Perfectly transparent dark brown colour solution was obtained on the reduction of $KMnO_4$ ($1.0×10^{-2}$ mol dm$^{-3}$) by sodium thiosulphate ($1.0×10^{-2}$ mol dm$^{-3}$) under neutral condition[53], which was stable for several weeks and was stored in black coated bottle to prevent photochemical reaction. The solution of colloidal $MnO_2$ was confirmed by the peak at $\lambda_{max}$ 375 nm in its absorption spectra recorded using Cary 50 Bio UV-visible spectrophotometer (Varian). This has also been confirmed by the precipitation of Mn(IV) on the addition of electrolytes like($SrCl_2$,

$BaCl_2$, $LiCl$, $NaCl$, $KCl$, $NH_4Cl$, $CaCl_2$ and $MgCl_2$, to the colloidal solution of $MnO_2$[54].

### Kinetic measurements

All the kinetic experiments were performed under pseudo-first order conditions where NOR concentration was ten fold excess over [$MnO_2$]. The reaction was initiated on the addition of NOR in the mixture containing $MnO_2$ and NaOH in both media. The progress of the reaction was monitored spectrophotometrically by monitoring the disappearance of colloidal $MnO_2$ at 375 nm at varying time intervals. From the linear plot of log(abs) versus time, the values of pseudo-first order rate constant were evaluated. Each kinetic reaction run was studied for 80% completion. The spectral changes of NOR ($1.2×10^{-5}$ mol dm$^{-3}$) solution during the oxidation of NOR by $MnO_2$ ($0.6×10^{-4}$ mol dm$^{-3}$) in basic media (NaOH, $1.0×10^{-3}$ mol dm$^{-3}$) at different time intervals at 298 K in the absence and presence of CTAB ($10.0×10^{-4}$ mol dm$^{-3}$) are shown in Fig. 1 and Fig. S1 (Supplementary Data) respectively.

### Stoichiometry and product analysis

Various sets of reaction mixtures consisting of NOR, NaOH with excess $MnO_2$ were equilibrated for 72 h at 298 K. After completion of the reaction, unconsumed $MnO_2$ was determined. It was observed that one mole of NOR was oxidized by one mole of $MnO_2$, exhibiting 1:1 ratio for the consumption of reductant to oxidant.
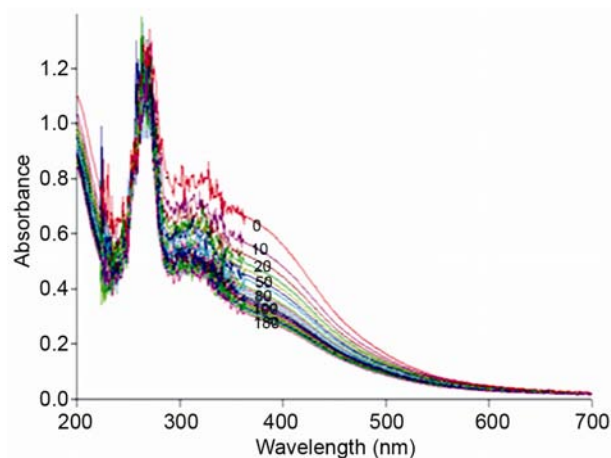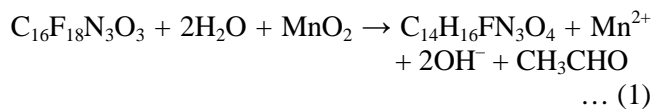
$$C_{16}F_{18}N_3O_3 + 2H_2O + MnO_2 \rightarrow C_{14}H_{16}FN_3O_4 + Mn^{2+}$$
$$+ 2OH^- + CH_3CHO$$
$$\ldots (1)$$



Fig. 1 – UV-visible spectral changes during the oxidation of norfloxacin by colloidal $MnO_2$ in alkaline medium at 298 K. {React. cond.: [NOR] = $1.2×10^{-5}$; [$MnO_2$] = $0.6×10^{-4}$; [NaOH] = $1.0×10^{-3}$ mol dm$^{-3}$); time interval = 10 min}.

After completion of the reaction, reaction mixture was treated with ether and was shaken properly. Upper layer of ether with dissolved organic compound separated out and was evaporated to obtain the oxidation product of NOR. GC-ESI-MS analysis of the NOR reaction illustrated the presence of product with molecular mass and molecular formula $m/z$ 310 and $C_{14}H_{16}O_4FN_3$ respectively, which indicates loss of $C_2H_2$ at the piperazinyl substituent resulting in opening of the piperazinyl ring and addition of oxygen atom that produces hydroxyl derivatives (Supplementary Data, Fig. S2)[54,55].

To investigate the presence of free radicals in reaction mixture, the experiment was performed with acrylonitrile in the reaction mixture, kept in an inert atmosphere for 24 h. Precipitate was formed after diluting the reaction mixture with methanol. This observation indicates that free radical was formed in the reaction mixture.

## Results and Discussion

### Effect of various parameters in absence of CTAB

The order of reaction with respect to [MnO₂] was monitored by varying the concentration of MnO₂ ($0.4\times10^{-4}$ to $1.8\times10^{-4}$ mol dm³) in the presence of [NOR] ($1.2\times10^{-3}$ mol dm³) and [NaOH] ($1.0\times10^{-3}$ mol dm³) at 298 K. It was found that the rate constant value decreased with increasing [MnO₂] (Fig. 2 and Table S1, Supplementary Data). The decrease in the rate constant value may be due to the possibility of flocculation of colloidal MnO₂ particles[56-59].

