# Oxidative degradation of Potassium Dioxalato Diaquo Chromate (III) by water soluble colloidal Manganese Dioxide in acid medium

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## ABSTRACT

*The Oxidative degradation of Potassium dioxalato diaquo Chromate (III) by water soluble colloidal Manganese Dioxide in acid medium has been studied with varying concentration of the complex, colloidal $MnO_2$ and $HClO_4$ solution. This oxidation process obeys pseudo $1^{st}$ order kinetics with respect to colloidal $MnO_2$, $1^{st}$ order kinetics with respect to concentration of the complex and concentration of $HClO_4$.*

**Key words**: Colloidal $MnO_2$, Kinetics, Catalytic oxidation, Rate constant etc.

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## INTRODUCTION

Manganese dioxide has been most extensively studied due to its good oxidizing property [1-4] and reasonably high catalytic activity [5-9]. It is one of the most extensively used heterogeneous catalysts for a variety of organic and inorganic transformations in gaseous as well as liquid phases. However, its use in homogeneous catalyst is limited because of its insolubility under ordinary reaction conditions. In order to remove this limitation, the idea of preparation of colloidal $MnO_2$ came to the mind of different researcher across the globe. As the colloidal manganese dioxide is water-soluble it can be used as a homogeneous catalyst for many reactions.

Several forms of stable and perfectly transparent colloidal $MnO_2$, either in aqueous [10-11] or organic media [12] has been synthesized and the kinetic study of its oxidizing behavior in redox reaction were studied by conventional UV-visible spectrophotometeric method [13]. Keeping these in view, the kinetics and mechanism of oxidation of simple organic molecules like oxalic acid, lactic acid, D-fructose etc by colloidal $MnO_2$ have been studied [14-21]. Benito and his co-workers at University of Barcelona, Spain have extensively studied the synthetic parameters (like coagulation and stabilization) and catalytic properties of colloidal manganese dioxide. The coagulation of colloidal $MnO_2$ by divalent metal cation, oxidation of Mn(II), formic acid and oxalic acid etc have been reported [14,16,22,23]. Photo induced reaction between colloidal $MnO_2$ and some organic compounds of environmental importance have been reported [24]. It is known that carboxylic acid (oxalic acid, malonic acid etc.) and amino acid (glycine, alanine, iminodiacetic acid, pyridine-2/3- carboxylic acid etc.) are bound to a variety of metal ions in biological and chemical systems. The rate and mechanism of oxidation of these bound ligands is different from those of free ligands. A detailed kinetic study is needed to assess the oxidizing ability of colloidal $MnO_2$ towards these coordinated ligands and also to predict the most probable mechanism. This would add further input on its application in reaction of chemical and biological importance.

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The present work deals with the study of the oxidative degradation of Potassium Dioxalato Diaquo Chromate (III) by water soluble colloidal Manganese Dioxide in acid medium.

## EXPERIMENTAL SECTION

### 2.1. Preparation of Potassium dioxalato diaqua Chromate (III)
6grams of oxalic acid and 2 grams of Potassium dichromate was powdered in a dry mortar. The powder was mixed intimately by gentle regrinding in the mortar. The mixture was introduced into the center of a wet basin as compact heap. Then the mixture was further moistened for a few millimeters upwards from its base. The basin was covered with a watch glass and heated gently in a hot plate. After a short interval a vigorous spontaneous reaction set in and a deep coloured syrupy liquid was formed .Then 20ml of ethanol was added to it and the product was stirred with a spatula till it solidified. The deposited crystals were filtered in a suction pump, washed with cold water and finally alcohol.

### 2.2. Characterization of Potassium Dioxalato Diaqua Chromate (III)
### 2.2.1 Spectral study
The UV- visible spectral measurements of the prepared complex were made using Shimadzu UV-2450 and Systronics 119 double beam UV-visible spectrophotometers. Infrared spectra in KBr phase were recorded using Shimadzu IR-Affinity-1 FT-IR spectrophotometer available at our Department. The spectra were recorded at a resolution 4 cm$^{-1}$ and averaging 32-64 scans in the range of 4000-400cm$^{-1}$.

