

Oxidation of Citric Acid using Colloidal MnO_2 in the Presence of Non-ionic Surfactant Tween-80

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Abstract

Introduction: In the geochemistry of the ocean, MnO_2 is a significant phase. It has a significant role in the formation of hydrous iron oxide and manganese nodules. **Materials and Methods:** The UV-Vis spectrum at 390 nm was used to characterize water soluble colloidal MnO_2 . Non-ionic surfactant such as Tween 80 used for this investigation. **Results and Discussion:** The kinetics of the oxidation of citric acid by water soluble colloidal MnO_2 in the presence of Tween-80 surfactant have been reported for the 1st time. There is no effect of ionic surfactants CTAB and SDS. The reaction proceeds through the adsorption of lactic acid on the surface of the colloidal particles. **Conclusion:** The non-ionic surfactant Tween-80 showed a catalytic effect up to certain concentrations thereafter an inhibitory effect follows. Non-ionic surfactant Tween-80 by bringing the reactants close and closer due to multiple hydrogen bonding. In doing so rate increased.

Keywords: Citric acid, MnO_2 (Colloidal), Oxidation, Surfactant, Tween-80

INTRODUCTION

In marine geochemistry, MnO_2 is a crucial phase.^[1] It has a significant role in the formation of hydrous iron oxide and manganese nodules. Positive correlations between Mn and other elements are frequent in sedimentary materials, and adsorption onto the surface of manganese dioxide is one of the most recognized mechanisms.^[2]

Because of this, MnO_2 plays an essential role in the scavenging of trace metals and other anions, such as phosphates and chromates, in freshwater and marine ecosystems. Differences in the surface charges of the two substances have been used to explain why manganese-rich sediments and manganese nodules have considerably bigger concentrations of rare metals than silica-rich sediments.

Manganese dioxide is one of the most appealing inorganic materials when compared to all other non-noble metals or transition metal oxides currently being studied. This is due to its

physical and chemical properties as well as its low cost and environmentally friendly makeup.^[3] Manganese dioxide becomes a natural candidate as an oxidant, particularly in catalysis.^[3]

Many different synthetic procedures have been published for the manufacture of manganese dioxide materials since it is broadly accepted that their performance is greatly influenced by both their morphologies and crystallographic shapes. However, because to their low cost, gentleness, ease, and application without extra templates and apparatus, solution-based synthesis and use of metal oxide nanoparticles demand special notice.^[4] Due to their huge specific surface area and the ability to observe reactions using UV-visible spectrophotometry, water-soluble colloidal forms, such as

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those mentioned above, have elevated catalytic and oxidizing activity.

Organic acid reactions have been thoroughly explored^[5-8] with a focus on the estimation of kinetic parameters. Perez-Benito *et al.*^[5] have described a method for the manufacture of water-soluble colloidal manganese dioxide. There are also some findings on the reduction of colloidal manganese dioxide by organic acids in the presence of micelle-forming surfactants,^[9-12] which play very different roles in surface reactions and micellar catalysis. Perez Benito *et al.* disclosed for the 1st time, the preparation of colloidal MnO₂ prepared by action of KMnO₄ and Na₂S₂O₃ under neutral conditions was fully transparent and stable. In such type of reactions, reactants are adsorbed on the surface of the colloidal particles. Both inorganic and organic compounds have been subjected to the oxidizing and catalytic effects of MnO₂ (in an aqueous suspension). Water soluble colloidal MnO₂ is also significant because they function as active auto^[13-17] catalysts in numerous oxidations of permanganates.

MATERIALS AND METHODS

Experimental

All the chemicals used were analytical grade.

Characterization of colloidal MnO₂

The UV-Vis spectrum used to describe the colloidal solution revealed a broad band covering the whole visible region of the spectrum with uniformly decreasing wavelength absorption as well as a single broad band of high intensity at 390 nm. It is corroborated by the findings^[18-20] that the stabilized spectrum belongs to water-soluble colloidal MnO₂. By observing the absorbance of several solutions of colloidal MnO₂, it was revealed that the wavelength of 390 nm was appropriate for verifying the Beer-Lambert law's fulfillment. The findings demonstrate that in the present investigations, the law is followed.