To study the effect of [NOR] on the rate of reaction, the reaction was carried out at fixed concentration of all other reactants, while the NOR
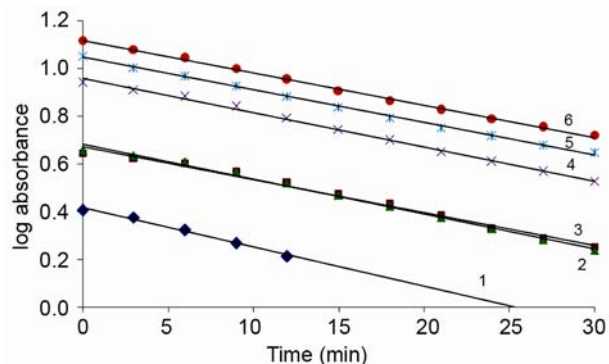
concentration was varied in the range of $0.6\times10^{-3}$ to $3.0\times10^{-3}$ mol dm³ at 298 K (Table S1). The value of rate constant was increased with increasing [NOR] linearly. Positive fractional order was obtained as a function of [NOR] with slope 0.676 ($R^2 = 0.995$) (Fig. 3).

The effect of [NaOH] on the reaction rate was studied at fixed concentration of NOR and MnO₂ at 298 K. The rate constant decreased with increasing NaOH concentration (Table S1). The result exhibit a negative fractional order with respect to [OH⁻] with a slope equal to -0.362 ($R^2 = 0.999$) (Fig. 4a).

The effect of ionic strength on the reaction rate was studied by varying [KNO₃] (from $2.0\times10^{-3}$ to $8.0\times10^{-3}$ mol dm³) at fixed [NOR], [NaOH] and [MnO₂] at 298 K. In the absence of the surfactant, the reaction rate was almost constant. According to the theory of Bronsted and Bjerrum[60] this indicates that ionic strength did not influence the rate of reaction.

In order to investigate the effect of dielectric constant (polarity) of the medium on the reaction rate, experiments were performed in aqueous media using acetic acid with varying proportions as elucidated by the following equation.

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

here $k_0'$ is the rate constant in a medium of infinite dielectric constant, $Z_A$ and $Z_B$ are the charges of reacting ion, $d_{AB}$ refers to the size of activated complex, $T$ is absolute temperature and $D$ is dielectric constant of the medium. The effect of dielectric constant was studied on the addition of 2–10% acetic acid. It was observed that the reaction rate increased
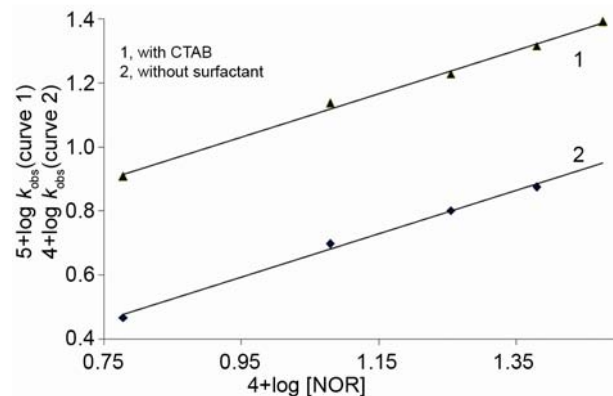


Fig. 2 – First order plots for the oxidation of norfloxacin by colloidal MnO₂ in aqueous media at 298 K. {React. cond.: [NOR] = $1.2\times10^{-3}$ mol dm³; [NaOH] = $1.0\times10^{-3}$ mol dm³; [MnO₂] = (1) $0.4\times10^{-4}$; (2) $0.6\times10^{-4}$; (3) $0.9\times10^{-4}$;(4) $1.2\times10^{-4}$; (5) $1.5\times10^{-4}$; (6) $1.8\times10^{-4}$ mol dm³}.