### 2.2.2 Elemental Analysis
The purity of the complex was checked by elemental analyses. The metallic and ligand components in the complex were estimated by standard wet chemical analysis as described below.

### Analysis of Chromium
0.15 g of the complex was weighed out accurately and dissolved in 50 ml of distilled water. The resulting solution was acidified with 3 ml of concentrated sulphuric acid. To that 15 g of solid potassium bromate was added and then boiled for 10 minutes. A solution of ammonium sulphate prepared by dissolving 5 g of it in hot water was then added to the boiling solution of the complex in which chromium now present entirely as chromic acid. The resultant solution was further boiled for about 45 min till all the excess of bromine escaped. The boiled solution was left for 2 h. 10 ml of normal sulphuric acid was added to it and again boiled for about 10 min. The liquid was cooled and then 10ml of concentrated hydrochloric acid was added to it followed by 1 g of solid potassium iodide and kept in a dark place. The liberated iodine was titrated with decinormal $Na_2S_2O_3$ solution. Chromium content of the complex was calculated from the following relationship:

1 cm$^3$ of 1 mol dm$^{-3}$ $Na_2S_2O_3$=0.05199 g of Cr(III).

### Analysis of oxalate
 0.3 g of the complex was taken into a 250ml beaker.10ml of water and 10ml of 10% solution of KOH was added to it. The mixture was then boiled until no more green precipitate formed. The chromic hydroxide precipitate was filtered off using what man 41 No. filter paper and washed with hot water. Then the united filtrate and the washings were acidified with 6N $H_2SO_4$ and titrated at about 70$^0$C with N/10 $KMnO_4$ solution. Oxalate content of the complex was calculated from the following relationship:

1 cm$^3$ of N/10 KMnO4 solution = 0.00411 g of $C_2O_4^{2-}$

### 2.3. Chemicals used
Analytical grade reagents were used for preparation of all standard solutions. For synthesis of complexes and colloidal $MnO_2$, analytical grade chemicals were also used as far as practicable. All solutions were prepared in doubly distilled water.

### 2.4. Preparation of Colloidal $MnO_2$
A dark-brown Colloidal $MnO_2$ (5.0 x 10$^{-4}$M) Solution was prepared by reducing $KMnO_4$ with a stoichiometric amount of $Na_2S_2O_3$ according to the reaction,

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$$8\ MnO_4 + 3S_2O_3^2 + 2\ H^+ \longrightarrow 8\ MnO_2 + 6\ SO_4^2 + H_2O$$

A 2L volumetric flask was filled with water to around 4/5 of its capacity. 20ml of $Na_2S_2O_3$ ($1.88 \times 10^{-2}M$) solution was added to it. Then 2ml of $KMnO_4$ (0.2M) Solution was added & the mixture was diluted to 2-L with more water. Each addition was followed of homogenization by gentle shaking. A dark brown coloured colloidal solution was obtained, remaining perfectly transparent at least for several months.

### 2.5. Characterization of Colloidal MnO₂
The colloid's UV-Vis spectrum was recorded with Shimadzu UV-2450 and Systronics 119 double beam UV-visible spectrophotometers and showed a large band covering the whole visible region of the spectrum, with absorbance uniformly decreasing with increasing wave length, as well as a wide maximum at 300-400 nm.

### 2.6. Kinetics of Spectrophotometric measurement
The reaction was initiated by adding the required quantity of colloidal $MnO_2$ maintained at constant temperature to the mixed solution of $HCO_4$ and the complex maintained at the same temperature. The zero time was taken when half of the colloidal $MnO_2$ solution was added. The rate of disappearance of $MnO_2$ was monitored at 375 nm at different time intervals with a UV-Visible Spectrophotometer, using a cell of path length 1cm. The pseudo-first order rate constants were calculated from the slopes of plots of log (absorbance) versus time. The first-order plots in almost all cases were linear to 80% completion of the reaction with correlation coefficient ~0.998.

