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Research Article

Soluble Colloidal Manganese Dioxide: Formation, Characterization and Application in Oxidative Kinetic Study of Ciprofloxacin

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Abstract

Soluble colloidal manganese dioxide was formed by reduction of potassium permanganate with sodium thiosulphate in neutral aqueous medium at 25 ºC. The obtained nano-sized colloidal manganese dioxide was found to be dark reddish-brown in color and stable for several months. The formation of manganese dioxide was confirmed by UV-visible spectrophotometer and determination of oxidation state of Mn species in manganese dioxide. The effect of different concentration of sodium thiosulphate on the formation of manganese dioxide was also studied. The nano-sized colloid manganese dioxide was characterized by transmission electron microscopy and Fourier transform infrared spectrophotometer. The formed soluble colloidal manganese dioxide was used as an oxidant in oxidation of ciprofloxacin in perchloric acid medium at 35 ºC. The reaction was first-order concerning to concentration of manganese dioxide and hydrogen ion but fractional order with ciprofloxacin. The results suggest formation of complex between ciprofloxacin and manganese dioxide. The oxidation products were also identified based on stoichiometric and characterization results.

Keywords: Soluble colloidal manganese dioxide; Ciprofloxacin; Characterization; Kinetics; Oxidation

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1. Introduction

Manganese dioxide (MnO_2) is one of the most important oxidizing agent for both organic and inorganic compounds [1,2] with an oxidation potential of 1.23 V [3]. Due to its importance such as the low toxicity, low cost, electrochemical behavior, environmental compatibility and ease of handling, many researchers have been developed different methods for preparation of soluble colloidal MnO_2 [4-6]. Soluble colloidal MnO_2 is generally formed by the reduction of MnO_4^- ion in aqueous solution with many reductants including Mn^{2+} ion [7]. Perez-Benito *et al.* [8-10] have also been reported as a method for preparation of perfectly transparent dark brown water-soluble colloidal manganese dioxide sols by the permanganate-thiosulphate reaction in aqueous neutral conditions. The formed soluble colloidal MnO_2 has been characterized by different instrumental techniques and determined by iodometric method [11-13]. The existence of manganese(IV) in the aqueous solution in colloidal form and as negatively charged species has been reported in the literature [14-16], and the oxidizing ability is limited under ordinary conditions due to its insolubility [17]. In fact, manganese oxides have been shown to be capable of ox-

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idizing a wide range of organic contaminants [18-21]. It has reactive surfaces that play important role in transformation of organic pollutants such as synthetic hormones, anti-inflammatory drugs, antibacterial agents, bisphenol A, phenols, sulfides, 2-mercaptobenzothiazole (2MBT), and sulfadiazine in soil and aquatic environment [22,23]. The kinetics and mechanism of oxidation of simple organic reactants like lactic acid, aspartic acid, oxalic acid, mandelic acid, amino acid, D-fructose, D-glucose, Cysteine and glutathione [12,24-29], *etc*. by colloidal MnO_2 have been studied.

Ciprofloxacin (CIP) {1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(piperazine-1-yl)-quinolone-3-carboxylic acid}, a common fluoroquinolone is a primary degradation product of enrofloxacin. It is a second-generation fluoroquinolone antimicrobial agent and possesses two relevant ionizable functional groups: a basic piperazinyl group and a carboxylic group which is required for antimicrobial activity. Because of their continued use, the environment impact of such antibacterial agents is of serious concern for public health, so for requires development of the various oxidation process for the transformation and degradation of fluoroquinolones in water. The literature survey reveals that the oxidation of CIP by many oxidants, such as: hexacyanoferrate(III), chloramine-B, Cl_2, ClO_2, $CeSO_4$, and Fe(VI) [30-34], have been carried out in either alkaline or acidic medium. Studies reveal that the piperazine moiety of CIP is the predominant oxidative site for oxidation [35-39] Literature survey confessed that the kinetics and mechanism of degradation of some antibiotics by colloidal MnO_2 in aqueous acidic/alkaline medium have been studied earlier [40-42]. Yuan-Li *et al* [43] reported that transformation pathway of levofloxacin in the manganese oxide system involving oxidation and dealkylation while the antibacterial activity was not markedly affected by addition of MnO_2. Zhang & Haung [44] also reports the antibacterial agents are highly susceptible to metal oxide- facilitated oxidation and exhibit complex reaction kinetics, which are affected by reaction conditions. However, the details of CIP oxidation by colloidal MnO_2 in an aqueous acidic medium are yet unknown. Therefore, the aim of this paper is the formation of colloidal MnO_2, characterized them by different instrumental techniques and its application in the oxidation of CIP in aqueous acidic medium with kinetic and mechanistic aspects.