Fig. 3 – Effect of [NOR] on $k_{obs}$ for the oxidation of norfloxacin by colloidal MnO₂ in the absence (Curve 1) and presence (Curve 2) of CTAB. {React. cond.: [MnO₂] = $1.2\times10^{-4}$ mol dm³; [NaOH] = $1.0\times10^{-3}$ mol dm³; [CTAB] = $10.0\times10^{-4}$ mol dm³ at 298 K}.
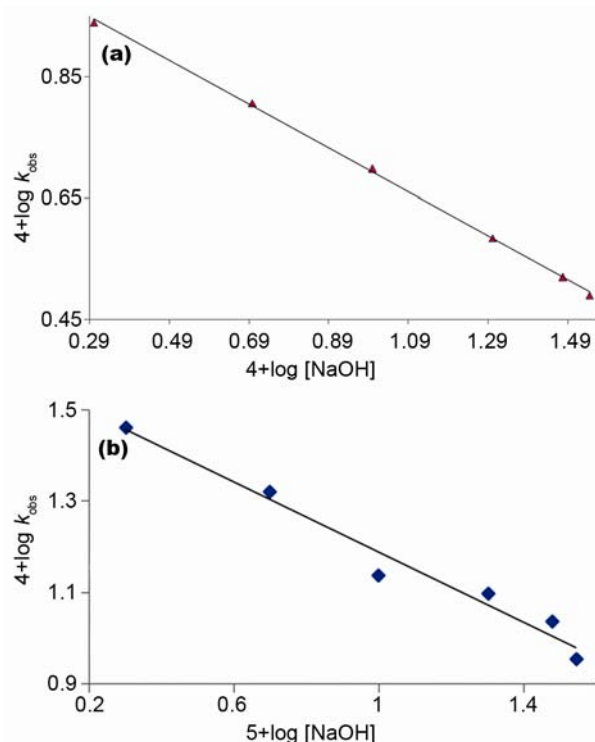
Fig. 4 – Effect of [NaOH] on $k_{obs}$ for the oxidation of norfloxacin by colloidal $MnO_2$ in (a) absence of surfactant, and (b) presence of CTAB. {React. cond.: $[MnO_2] = 1.2 \times 10^{-4}$ mol $dm^{-3}$; [NOR] = $1.2 \times 10^{-3}$ mol $dm^{-3}$; [CTAB] = $10.0 \times 10^{-4}$ mol $dm^{-3}$; [NaOH] = $0.2 \times 10^{-3}$, $0.5 \times 10^{-3}$, $1.0 \times 10^{-3}$, $2.0 \times 10^{-3}$, $3.0 \times 10^{-3}$ and $3.5 \times 10^{-3}$ mol $dm^{-3}$ at 298 K}.



Fig. 5 – Effect of dielectric constant on $k_{obs}$ for the oxidation of norfloxacin by colloidal $MnO_2$. {React. cond.: $[MnO_2] = 1.2 \times 10^{-4}$ mol $dm^{-3}$; [NaOH] = $1.0 \times 10^{-3}$ mol $dm^{-3}$; [CTAB] = $10 \times 10^{-4}$ mol $dm^{-3}$ at 298 K}.



Fig. 6 – Effect of temperature on the pseudo-first-order rate constant for the oxidation of norfloxacin by colloidal $MnO_2$. {React. cond.: $[MnO_2] = 1.2 \times 10^{-4}$ mol $dm^{-3}$; [NaOH] = $1.0 \times 10^{-3}$ mol $dm^{-3}$; [CTAB] = $10.0 \times 10^{-4}$ mol $dm^{-3}$; temp. (K) = 293, 298, 303, 308, 313, 318}.

gradually with increasing percentage of acetic acid (Supplementary Data, Table S2). A linear plot of log $k_1$ versus $1/D$, with positive slope was obtained (Fig. 5), indicating an interaction between a charged species and a dipole molecule[61,62].

In order to observe the effect of externally added Mn(II), Mn(II) was added in the reaction mixture. It has been observed that the rate of reaction remained constant with varying proportion of [Mn(II)] ($0.2 \times 10^{-5}$ to $1.2 \times 10^{-5}$ mol $dm^{-3}$) keeping other experimental conditions constant (Supplementary Data, Table S3).

**Effect of various parameters in presence of CTAB**

Preliminary experiments were performed for the oxidation of NOR by colloidal $MnO_2$ in the presence of CTAB. Reaction was carried out under pseudo-first order condition as a function of $[MnO_2]$. It was observed that the reaction rate gradually decreased ($1.53 \times 10^{-4}$ to $0.84 \times 10^{-4}$ $s^{-1}$) with increasing concentration of $MnO_2$ ($0.4 \times 10^{-4}$ to $1.8 \times 10^{-4}$ mol $dm^{-3}$), this may be due to the flocculation of colloidal $MnO_2$ particles (Supplementary Data, Fig. S3). The behaviour with respect to [NOR] in the presence of
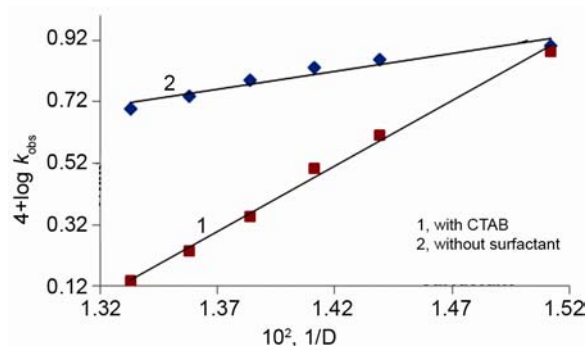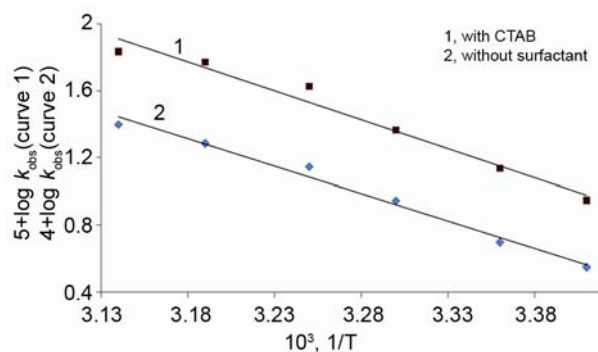
micellar system (CTAB), reaction rate was found to increase ($0.81 \times 10^{-4}$ to $2.46 \times 10^{-4}$ $s^{-1}$) with increasing NOR concentration ($0.6 \times 10^{-3}$ to $3.0 \times 10^{-3}$ mol $dm^{-3}$) (Fig. 3). On increasing concentration of NaOH ($0.2 \times 10^{-3}$ to $3.5 \times 10^{-3}$ mol $dm^{-3}$), and keeping other reactants constant, the value of $k_{obs}$ decreased ($1.52 \times 10^{-4}$ to $1.30 \times 10^{-4}$ $s^{-1}$) (Fig. 4b). [Mn(II)] and ionic strength of the medium did not influence the reaction rate in the presence of cationic surfactant. The rate of reaction increased with increasing percentage of acetic acid as solvent, a similar effect was observed in the aqueous medium (Fig. 5).