### RESULTS AND DISCUSSION

### 3.1 Characterization of colloidal MnO₂
The colloid's UV-Vis spectrum was recorded with a Shimadzu UV-2450 spectrophotometer, and showed a large band covering the whole visible region of the spectrum, with absorbance maxima at 375 nm (Fig1). So the wavelength of 375nm was chosen to follow the kinetic runs.
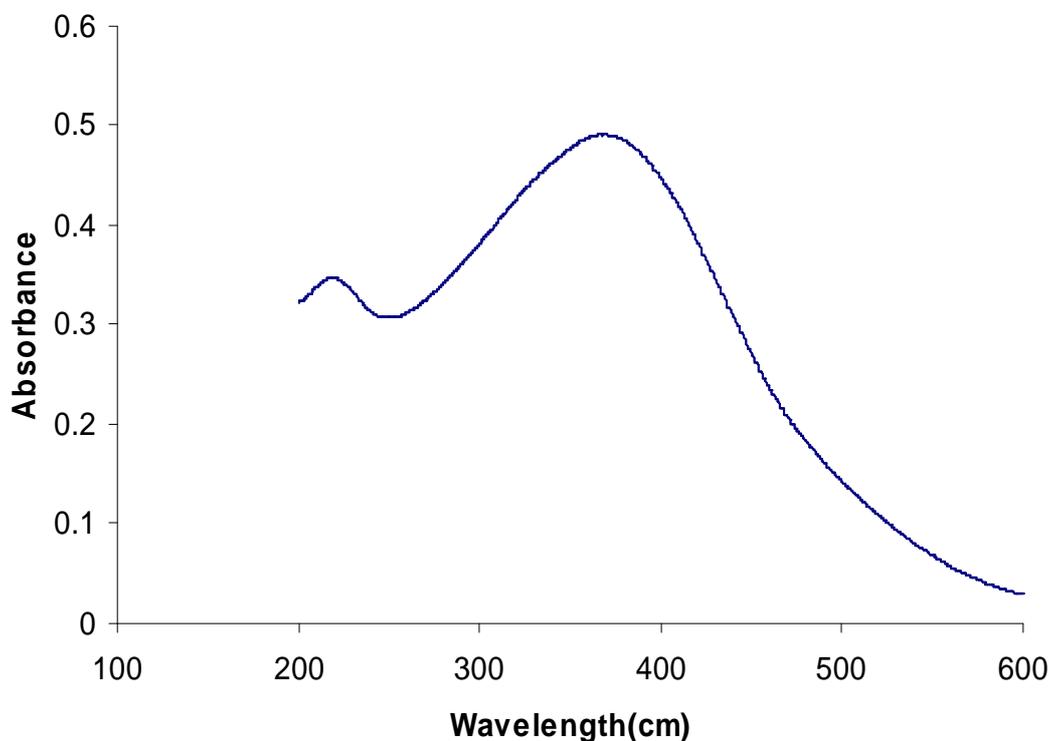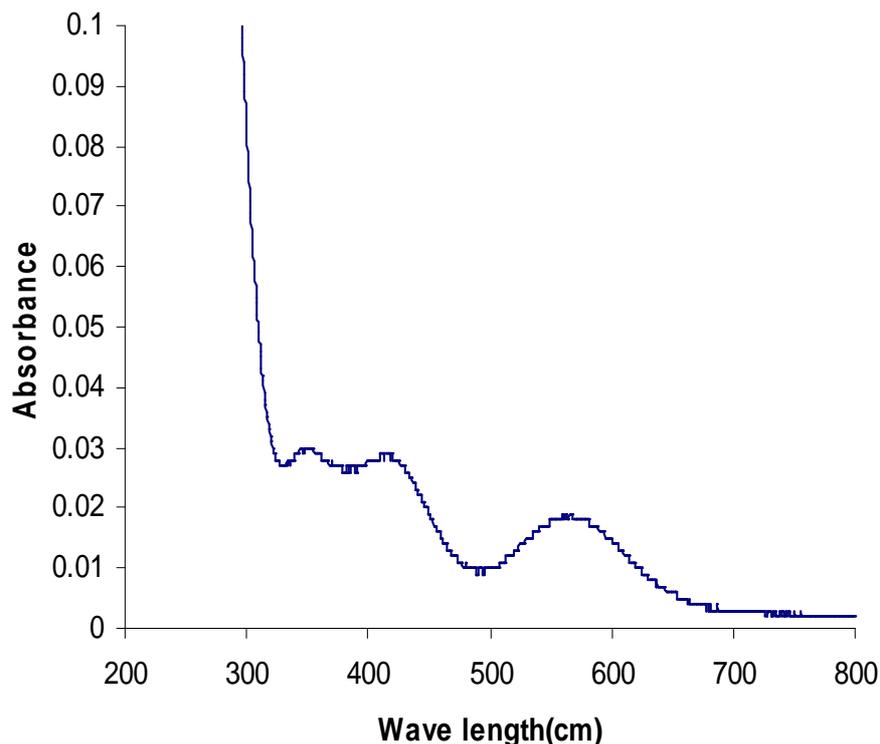