2. Materials and Method

2.1 Materials

Ciprofloxacin hydrochloride was purchased from KORES India Limited, Mumbai, was used in the experiment. A solution was always freshly prepared by dissolving a known amount of the CIP in double-distilled water. To maintain the acidity and ionic strength of the reaction perchloric acid (MERCK) and sodium perchlorate (MERCK) were used, respectively. Other reagents employed in this study were either of AnalaR or guaranteed reagent grade and were used as received. Doubly distilled water was employed throughout the study; second distillation was from alkaline potassium permanganate solution in an all glass assembly.

2.2 Formation of MnO_2

For the formation of water-soluble colloidal MnO_2, required volume of $Na_2S_2O_3$ solution (20 cm^3, 2.0×10^{-2} $mol.dm^{-3}$) was added to a standard solution of $KMnO_4$ (10 cm^3, 0.1 $mol.dm^{-3}$) and reaction mixture was diluted with required volume of water in 2 dm^{-3} standard flask [10] The resulting solution was dark brown and perfectly transparent and stable for several weeks. The absorption spectrum of the reaction mixture consists of one broadband covering the whole visible region of the spectrum with λ_{max} 390 nm. The studies were performed at different concentration of $Na_2S_2O_3$ to investigate formation and particle size of colloidal MnO_2.

2.3 Characterizations

For the preliminary characterization of formed colloidal MnO_2 and kinetic measurements, a Peltier accessory (temperature-Controlled) attached to a double beam, the UV-Visible spectrophotometer (U.V.3000$^+$ LABINDIA, Mumbai) with U.V. path length 1.0 cm in the spectral range 200-800 nm, was used. Transmission Electron Microscopy (TEM) was used to study the morphology of colloidal MnO_2. Samples for TEM analysis were prepared by drop-coating MnO_2 suspension onto carbon-coated copper grid. The film on the TEM grid was allowed to stand for 2 minutes, following then the extra solution was removed using a blotting paper and the grid allowed drying before measurement on TEM (Model-Tecnai G^2 20 (FEI) S-Twin) instrument. Additionally, the presence of metal in the sample was analyzed by energy-dispersive X-ray (EDX) spectrometer. Stability and an average size of colloidal MnO_2 have been investigated by zeta sizer and zeta potential (Zetasizer ver.

7.11, Malvern). The spectrum of colloidal MnO_2 and oxidation product were recorded from Fourier Transform Infrared (FT-IR) Spectrophotometer (ALPHA-T, Bruker, Germany) in the range of 400-4000 cm^{-1} by mixing sample with dried KBr (in 1:20 weight ratio) with a resolution of 4 cm^{-1}. Liquid Chromatography Mass Spectroscopy (LC-MS), (Q-TOF Micromass, WATERS Company, UK), was used for oxidation product analysis over a mass scan range of 50-1000 m/z.

2.4 Kinetic Measurements

In all the kinetic runs, the oxidation of CIP by colloidal MnO_2 was carried out under pseudo first-order condition. The required concentrations of reactants (CIP, $HClO_4$, and $NaClO_4$) were taken in the glass stopper Erlenmeyer flask and the reaction was initiated by addition of required concentration of colloidal MnO_2 at 35 ºC. The progress of the reaction was followed by monitoring absorbance of MnO_2 at 390 nm in UV-Visible spectrophotometer at different time intervals (Figure 1). All the kinetics runs were followed up to 80% completion of the reaction. The pseudo first-order rate constants (k_{obs}) were evaluated from plots of log (absorbance) versus time.