**Effects of temperature and thermodynamic activation parameters**

The kinetic experiments were studied at six different temperature, viz., 293, 298, 303, 308, 313 and 318 K at fixed concentration of [NOR], $[MnO_2]$ and [NaOH] in the absence and presence of CTAB. The reaction rate was found to increase with increasing temperature (Table S4 and Fig. 6). From

the linear plot of log $k_{obs}$ versus $1/T$, using Arrhenius equation, activation energy and other thermodynamic activation parameters were obtained for both the media (Table 1). High negative value of entropy of activation ($\Delta S^{\#}$) indicates that more ordered activated complex was formed in the micellar phase. The more highly positive values of enthalpy of activation ($\Delta H^{\#}$) and Gibb's free energy ($\Delta G^{\#}$) indicate that highly solvated transition state was formed during the course of the reaction.

Table 1 – Thermodynamic activation parameters in the absence and presence of surfactant

| Thermodynamic parameters | Absence of CTAB | Presence of CTAB |
|---|---|---|
| $E$a (kJ mol⁻¹) | 63.38 | 67.26 |
| $\Delta H^{\#}$ (kJ mol⁻¹) | 60.90 | 64.79 |
| $\Delta S^{\#}$ (J K⁻¹ mol¹) | - 95.48 | -93.18 |
| $\Delta G^{\#}$ (kJ mol⁻¹) | 89.35 | 92.55 |
| logPz | 7.80 | 7.92 |



…(3)

…(4)

…(5)

…(6)

…(7)
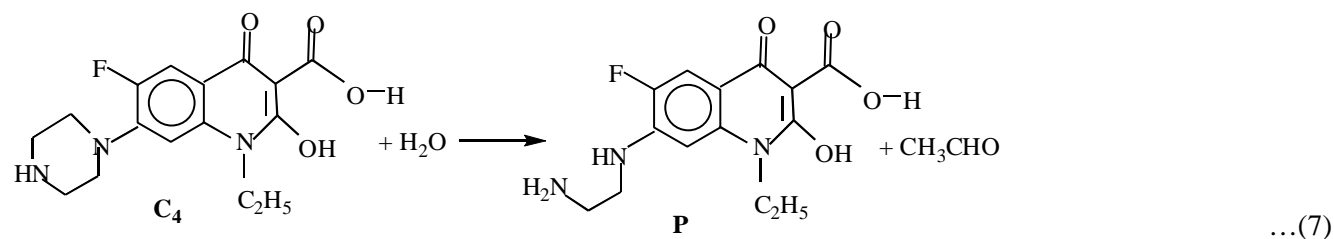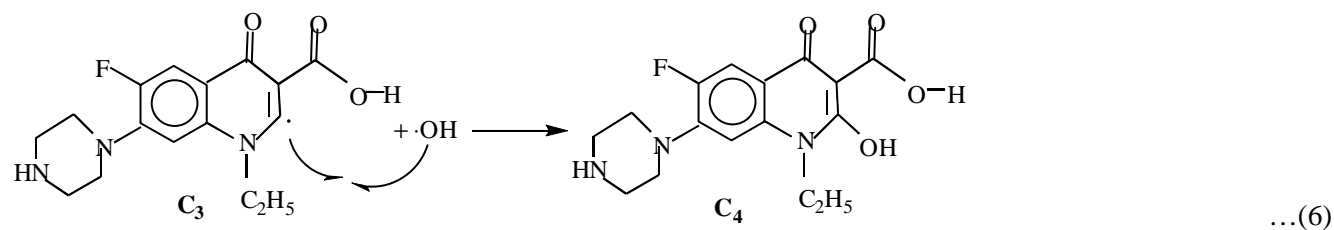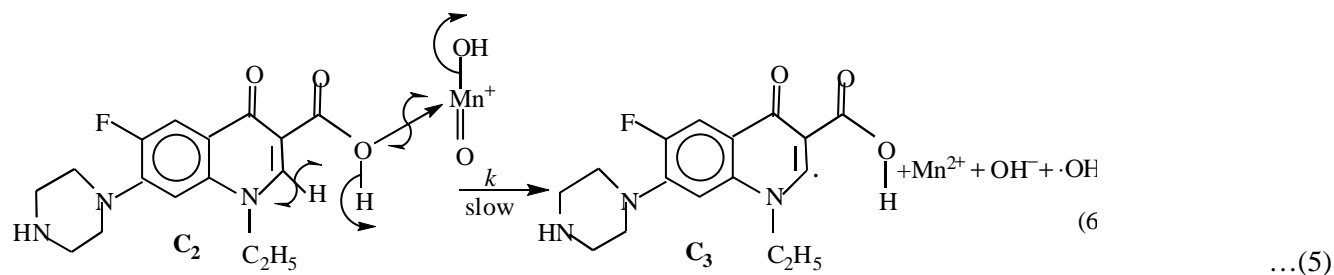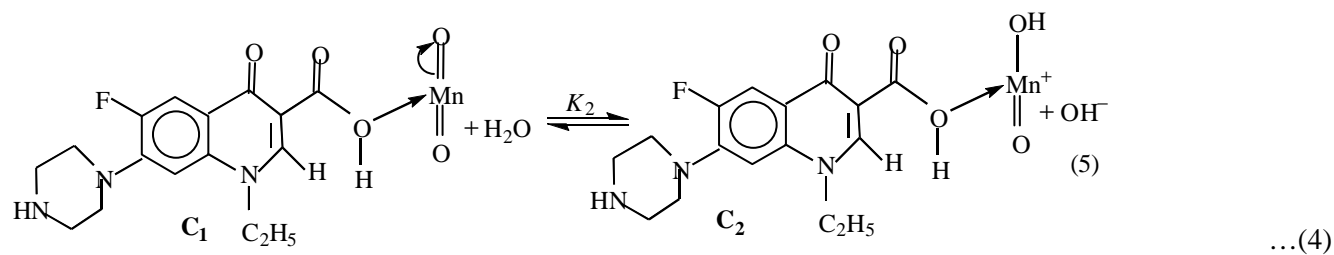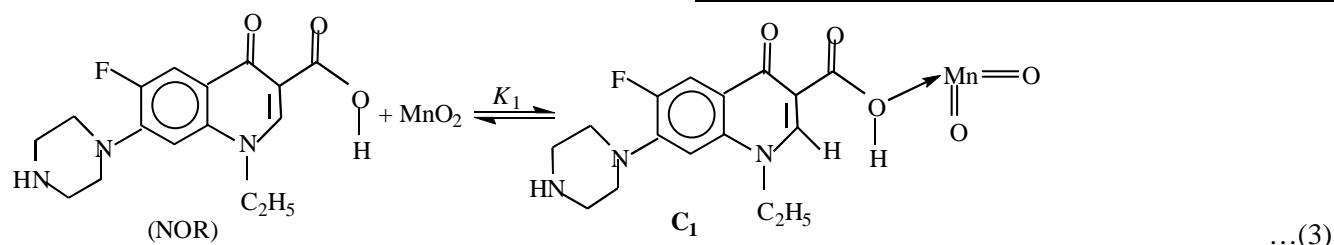
Reaction path for the oxidation of norfloxacin by MnO₂

