

OXIDATIVE DEGRADATION OF CIPROFLOXACIN BY WATER SOLUBLE COLLOIDAL
MNO₂ IN MICELLAR MEDIA**Neelam Sen****neelam969142@gmail.com**

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ABSTRACT

This work aimed at demonstrating the oxidative degradation of fluoroquinolone antimicrobial ciprofloxacin (CIP) by water soluble colloidal MnO₂ in acidic medium has been studied spectrophotometrically in the presence of micelles at 298K. The rate of reaction was found first order with respect to [MnO₂], [PCM] and [H₂SO₄]. The rate constant decreased with decreasing dielectric constant of the medium. Ionic strength did not influence rate of reaction. CTAB enhanced the reaction rate i.e. with a progressive increase in [CTAB], the catalytic role of CTAB has been explained by Menger-Portnoy model and Piskiewicz model. Oxidation product was identified and thermodynamic activation parameters have been calculated with the help of Arrhenius equation.

Keywords: Oxidation, Kinetics, Colloidal manganese dioxide, Paracetamol, Micellar catalysis.

INTRODUCTION

Manganese dioxide (MnO₂) 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 MnO₂ [4-6]. Soluble colloidal MnO₂ is generally formed by the reduction of MnO₄⁻ *

Corresponding Author. E-mail: v_devra1@rediffmail.com (V. Devra); Mobile No. 91-9352602303 Received: 18th July 2019; Revised: 27th August 2019; Accepted: 13th September 2019; Available online: 28th February 2020; Published regularly: April 2020 ion in aqueous solution with many reductants including Mn²⁺ 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 MnO₂ 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 oxidizing 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, antiinflammatory 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 MnO₂ 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, Cl₂, ClO₂, CeSO₄, 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 MnO₂ 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 MnO₂. 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 MnO₂ in an aqueous acidic medium are yet unknown. Therefore, the aim of this paper is the formation of colloidal MnO₂, 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 MnO₂ For the formation of water-soluble colloidal MnO₂, required volume of Na₂S₂O₃ solution (20 cm³, 2.0×10⁻² mol.dm⁻³) was added to a standard solution of KMnO₄ (10 cm³, 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 maxλ whole visible region of the spectrum with 390 nm. The studies were performed at different concentration of Na₂S₂O₃ to investigate formation and particle size of colloidal MnO₂.

RESULTS AND DISCUSSION

Characterization of MnO₂ Formation of colloidal MnO₂ 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 [Na₂S₂O₃](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 MnO₂ was produced. As the [Na₂S₂O₃] 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 MnO₂ at higher [Na₂S₂O₃]. However, maximum absorption band was obtained at 2.0×10⁻⁴ mol dm⁻³, suggesting optimum concentration of Na₂S₂O₃ for the formation of colloidal MnO₂. 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 MnO₂ (Figure 3). TEM analysis was carried out to determine size and shape of colloidal MnO₂; the images show that the formed particles were needle shape (Figure 4(a)) with average size 20.59

nm at $[\text{Na}_2\text{S}_2\text{O}_3] = 2.0 \times 10^{-4} \text{ mol.dm}^{-3}$. Whereas, at higher $[\text{Na}_2\text{S}_2\text{O}_3]$, 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 $15660 \text{ dm}^3.\text{mol}^{-1}.\text{cm}^{-1}$ 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 $35 \text{ }^\circ\text{C}$ for 12 h to ensure the completion of the reaction. The excess of MnO_2 was estimated 3 Hydrogen ion dependence Hydrogen ion concentration was varied from 1.0×10^{-4} to $4.0 \times 10^{-4} \text{ mol.dm}^{-3}$ 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 $10.0 \times 10^{-4} \text{ mol.dm}^{-3}$ 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 MnO₂ 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 MnO₂ 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 HMnO₂ 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). (5) (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 (R² = 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 10.5×10², 15.2×10², 20.7×10² /dm³.mol⁻¹ from the ratio of intercept

CONCLUSION

The present study reports highly stable needle-shaped colloidal nano-sized MnO₂ was formed by simple laboratory equipment in ambient condition. The characterization results reveal that formed colloidal MnO₂ 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 MnO₂ has been first time investigated in aqueous acidic medium. The reaction follows firstorder kinetics concerning to MnO₂ and H⁺ ion under first-order reaction conditions. Results and mechanism indicate that HMnO₂ is reactive species of MnO₂. 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 MnO₂ in aqueous acidic medium.

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