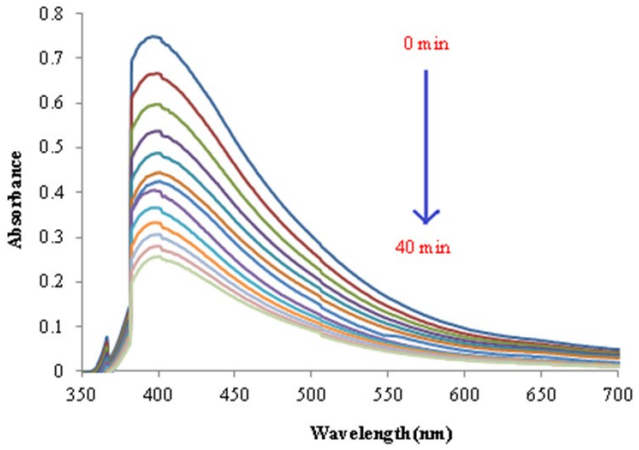


Figure 1. UV-visible absorption spectra of absorbance versus wavelength during the oxidation of ciprofloxacin by colloidal MnO_2 in acidic medium at 35 ˚C. $[MnO_2]$ = 5.0×10^{-5}, [CIP] = 2.0×10^{-4}, $[H^+]$ = 2.0×10^{-4} and I = 4.0×10^{-4} / mol.dm^{-3}.

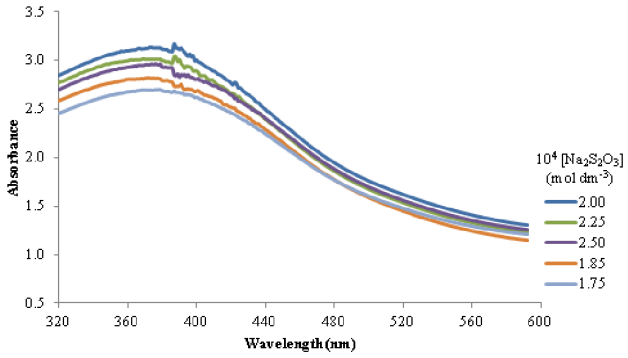


Figure 2. UV-visible absorption spectra of absorbance versus wave length of the mixtures containing a fixed amount of $KMnO_4$ (2.0×10^{-4} mol.dm^{-3}) and varying amounts of $Na_2S_2O_3$ at 35 ºC.

3. Results and Discussion

3.1 Characterization of MnO_2

Formation of colloidal MnO_2 by reduction of permanganate ions by sodium thiosulfate was studied by UV–Vis spectroscopy. The effect of different concentrations of sodium thiosulfate on the formation and particle size of nanoparticles were also investigated (Figure 2). At lower $[Na_2S_2O_3]$(1.75×10^{-4} mol.dm^{-3}), a weak absorption band at 390 nm was observed, indicating that due to insufficient reduction relatively low concentration of MnO_2 was produced. As the $[Na_2S_2O_3]$ increases up to 2.0×10^{-4} mol.dm^{-3}, the intensity of absorption band at 390 nm increases after that absorption band becomes lower, indicating precipitation of colloidal MnO_2 at higher $[Na_2S_2O_3]$. However, maximum absorption band was obtained at 2.0×10^{-4} mol dm^{-3}, suggesting optimum concentration of $Na_2S_2O_3$ for the formation of colloidal MnO_2. The resulting solution was dark reddish-brown and perfectly transparent and stable for several weeks.

The energy dispersive spectrometer spectrum indicates the Mn and O elements present in synthesized sample confirming the formation of colloidal nano-sized MnO_2 (Figure 3). TEM analysis was carried out to determine size and shape of colloidal MnO_2; the images show that the formed particles were needle shape (Figure 4(a)) with average size 20.59 nm

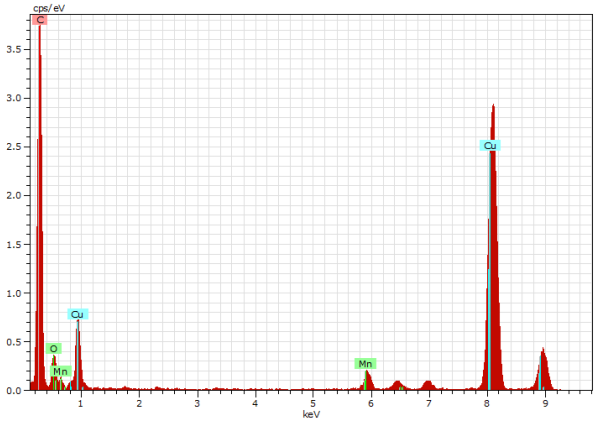


Figure 3. EDX analysis of synthesized colloidal MnO_2.