**Scheme 1**

### Reaction mechanism

Scheme 1 shows that in a prior equilibrium step, NOR combine with $MnO_2$ to form $C_1$ complex, which further hydrolyzes in a second equilibrium step to generate hydroxyl ion and $C_2$ complex. In the next step, the rate determining step (slow) transferred one electron from NOR to $MnO_2$ to produce $C_3$ complex (radical intermediate), $Mn^{2+}$, hydroxyl ion and radical. Now this $C_3$ complex reacts with hydroxyl radical to produce $C_4$ complex and after hydrolysis of $C_4$ complex, final product (P) was obtained (Eq. 7).

From Scheme 1 representing the reaction path for the oxidation of NOR by $MnO_2$, the rate law derived from Eq. (6) can be deduced as Eq. (8).

$$\text{rate} = k\,[C_2] \qquad \qquad \dots (8)$$

From Eq. (4), we have Eq. (9),

$$[C_1] = K_1\,[NOR]\,[MnO_2] \qquad \dots (9)$$

From Eq. (5) and Eq. (9), we get Eq. (10).

$$[C_2] = \frac{K_1 K_2 [NOR]\,[MnO_2]}{[OH^-]} \qquad \dots (10)$$

Putting the value of $[C_2]$ from Eq. (10) in Eq. (8), we have Eq. (11)

$$\text{rate} = \frac{k K_1 K_2 [NOR]\,[MnO_2]}{[OH^-]} \qquad \dots (11)$$

At any time of the reaction, the total concentration of $MnO_2$, i.e., $[MnO_2]_T$ can be shown as

$$[MnO_2]_T = [MnO_2] + [C_1] + [C_2] \qquad \dots (12)$$

Substituting the values of $[C_1]$ and $[C_2]$ from Eqs (9), (10) and applying approximation method, we get Eq. (13).

$$[MnO_2] = \frac{[MnO_2]_T}{1 + K_1 [NOR] + K_1 K_2 [NOR]/[OH^-]} \quad \dots (13)$$

Substituting the value of $[MnO_2]$ from Eq. (13) in Eq. (11), we get Eq, (14).

$$\text{rate} = \frac{k K_1 K_2 [NOR]\,[MnO_2]_T}{\{[OH^-] + K_1 K_2 [NOR]\}} \qquad \dots (14)$$

Equation (14) is the final rate law on the basis of which the observed kinetic orders with respect to each reactant of the reaction can very easily be explained.

By reversing Eq. (14), we have Eq. (15)

$$\frac{[MnO_2]_T}{\text{rate}} = \frac{1}{k_{obs}} = \frac{[OH^-]}{k K_1 K_2 [NOR]} + \frac{1}{k} \qquad \dots (15)$$

According to Eq. (15) a linear plot between $1/k_{obs}$ versus $1/[NOR]$ or $[OH^-]$ is obtained having a positive intercept on y-axis (Figs 7 & 8). Thus, the proposed reaction scheme supports the represented rate law Eq. (14).