**Fig.1. UV-Visible Spectra of Colloidal MnO₂**

**3.2 Characterization of the complex**
**Elemental Analysis:-**
Amount of chromium and oxalate present in the complex were estimated by wet chemical methods. It was found that the complex contains 15.07% chromium and 47.89% of $C_2O_4^{2-}$.

**UV-Vis Spectra:-**
The UV-Vis spectrum of the complex was recorded with a Shimadzu UV-2450 spectrophotometer, and showed a large band covering the whole visible region of the spectrum, with absorbance maxima at 560 nm (Fig2).



**Fig.2. UV-Visible Spectra of potassium dioxalato diaqua Chromate(III)**

**IR Spectra:-**
The FT-IR Spectrum (Fig.3) of the complex displays bands at 3545, 3255, 3050 cm$^{-1}$ that are indicative of the co-ordinate water. The strong bands at 1609 and 1500cm$^{-1}$, may be due to c=0 stretching band. The complex also exhibit bands at 1400, 1250, 1140, 800cm$^{-1.}$

**3.3 Kinetic study**
The Kinetics of the oxidative degradation of Potassium Dioxalato Diaqua-Chromate(III) by colloidal $MnO_2$ in aqueous medium was studied by varying concentration of the complex from 2.8 x$10^{-4}$-4.8 x$10^{-4}$mol dm$^{-3}$ ,colloidal $MnO_2$ from 1.6x$10^{-5}$-2.8x$10^{-5}$ moldm$^{-3}$and $HClO_4$ concentration from 1x$10^{-3}$-2.2x$10^{-3}$ moldm$^{-3}$ .