at $[Na_2S_2O_3]$ = 2.0×10^{-4} mol.dm^{-3}. Whereas, at higher $[Na_2S_2O_3]$, TEM results (Figure 4(b)), suggesting that too many reducing agent cause aggregation of formed particle. It is possible due to the interaction between capping molecules bound to the surface of particles and secondary reduction process on surface of performed nuclei [36]. The results are well consistent with U.V. spectra in Figure 3. The selected area electron diffraction (SAED) pattern (Figure 4(b) inset) recorded colloidal MnO_2. The ring-like diffraction indicates that the particles are crystalline [11]. Zeta sizer (dynamic light scattering) and zeta potential have been suggested to play an important role in the size distribution and stability of synthesized soluble colloidal MnO_2, respectively. The zeta potential of colloidal MnO_2 was found to be -41.1 mV with average size 20.59 nm (Figure 5 (a) and (b)) revealing that surface of the particle was negatively charged that dispersed in the medium. To investigate chemical structure of the particles, FT-IR analysis was performed. Two absorption bands located at around 3400 and 1623 cm^{-1} correspond to O–H and H–O–H (Figure 6) [45].

The oxidation state of manganese species in the colloidal solution was also determined iodometrically at 390 nm based on the previous report [46]. The determined oxidation state of Mn species in MnO_2 was (+4.16), was confirming the formation of MnO_2 [47]. The molar extinction coefficient of colloidal MnO_2 was found to be 15660 dm^3.mol^{-1}.cm^{-1} that in a good agreement with previous study [48].

3.2 Stoichiometry and Product Analysis

The stoichiometry of the reaction was determined with various ratios of experiments at excess of MnO_2 over CIP in acid perchlorate medium at 35 ºC for 12 h to ensure the completion of the reaction. The excess of MnO_2 was esti-

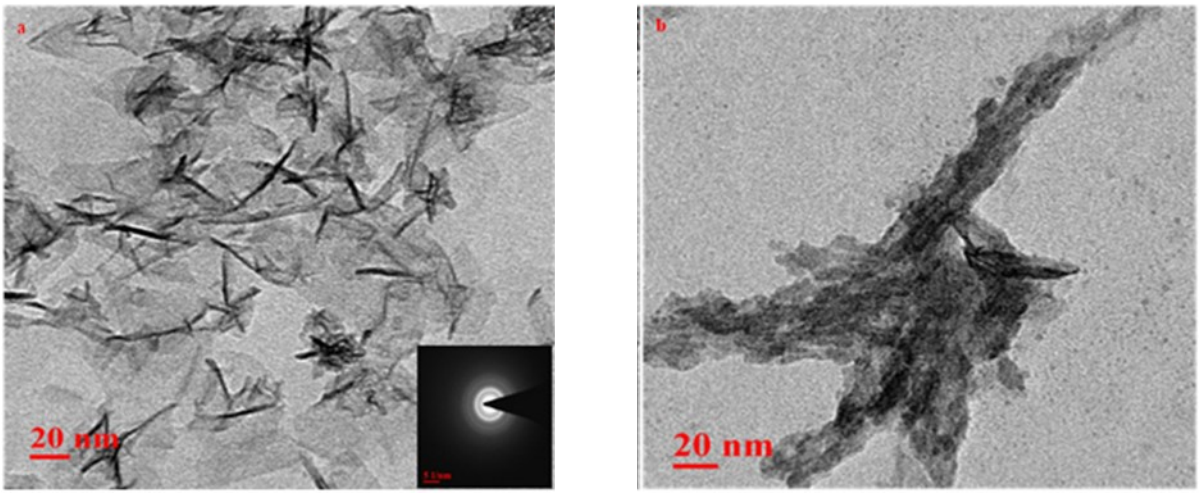


Figure 4. TEM of synthesized colloidal MnO_2 at optimum conditions and inset SAED pattern (a); TEM of synthesized colloidal MnO_2 at higher $[Na_2S_2O_3]$ (b).