### Determination of CMC

The critical micelle concentration (CMC) was determined by conductivity measurements (Systronic digital conductivity meter 304). The values of CMC of CTAB in the presence and absence of reactants (NOR and $MnO_2$) were determined from the breaking point of nearly two straight line portions of the plot of specific conductivity versus [surfactant]. The CMC of surfactants is sensitive to the nature of the reactants and also depends upon the conditions of reaction. The obtained CMC values under various experimental conditions are given in Table 2.
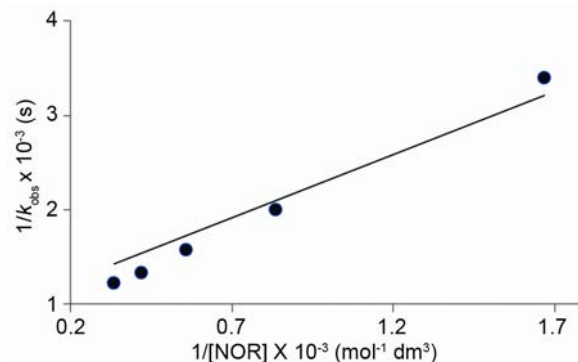


Fig. 7 – Verification of rate law for 1/[NOR] on the oxidation of norfloxacin by colloidal $MnO_2$ in the absence of surfactant at 298 K. {React. cond.: $[MnO_2] = 1.2 \times 10^{-4}$ mol dm$^{-3}$; [CTAB] = $10 \times 10^{-4}$ mol dm$^{-3}$; $[OH^-] = 1.0 \times 10^{-3}$ mol dm$^{-3}$}.
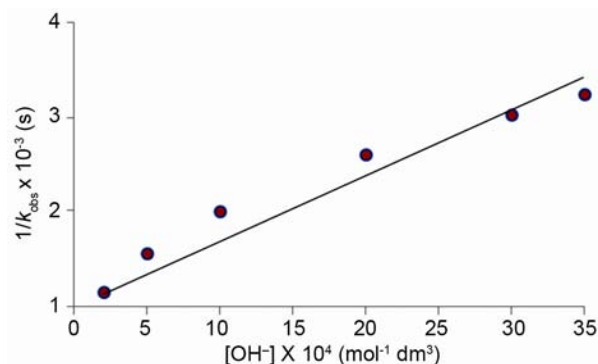


Fig. 8 – Verification of rate law for $[OH^-]$ of oxidation of norfloxacin by colloidal $MnO_2$ in the absence of surfactant at 298 K. {React. cond.: [NOR] = $1.2 \times 10^{-3}$ mol dm$^{-3}$; [CTAB] = $10 \times 10^{-4}$ mol dm$^{-3}$; $[MnO_2] = 1.2 \times 10^{-4}$ mol dm$^{-3}$}.

Table 2 – CMC values of CTAB under different experimental conditions at 298K

| Solution | CMC[a] ($\times 10^{-4}$ mol dm$^{-3}$) |
|---|---|
| water | 9.90 |
| water + MnO$_2$ | 5.15 |
| water + NaOH | 4.92 |
| water + NOR + MnO$_2$ + NaOH | 7.00 |

[a]Lit. value of CMC of CTAB at 298 K = $10.0 \times 10^{-4}$ mol dm$^{-3}$.

Table 3 – Effect of [CTAB] on the oxidation of norfloxacin with colloidal MnO$_2$ at 298 K. {React. cond.: [NOR] = $1.2 \times 10^{-3}$ mol dm$^{-3}$, [MnO$_2$] = $1.2 \times 10^{-4}$ mol dm$^{-3}$, [NaOH] = $1.0 \times 10^{-3}$ mol dm$^{-3}$}

| $10^4$[CTAB] (mol dm$^{-3}$) | $k_{obs} \times 10^4$ (s$^{-1}$) |
|---|---|
| 0.0 | 7.41 |
| 1.0 | 4.57 |
| 2.0 | 2.65 |
| 4.0 | 1.69 |
| 5.0 | 1.54 |
| 7.0 | 1.50 |
| 10.0 | 1.37 |
| 11.0 | 1.30 |
| 12.0 | 1.28 |

**Influence of [CTAB]**

To find out the effect of CTAB on the reaction rate, the kinetic experiments were performed by varying [CTAB] ($1.0 \times 10^{-4}$ to $12.0 \times 10^{-4}$ mol dm$^{-3}$) at fixed concentrations of all reactants at 298 K. Initially the rate of reaction decreased (from $7.41 \times 10^{-4}$ to $1.28 \times 10^{-4}$ s$^{-1}$) with increasing [CTAB] and then remained constant on further increasing the CTAB concentration (Table 3 and Fig. S4). The plot between $k_{obs}$ versus [CTAB] demonstrated the inhibitory effect of CTAB on $k_{obs}$. The inhibitory behaviour of cationic surfactant [CTAB] can be explained in terms of the pseudo-phase model proposed by Berezin's (Scheme 2). The inhibition effect of the surfactant may be due to the repulsion between the substrate (NOR-MnO$_2$) and surfactant molecules