**3.3.1. Rate dependence on colloidal $MnO_2$**
The order with respect to colloidal $MnO_2$ was determined by finding $K_{obs}$ at different initial concentrations of $MnO_2$ (1.6 x $10^{-5}$ to 2.8 x $10^{-5}$ mol dm$^{-3}$) with other parameters remaining fixed [$HClO_4$] = 1.0 x $10^{-3}$ mol dm$^{-3}$ [complex] =2.8x $10^{-4}$ mol dm$^{-3}$. It has been found that the values of rate constants remained constant for all concentrations of colloidal $MnO_2$ (table-1). The constant values of rate constants indicate that the rate is independent on concentration of colloidal $MnO_2$. According to the basic tenets of chemical kinetics the pseudo-first order rate constants should be independent of the initial concentration of colloidal $MnO_2$. So the reaction is pseudo 1$^{st}$ order with respect to colloidal $MnO_2$.
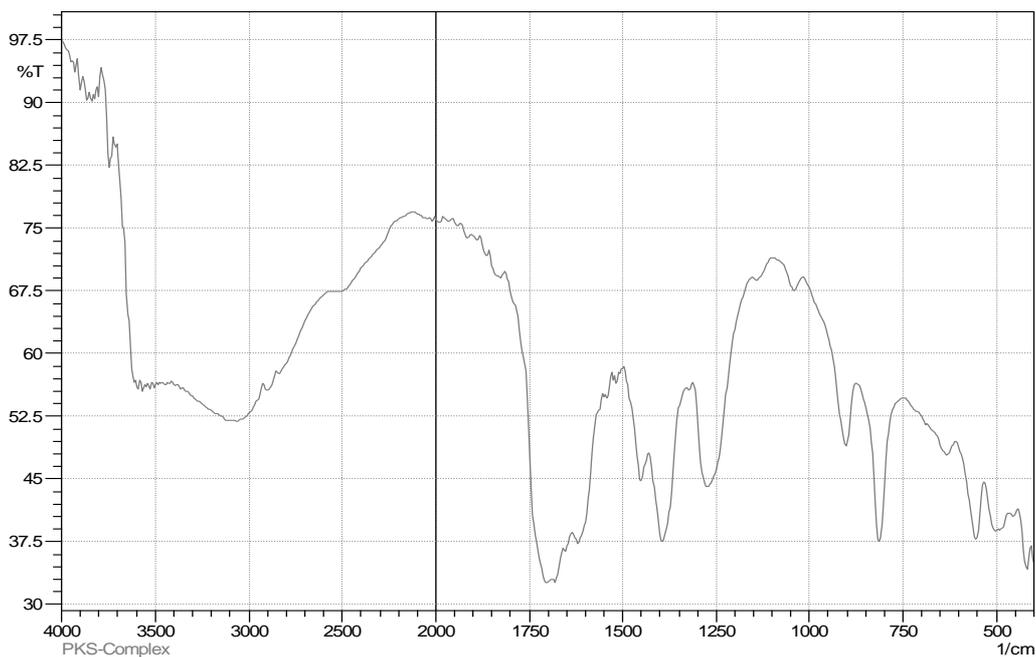
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**Fig.3. I.R. Spectra of Potassium dioxalato diaquo-chromate**

### 3.3.2. Rate dependence on [HClO$_4$]

The order with respect to HClO$_4$ was deduced from the values of $k_{obs}$ obtained at several [HClO4] (1.0 x10$^{-3}$ to 2.2 x 10$^{-3}$ mol dm$^{-3}$) with fixed [Coll.MnO2] (=2.8 x 10$^{-5}$ mol dm$^{-3)}$ and [complex] (=2.8x 10$^{-4}$ mol dm$^{-3}$). The values of rate constant increased with increase in [HClO$_4$]. A plot of log k versus log [HClO$_4$] is linear with slope 0.954 which confirmed that the reaction is first order with respect to [HClO$_4$] (fig.-4).

**Table -1: Effect of varying the [Colloidal MnO$_2$], [complex] and [HClO$_4$]   on the pseudo-first order rate constants for the oxidative degradation of Potassium Dioxalato Diaquo Chromate (III) complex by colloidal MnO$_2$**