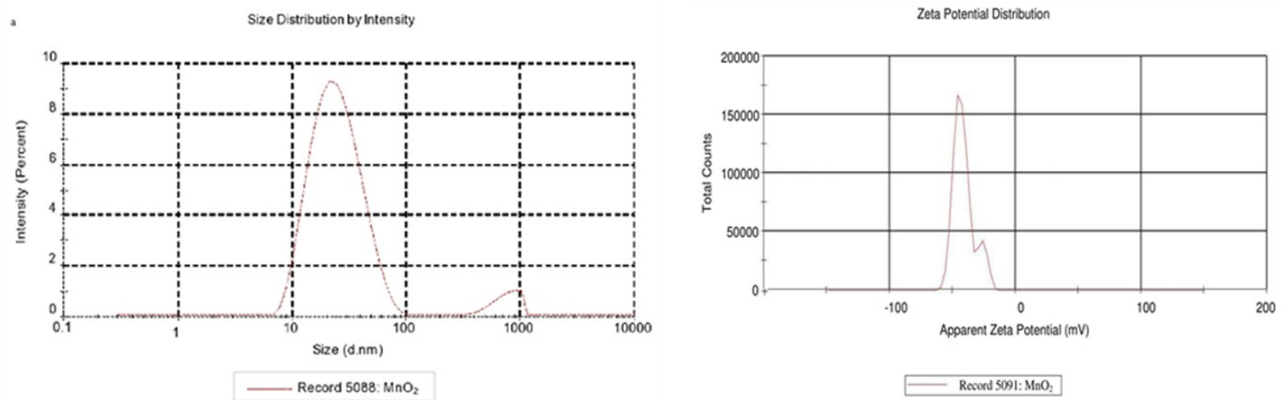
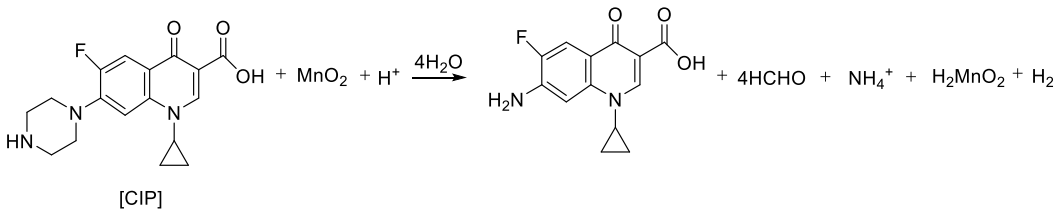


Figure 5. (a) Zeta sizer and (b) Zeta potential of synthesized colloidal MnO_2.



(1)

mated spectrophotometrically and the results correspond to the stoichiometry as represented by Equation (1). The product was separated with ether after the completion of the kinetic experiments. The main oxidative product {7-amino-1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-quinolone-3-carboxylic acid} was identified with the help of LC-MS and FT-IR analysis.

The major product was confirmed with the molecular ion of m/z 263 by LC-MS analysis, which corresponds to fully dealkylation of the piperazine ring [49] (Figure 7). It is due to the oxidation of piperazine moiety of CIP between oxidized centers and nitrogen atoms lead to distinctive mass loss m/z = 69. This can be ascribed by ring-opening, dealkylation and deamination process and finally yielded 7-amino fluoroquinolone product.

The deamination of CIP was confirmed by FT-IR analysis (Figure 8). The spectrum results confirm the –NH stretching of the –NH_2 group at 3375.45 cm^{-1} and the remaining bands are of the parent compound.

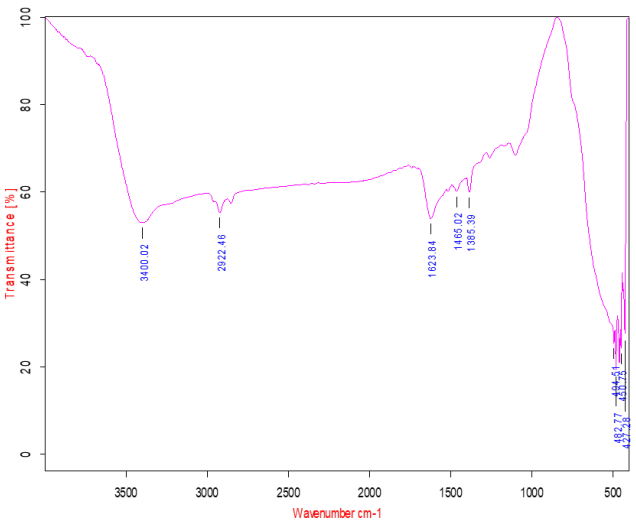


Figure 6. Fourier Transform Infrared spectra of synthesized colloidal MnO_2.

3.3 Kinetics of CIP Oxidation by Colloidal MnO_2

3.3.1 MnO_2 dependence

The concentration of MnO_2 was varied from 0.75×10^{-5} to 7.5×10^{-5} mol.dm^{-3} at two different concentrations of CIP (5.0×10^{-4} and 8.0×10^{-4}) but fixed $[H^+] = 2.0\times10^{-4}$ mol.dm^{-3} and I = 4.0×10^{-4} mol.dm^{-3} (adjusted by sodium perchlorate) at 35 °C. Pseudo-first order rate constants (k_{obs}) calculated from pseudo first-order plots (Figure 9) (R^2 = 1.0) were to be independent of MnO_2 concentration (Table 1) indicates reaction is first order concerning to MnO_2.