Berezin and co-workers[63] developed the first general treatment based on the pseudo-phase model, which explained spontaneous and bimolecular reaction among neutral and organic reactants. According to the Berezin's approach, a solution above the CMC may be expressed as a two phase system consisting of an aqueous and micellar pseudo phase. The reactants (substrate and oxidant) may be distributed as shown in (Scheme 2). The inhibition effect may be due to the repulsion between the substrate (NOR-MnO$_2$) and surfactant molecules.
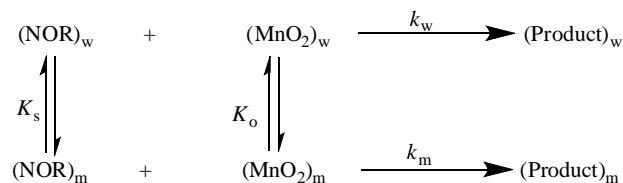


Distribution of substrate between aqueous and micellar phases

**Scheme 2**

For a bimolecular reaction, a quantitative rate expression in aqueous and micellar phase for the pseudo-first order rate constant is given by Eq. (16),

$$k_{obs} = \frac{k_w + k'_m K_s K_o (C_{Surf} - CMC)}{[1 + K_s(C_{Surf} - CMC)] \, [1 + K_o(C_{Surf} - CMC)]} \quad \ldots(16)$$

where $K_s$ and $K_o$ are the association constants of [NOR] and [MnO$_2$] with CTAB, respectively, $C_{surf}$ is the concentration of CTAB, $k'_m = (k_m/V)$, $V$ being the molar volume of the micelle and $k_w$ and $k_m$ are the pseudo-first order rate constants in aqueous and micellar systems, respectively. In present work, since the oxidant is a neutral species and substrates are small molecules, the interaction of hydrophilic and electrostatic will not be very large. As $C_{surf}$ is small, $k_w \gg k'_m K_s K_o (C_{surf} - CMC)$ and Eq. (16) can be written as Eq. (17).

$$k_{obs} = \frac{k_w}{[1 + (K_s + K_o)(C_{surf} - CMC)] + [K_s K_o (C_{surf} - CMC)^2]}$$
$$\ldots (17)$$

Again, as $(C_{surf} - CMC)$ is very small, the term containing $(C_{surf} - CMC)^2$ may be neglected, and Eq. (17) may be arranged to Eq. (18).

$$\frac{1}{k_{obs}} = \frac{1}{k_w} + \frac{K_s + K_o (C_{surf} - CMC)}{k_w} \quad \ldots (18)$$

A straight line with positive slope and intercept was obtained from the plot of $k_{obs}^{-1}$ versus $(C_{surf} - CMC)$. From the slope and intercept, the value of $k_w$ and $(K_s + K_o)$ were calculated and were found to be $5.94 \times 10^{-4}$ s$^{-1}$ and $3.57 \times 10^{-3}$ L mol$^{-1}$ respectively.

**Supplementary Data**

Supplementary data associated with this article, i.e., Figs S1-S4, and, Tables S1-S3, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(09)1059-1067_SupplData.pdf.

## Acknowledgement

## References

1   Vijayalakshmi A D, Rao K, Bhuyan A K & Rao N M, *Colloids Surf A*, 322 (2008) 66.

2   Bunton C A, Nome F, Quina F H & Romsted L S, *Acc Chem Res*, 24 (1991) 357.

3   Ahmad N, Kumar P, Hashmi A A & Khan Z, *Colloids Surf A*, 315 (2008) 226.

4   Rub M A, Asiri A M, Azum N, Khan A, Khan A A, Khan P, Rahman S B, Mohammed M & Kabir-ud-Din, *Thermochimica Acta*, 574 (2013) 26.

5   Jean Y & Ache H J, *J Am Chem Soc*, 99 (1977) 7504.

6   Mallick K, Jewrajka S & Pradhan N, *Current Sci*, 80 (2001) 1408.

7   Jones M & Leroux J, *Eur J Pharm Biopharm*, 48 (1999) 101.

8   Torchilin V P, *J Controlled Release*, 73 (2001) 137.

9   Kabir-ud-Din, Rub M A & Naqvi A Z, *J Colloid Interface Sci*, 354 (2011) 700.

10  Richmond W, Tondre C & Krzyzanowska E, *J Chem Soc Faraday Trans*, 91(1995) 657.

11  Piszkiewicz D, *J Am Chem Soc*, 99 (1977) 7695.

12  Andrabi S M Z, Malik M A & Khan Z, *Colloids Surf A*, 299 (2007) 58.

13  Katre Y R, Tripathi K, Joshi G K & Singh A K, *J Surf Deterg*, 9 (2006) 231.

14  Patil S, Katre Y R & Singh A K, *Colloids Surf A*, 308 (2007) 6.

15  Katre Y R, Tripathi K & Singh A K, *Ten Surf Det*, 51 (2014) 146.

16  Katre Y R, Singh M & Singh A K, *Ten Surf Det*, 48 (2011) 73.

17  Katre Y R, Goyal N & Singh A K, *Z Phys Chem*, 225 (2011) 107.

18  Katre Y R, Joshi G K & Singh A K, *J Dispersion Sci Technol*, 31 (2010) 108.

19  Katre Y R, Singh M, Patil S & Singh A K, *Acta Phys Chim Sin*, 25 (2009) 319.

20  Katre Y R, Singh M & Singh A K, *Colloid J*, 74 (2012) 391.

21  Katre Y R, Singh M & Singh A K, *J Dispersion Sci Technol*, 32 (2011) 903.

22  Katre Y R, Tripathi K, Joshi G K & Singh A K, *J Dispersion Sci Technol*, 32 (2011) 341.

23  Elmolla E S & Chaudhuri M, *Desalination*, 252 (2010) 46.

24  Kusari S, Prabhakaran D, Lamshoft M & Spiteller M, *Environ Pollut*, 157 (2009) 2722.

25  Sturini M, Speltini A, Maraschi F, Pretali L, Profumo A, Fasani E, Albini A, Migliavacca R & Nucleo E, *Water Res*, 46 (2012) 5575.