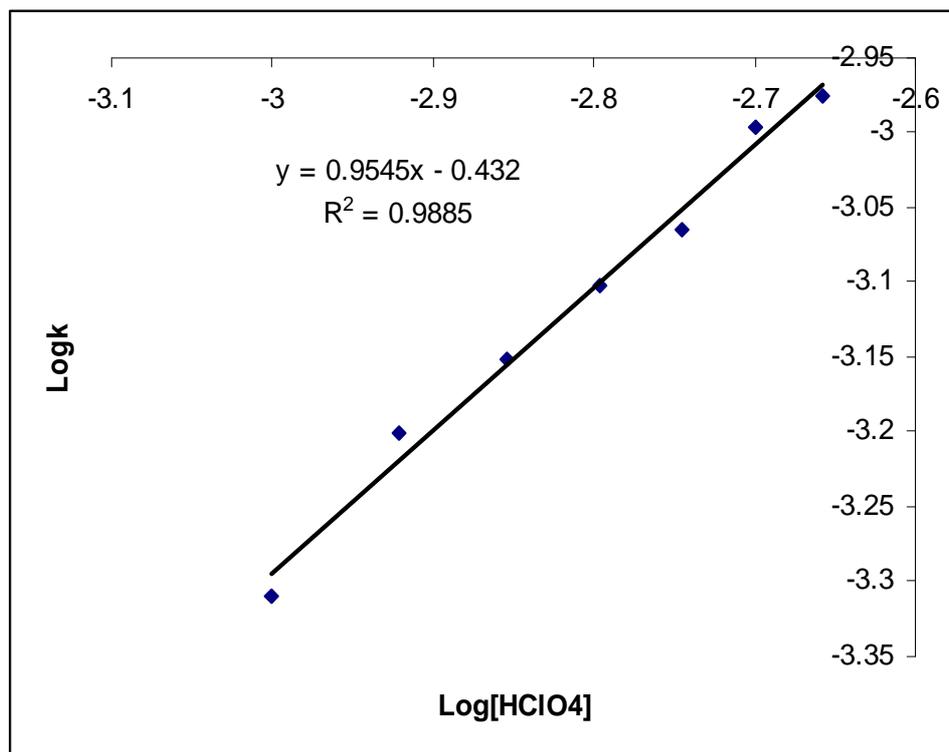| $10^5$[MnO$_2$]moldm$^{-3}$ | $10^4$[complex]mol dm$^{-3}$ | $10^3$[HClO$_4$]mol dm$^{-3}$ | $10^3$ k$_{abs}$ sec$^{-1}$ |
|---|---|---|---|
| 1.6 | | | 0.46 |
| 1.8 | | | 0.464 |
| 2.0 | | | 0.468 |
| 2.2 | 2.8 | 1 | 0.49 |
| 2.4 | | | 0.49 |
| 2.6 | | | 0.44 |
| 2.8 | | | 0.49 |
| | 2.8 | | 0.49 |
| | 3.2 | | 0.86 |
| 2.8 | 3.6 | 1 | 1.04 |
| | 4.0 | | 1.18 |
| | 4.4 | | 1.23 |
| | 4.8 | | 1.36 |
| | | 1.0 | 0.49 |
| | | 1.2 | 0.63 |
| | | 1.4 | 0.70 |
| 2.8 | 2.8 | 1.6 | 0.79 |
| | | 1.8 | 0.86 |
| | | 2.0 | 1.01 |
| | | 2.2 | 1.06 |

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**Fig.4. Log-log plot of concentration of Perchloric acid with rate constant**

### 3.3.3. Rate dependence on [complex]

The order with respect to complex was deduced from the values of $k_{obs}$ obtained at several [complex] ($2.8 \times 10^{-3}$ to $4.8 \times 10^{-3}$ mol dm$^{-3}$) with fixed [Coll.MnO2] ($= 2.8 \times 10^{-5}$ mol dm$^{-3)}$ and [HClO$_4$] ($= 1.0 \times 10^{-4}$ mol dm$^{-3}$). The values of rate constant increased with increase in    [complex]. A plot of log k versus log [complex] is linear with slope 1.081 which confirmed that the reaction is first order with respect to complex (fig.-5).
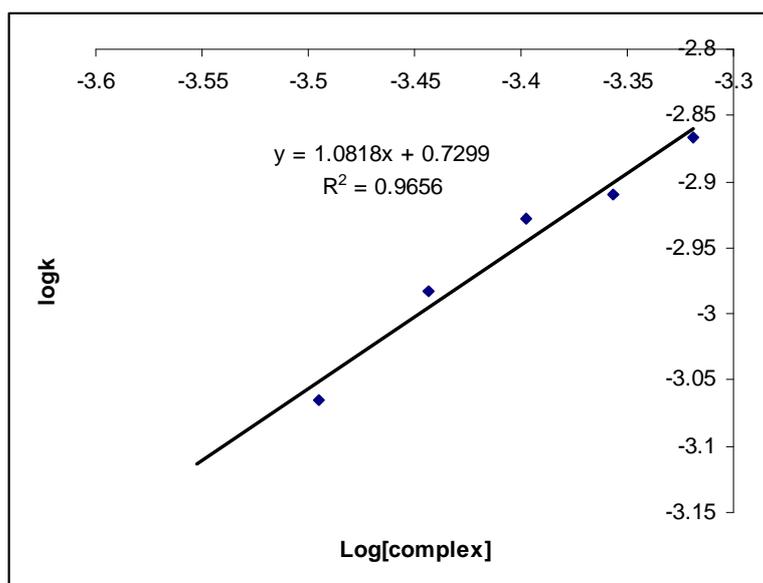