3.3.2 Ciprofloxacin dependence

The concentration of CIP was varied from 1.0×10^{-4} to 10.0×10^{-4} mol.dm^{-3} at a fixed concentration of other reaction ingredients at three temperatures viz. 30 ºC, 35 ºC, and 40 ºC. The rate of reaction initially increases and tends towards a limiting value with the higher concentration of the CIP ($R^2 \leq$ 0.908) showing frac-

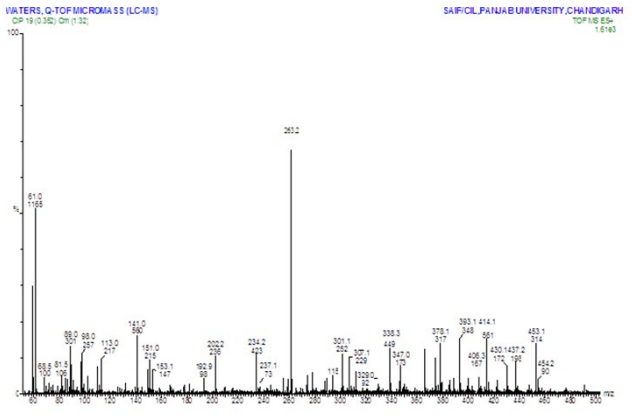


Figure 7. Liquid Chromatography Mass spectra of oxidation product of Ciprofloxacin.

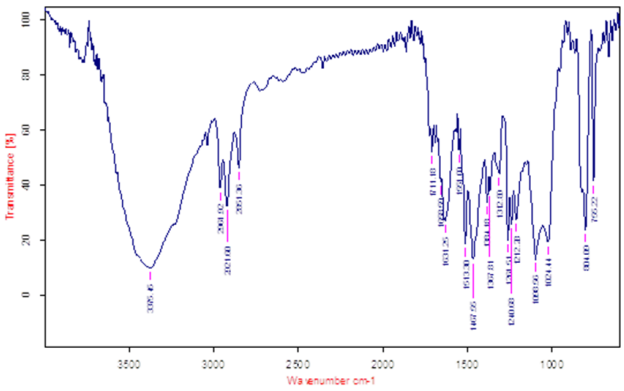


Figure 8. Fourier Transform Infrared spectra of the oxidation product of Ciprofloxacin by MnO_2 in aqueous acidic medium.

Table 1. First order rate constants (k_{obs}) for the reaction of ciprofloxacin with MnO_2 in aqueous acidic medium at I = 4.0×10^{-4} mol.dm^{-3} and Temperature = 308 K (S.D. = Standard Deviation)

10^5 [MnO_2] (mol.dm^{-3})	10^4 [CIP] (mol.dm^{-3})	10^4 [H^+] (mol.dm^{-3})	10^4 k_{obs} ± S.D. (s^{-1})
0.75	5.0	2.0	8.06 ± 0.03
1.0	5.0	2.0	8.10 ± 0.04
2.0	5.0	2.0	7.98 ± 0.09
3.0	5.0	2.0	8.02 ± 0.13
4.0	5.0	2.0	8.06 ± 0.19
5.0	5.0	2.0	8.00 ± 0.19
6.0	5.0	2.0	7.96 ± 0.28
7.5	5.0	2.0	8.05 ± 0.35
0.75	7.5	2.0	10.52 ± 0.03
1.0	7.5	2.0	11.02 ± 0.04
2.0	7.5	2.0	11.05 ± 0.08
3.0	7.5	2.0	10.95 ± 0.13
4.0	7.5	2.0	11.12 ± 0.19
5.0	7.5	2.0	11.10 ± 0.19
6.0	7.5	2.0	10.94 ± 0.27
7.5	7.5	2.0	11.00 ± 0.33
5.0	1.0	2.0	2.60 ± 0.03
5.0	2.0	2.0	4.52 ± 0.04
5.0	3.0	2.0	5.96 ± 0.07
5.0	4.0	2.0	7.10 ± 0.08
5.0	5.0	2.0	8.00 ± 0.19
5.0	6.0	2.0	8.72 ± 0.27
5.0	7.0	2.0	9.30 ± 0.33
5.0	8.0	2.0	9.64 ± 0.38
5.0	9.0	2.0	9.81 ± 0.42
5.0	10.0	2.0	9.92 ± 0.47
5.0	5.0	1.0	4.02 ± 0.03
5.0	5.0	1.5	5.96 ± 0.06
5.0	5.0	2.0	8.00 ± 0.08
5.0	5.0	2.5	10.02 ± 0.13
5.0	5.0	3.0	12.10 ± 0.17
5.0	5.0	3.5	14.04 ± 0.19
5.0	5.0	4.0	15.98 ± 0.27

tional order dependence concerning to CIP (Table 1).