RESULTS AND DISCUSSION

Kinetic measurement

The water-bath used for the kinetic studies was built in the laboratory using parts that were readily available on the market and maintained at constant temperatures. A three-necked reaction vessel with a double-surface water condenser was used to combine a mixture of the necessary proportions of all the reactants (aside from the oxidant) and stop evaporation. The resultant solution was then placed in the reaction vessel and submerged in the water bath set to the necessary temperature, where it was allowed to stand for 30 min to reach equilibrium.

The required volume of thermally equilibrated oxidant colloidal MnO₂ solution was then added to start the reaction. To maintain an inert atmosphere and stir the reaction mixture, purified nitrogen gas was bubbled through the mixture. When half of the colloidal MnO₂ solution had been added, the zero-time was measured. Using a Shimadzu-1800 UV-visible spectrophotometer to track the disappearance of colloidal MnO₂ at 390 nm (the maximum of colloidal MnO₂), the progress of the reaction was seen spectrophotometrically. Usually, the response was carried out to at least 80% of its potential. The reductant in excess was retained, establishing pseudo-first order requirements.

Least-squares method of the data was used to estimate the values of the pseudo-first-order rate constants in the presence of surfactants (k_{ψ}) from the slopes of the typical log (absorbance) versus time plots. The data were consistent as

Table 1: Rate constants for the oxidation of citric acid by colloidal MnO₂ in the presence of Tween 80a keeping citric acid and colloidal MnO₂ fixed

10 ⁵ [Tween-80] (mol dm ⁻³)	10 ³ k _{ψ1} (s ⁻¹)	10 ³ k _{ψ2} (s ⁻¹)
0.0	0.9	3.1
1.25	1.0	4.1
2.5	1.4	4.5
3.75	1.5	5.1
5.0	2.2	5.2
6.25	2.3	5.3
7.5	2.2	5.2

^aReaction conditions. [MnO₂] = 8.0 × 10⁻⁵ mol dm⁻³, [citric acid] = 16.0 × 10⁻⁴ mol dm⁻³, [HClO₄] = 10.0 × 10⁻⁴ mol dm⁻³, temperature = 30°C.

Table 2: Rate constants for the reduction of colloidal MnO₂ by citric acid in the presence of Tween-80 keeping Tween-80 fixed

10 ⁴ [citric acid] (mol dm ⁻³)	10 ³ k _{ψ1} (s ⁻¹)	10 ³ k _{ψ2} (s ⁻¹)
16.0	2.2	5.2
24.0	2.3	5.4
28.0	2.4	5.5
32.0	2.5	5.7
40.0	2.6	5.9
10 ⁵ [MnO ₂] (mol dm ⁻³)		
2.0	2.5	5.7
3.2	2.4	5.6
4.0	2.3	5.7
6.0	2.2	5.4
8.0	2.2	5.2

established by several kinetic runs. The findings are displayed in Tables 1 and 2.

To see the effect of [MnO₂] and [citric acid], a series of kinetic runs were performed at fixed [Tween-80] ($=5 \times 10^{-5}$ mol dm³). The k_{ψ} ($k_{\psi 1}$ and $k_{\psi 2}$) values calculated are summarized in Table 2. It is noted that Tween-80 on k_{ψ} [Table 1] is catalytic up to a certain concentration thereafter, an inhibitory effect follows.

CONCLUSION

Oxidation of citric acid by colloidal MnO₂ in the presence of a surfactant Tween-80 has been documented for the 1st time. Citric acid adheres to the surface of the colloidal particles, causing the process to occur. Due to numerous hydrogen bonds, the non-ionic surfactant Tween-80 demonstrated a catalytic effect by bringing the reactants closer. Because of its unique physical and chemical properties, wide range of uses in biosensors, ion-exchange, molecular adsorption, catalysis, and energy storage, as well as because it is inexpensive and environmentally friendly.

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