26  Darwish I A, Sultan M A & Al-Arfaj H A, *Talanta*, 78 (2009) 1383.

27  Golet E M, Xifra I, Siegrist H, Alder A C & Giger W, *Environ Sci Technol*, 37 (2003) 3243.

28  Castiglioni S, Bagnati R, Calamari D, Fanelli R & Zuccato E J, *J Chromatogr A*, 1092 (2005) 206.

29  Xu W, Zhang G, Li X, Zou S, Li P, Hu Z & Li J, *Water Res*, 41 (2007) 4526.

30  Crdoba-D´ıaz M, Crdoba-Borrego M & Crdoba-D´ıaz D, *J Pharm Biomed Anal*, 18 (1998) 565.

31  Rahman N, Ahmad Y & Azmi S N H, *Eur J Pharm Biopharm*, 57 (2004) 359.

32  Zhang J, Li Z J, Ge G F, Sun W C, Liang Y C & Wu L S, *J Environ Sci*, 21 (2009) 632.

33  Lawrenson R A & Logie J W, *J Antimicrob Chemother*, 48 (2001) 895.

34  Sumano L H, Ocampo C L, Brumbaugh G W & Lizarraga R E, *Br Poult Sci*, 39 (1998) 42.

35  Calamari D, Zuccato E, Castiglioni S, Bagnati R & Fanelli R, *Environ Sci Technol*, 37 (2003) 1241.

36  Robinson A A, Belden J B & Lydy M J, *Environ Toxicol Chem*, 24 (2005) 423.

37  Doorslaer X V, Demeestere K, Heynderickx P M, Langenhove H V & Dewulf J, *Appl Catal B*, 101 (2011) 540.

38  Horvath O, Gergo Z B, Marosfi J & Zsilak Z, *Colloid Polym Sci*, 286 (2008) 51.

39  Chirkst D E, Cheremisina O V, Sulimova M A, Kuzhaeva A A & Zgonnik P V, *Russ J Gen Chem*, 81 (2011) 704.

40  Lorphensri O, Intravijit J, Sabatini D A, Kibbey T C G, Osathaphan K, Saiwan C, *Water Res*, 40 (2006) 1481.

41  Liu W, Zhang J, Zhang C & Ren L, *Chem Eng J*, 171 (2011) 431.

42  Paul T, Miller P L & Strathman T J, *Environ Sci Technol*, 41 (2007) 4720.

43  Chen M & Chu W, *J Hazard Mater*, 219-220 (2012) 183.

44  Dodd M C, Shah A D, Gunten U V & Huang C, *Environ Sci Technol*, 39 (2005) 7065.

45  Shrivastava A, Singh A K, Sachdev N, Shrivastava D R, Katre Y R, Singh S P, Singh M & Mejutog J C, *J Mol Catal A Chem*, 361 (2012) 1.

46  An T C, Yang H, Song W H, Li G Y, Luo H Y & Cooper W J, *J Phys Chem A*, 114 (2010) 2569.

47  Rivas J, Encinas A, Beltran F & Graham N, *J Environ Sci Health A*, 46 (2011) 944.

48  Wang P, He Y L & Huang C H, *Water Res*, 44 (2010) 5989.

49  Naik P N, Chimatadar S A & Nandibewoor S T, *Ind Eng Chem Res*, 48 (2009) 2548.

50  Perez-Benito J F & Lee D G, *Can J Chem*, 63 (1985) 3545.

51  Perez-Benito J F, Brillas E & Pouplana R, *Inorg Chem*, 28 (1989) 390.

52  Perez-Benito J F & Arias C, *J Colloid Interface Sci*, 149 (1992) 92.

53  Ilyas Mohd, Malik M A & Khan Z, *Colloid Polym Sci*, 285 (2007) 1169.

54  Liu C, Nanaboina V, Korshin G V & Jiang W, *Water Res*, 46 (2012) 5235.

55  Zhang H & Huang C H, *Environ Sci Technol*, 39 (2005) 4474.

56  Qamruzzaman & Nasar A J, *Ind Eng Chem*, 20 (2014) 897.

57  Akram Mohd, Altaf Mohd & Kabir-ud-Din, *Colloids Surf B*, 82 (2011) 217.

58  Akram Mohd, Altaf Mohd & Kabir-ud-Din, *Colloids Surf B*, 82 (2011) 217.

59  Kabir-ud-Din, Fatma W & Khan Z, *Colloids Surf A*, 234 (2004) 159.

60  Ramalingaiah, Jagadeesh R V & Puttaswamy, *J Mol Catal A Chem*, 265 (2007) 70.

61  Entelis S G & Tiger R P, *Reaction Kinetics in the Liquid Phase* (Wiley, New York) 1976.

62  Singh A K, Negi R, Katre Y R & Singh S P, *J Mol Catal A Chem*, 302 (2009) 36.

63  Berezin I V, Martinck K & Yatsimirskii A K, *Russ Chem Rev (Eng Trans)*, 42 (1973) 787.