3.3.3 Hydrogen ion dependence

Hydrogen ion concentration was varied from 1.0×10^{-4} to 4.0×10^{-4} mol.dm^{-3} employing perchloric acid at a fixed concentration of other reactants and conditions. The rate of reaction increases with increasing concentration of H^+ (R^2 = 1.0) showing first-order reaction concerning to H^+ concentration (Table 1).

3.3.4 Ionic strength dependence

Ionic strength was varied from 2.0×10^{-4} to 10.0×10^{-4} mol.dm^{-3} employing sodium perchlorate keeping constant concentration of other reactants and conditions. However, the rate of reaction remains unaffected by the change in ionic strength (Table 1). The negligible effect of ionic strength on the rate of reaction suggests that the reaction is either between two neutral species or a neutral and a charged species [50].

3.3.5 Test for free radical

The possible intervention of free radicals during the oxidation reactions was examined by a polymerization test. Known amounts of acrylonitrile scavenger are added to reaction mixtures, which are kept for 6 h in an inert atmosphere. On dilution of the mixtures with methanol, white precipitates are formed, thus confirming the presence of free radicals intervention in these reactions. The blank experiment of reacting MnO_2 and CIP alone with acrylonitrile did not induce polymeric species under the same conditions. This indicates that the reactions proceeded via free radical pathways.

3.4 Mechanism

According to Scheme 1 ciprofloxacin reacts with MnO_2 and complex is obtained in first equilibrium step. Further complex combines with H^+ to give free radical in the rate determining step. This free radical again reacts with $HMnO_2$ to give final products. The rate being first-order dependence of H^+ ion concentration, a reaction mechanism consisting of Scheme (1) can be proposed (Equations (2-4).

The proposed mechanism leads to the rate law (5) and (6).

$$-\frac{d[Mn(IV)}{dt} = \frac{kK[Mn(IV)][CIP][H^+]}{1+K[CIP]} \quad (5)$$

$$k_{obs} = \frac{kK[CIP][H^+]}{1+K[CIP]} \quad (6)$$

The double reciprocal plot between $(k_{obs})^{-1}$ and $[CIP]^{-1}$ was made from Equation (6) that yield a straight line with non-zero intercept (R^2 = 0.999) (Figure 10). The value of '*k*' to be 1.40×10^{-3}, 1.90×10^{-3}, 2.44×10^{-3}/s^{-1} from intercepts and value of '*K*' to be 10.5×10^2, 15.2×10^2, 20.7×10^2 /dm^3.mol^{-1} from the ratio of intercept

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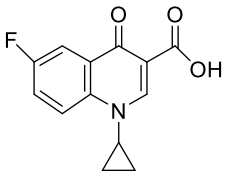


Scheme 1. Proposed mechanism for the oxidation of CIP by MnO_2.

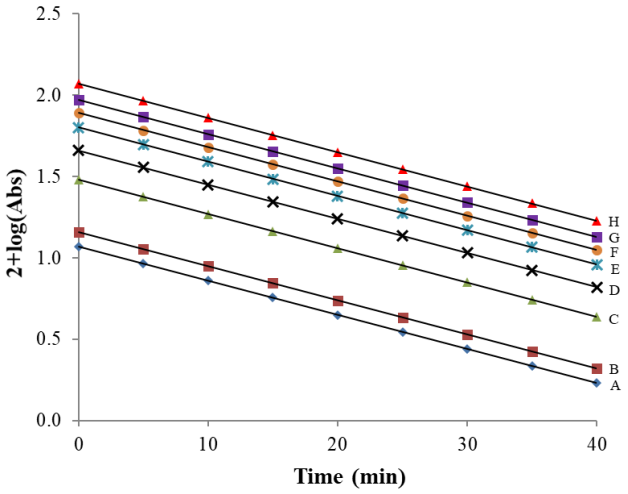


Figure 9. Variation of MnO_2 by the plots of log Absorbance versus Time. [CIP] = 5.0×10^{-4}, $[H^+]$ = 2.0×10^{-4}, I = 4.0×10^{-4} and 105 $[MnO_2]$ = (A) 0.75; (B) 1.0; (C) 2.0; (D) 3.0; (E) 4.0; (F) 5.0 (G) 6.0; (H) 7.5 /mol.dm^{-3}.