**Fig.5. Log-log plot of concentration of Potassium Dioxalato Diaqua Chromate (III) with rate constant**

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**3.2.4. Effect of time on oxidative degradation of the complex by colloidal MnO2**
Effect of time on oxidative degradation of the complex by colloidal MnO2 was studied by taking [Coll.MnO2] (=2.8 x $10^{-5}$ mol $dm^{-3}$), [complex] (=2.8x $10^{-4}$ mol $dm^{-3}$) and [$HClO_4$] (=1.0x$10^{-4}$ mol $dm^{-3}$).   The rate of degradation increases with regular interval of time (Fig-6).
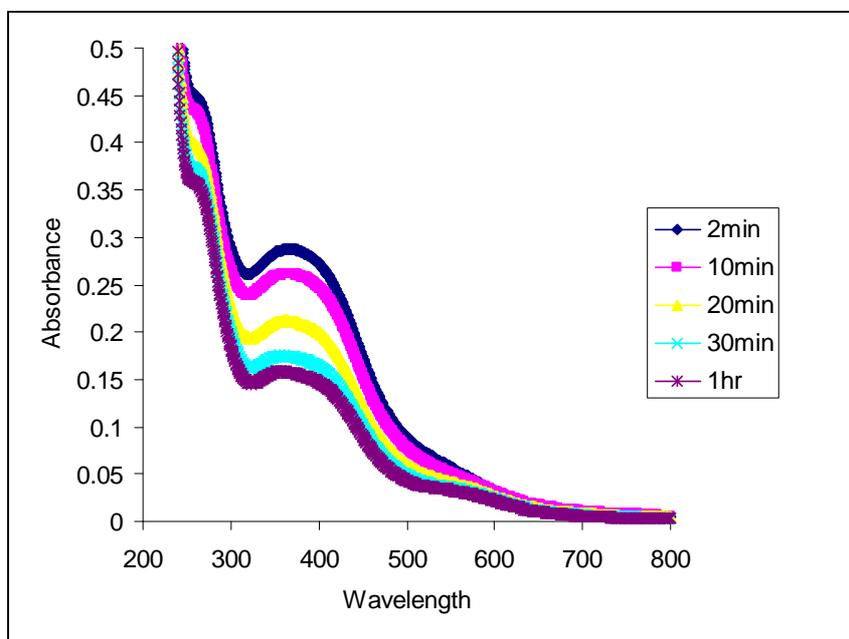


**Fig:-6.  Effect of time on oxidative degradation of the complex by colloidal MnO$_2$**

**CONCLUSION**

The colloidal $MnO_2$ first prepared by Perez- Benito et al. can be used for the Oxidative Degradation of Potassium Dioxalato Diaqua Chromate (III) Complex in acid medium. This oxidation process obeys pseudo 1st order kinetics with respect to concentration of colloidal $MnO_2$, however it obeys 1st order kinetics with respect to concentration of complex and concentration of $HClO_4$.

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