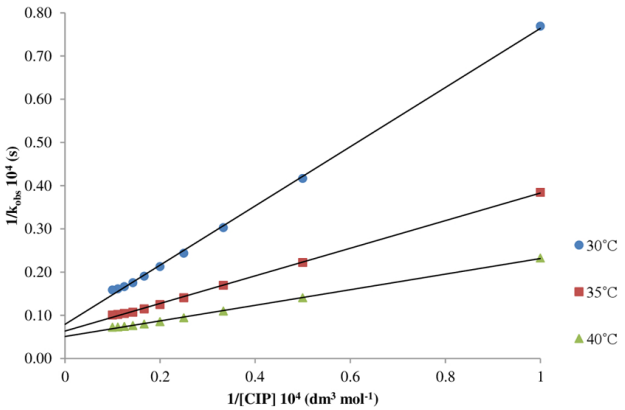
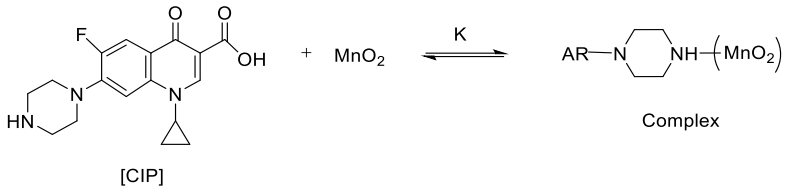


Figure 10. Plot of $1/k_{obs}$ verses 1/[CIP] at three temperatures. $[MnO_2]$ = 5.0×10^{-5}, $[H^+]$ = 2.0×10^{-4} and I = 4.0×10^{-4} /mol.dm^{-3}.



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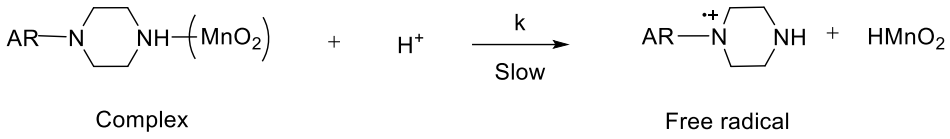

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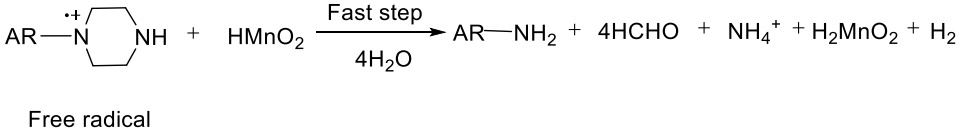

(4)

and slope at 30 ºC, 35 ºC, and 40 ºC respectively were calculated at I = 4.0×10^{-4} mol.dm^{-3}. The enthalpy and energy of activation for the rate-determining step were calculated to be 32.48 kJ.mol^{-1} and 35.04 kJ.mol^{-1} at 35 ºC respectively. The values are closer to earlier study [51]. The value of entropy of activation (ΔS) = -92.27 JK^{-1} mol^{-1} express the formation of intermediate complex and such an activated complex is more ordered than the reactants due to loss of degree of freedom. The value of ΔG = 92.06 kJ.mol^{-1} suggests enhanced formation of the intermediate with raising temperature as well as nonspontaneous complex formation.

4. Conclusion

The present study reports highly stable needle-shaped colloidal nano-sized MnO_2 was formed by simple laboratory equipment in ambient condition. The characterization results reveal that formed colloidal MnO_2 were needle shape with an average size 20.59 nm and crystalline in nature. A kinetic and mechanistic study of CIP oxidation by formed colloidal MnO_2 has been first time investigated in aqueous acidic medium. The reaction follows first-order kinetics concerning to MnO_2 and H^+ ion under first-order reaction conditions. Results and mechanism indicate that $HMnO_2$ is reactive species of MnO_2. Since dealkylated products are obtained in the present study, it is evident that the products of the title reaction have an antimicrobial activity after oxidation. Thus the degradation of fluoroquinolones plays an important role in the field of wastewater treatment. The kinetic results have also been used to evaluate various activation parameters associated with the degradation of CIP by MnO_2 in aqueous acidic medium.

Acknowledgments

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