

Research Article

Degradation of Methomyl by Colloidal Manganese Dioxide in Acidic Medium

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Aligarh Muslim University, Aligarh – 202 002, India.**Abstract**

The kinetics of the degradation of methomyl by water soluble colloidal MnO_2 in acidic medium (HClO_4) has been studied spectrophotometrically. The experiments have been performed under the pseudo-first-order reaction conditions with respect to MnO_2 . To determine the rate constant as functions of [methomyl], $[\text{MnO}_2]$ and $[\text{HClO}_4]$, the pseudo-first-order reaction conditions have been maintained throughout the entire kinetic runs. The degradation has been observed to be first-order with respect to MnO_2 while fractional-

order in both methomyl and HClO_4 . The rate constant for the degradation of methomyl by MnO_2 has been observed to be decreased with increasing concentration of latter, which is due to flocculation of its colloidal particles. The kinetic data have been exploited to generate the various activation parameters for the oxidative degradation of methomyl by colloidal MnO_2 .

***Correspondence**A. Nasar
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Contact: +91 9415842475**Keywords:** Kinetics, Methomyl, Manganese dioxide, Degradation, Pseudo-first order.**Introduction**

Methomyl, $\text{C}_5\text{H}_{10}\text{O}_2\text{N}_2\text{S}$ (IUPAC name, S-methyl-N-[(methylcarbamoyl)oxy]thioacetimidate) is a broad spectrum insecticide introduced in 1966 [1,2]. It acts by inhibiting the cholinesterase, an essential enzyme necessary for the functioning of nervous system, and widely used to control insects in vegetables, certain fruits, field crops and commercial plantation. In spite of high efficiency for crop protection against insects, methomyl has been considered as matter of environmental concern. WHO (World Health Organization), EPA (Environmental Protection Agency, USA) and EC (European Commission) have categorized this pesticide as a very toxic and hazardous material [3]. Due to high solubility in water (57.9 g dm^{-3} at 25°C) and low sorption affinity to soil it has potential to contaminate the ground and surface water in agricultural areas [3]. The presence of methomyl in water has been detected in different regions and location, by and large, all over the world [4-10]. This insecticide is quite persistence and particularly in ground water and its estimated half-life is more than 50 weeks [11]. Thus the application of methomyl in agricultural field is associated with the significant risk to aquatic system and water resources. Therefore degradation of pesticide in soil is essential to eliminate or minimize the

contamination of water resources. Moreover an efficient and cheaper method would also be helpful in treatment of waste water contaminated by methomyl. In fact the fate of an insecticide in soil is governed by the transformation process based on the splitting of molecules which includes chemical, photochemical and biological degradation. However, methomyl is more prone for photodegradation and it has been reported that its half-life is reduced from about a year in ground water to 6 days in surface water, i.e. water with aeration and sunlight [11]. The photochemical degradation of this compound under different conditions has been thoroughly studied by different research groups [3,12-21]. Biodegradation studies on methomyl have also been conducted by several workers [e.g.,11,21-23]. Furthermore many pesticides and other organic substances are known to undergo chemical decomposition in presence of manganese compounds and especially its dioxide (MnO_2). In fact manganese is 12th most abundant element in earth's crust and available from 7 to 9000 ppm depending upon region with an average value of 440 ppm [24]. The MnO_2 particles present in earth's crust and natural water have potential to oxidize the humic and organic substances including pesticides. However, oxidizing power of MnO_2 is limited due to its insolubility under ordinary conditions. Fortunately, in recent years perfectly transparent

colloidal solution of MnO_2 has been prepared by the reducing the neutral or slightly acidic potassium permanganate solution with sodium thiosulfate. The water soluble colloidal MnO_2 has successfully been used for the oxidative degradation of a number of compounds [25-41]. As so far the degradation of methomyl by MnO_2 has not been studied it has been considered worth to conduct experiments in this direction. In the present investigation the degradation kinetics of methomyl by water soluble colloidal MnO_2 in acidic medium has been performed and the results have been analyzed in term of different activation parameters associated with the process.

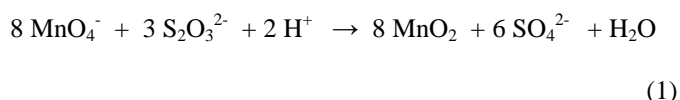
Experimental

Materials and Reagents

Commercial grade methomyl (E.I. Du Pont, India) and Analytical Reagent grade each potassium permanganate and sodium thiosulfate (Qualigens, India); and perchloric acid (CDH, India) were used in the present investigation. All the solutions were prepared in doubly distilled deionized water.

Preparation of Colloidal MnO_2 and other Stock Solutions

The stock solution of colloidal MnO_2 ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$) was prepared by the method described by Perez-Benito et al. [27]. The preparation involves the reduction of potassium permanganate by sodium thiosulfate in aqueous medium according to the following stoichiometry:



The required volume of sodium thiosulfate solution (20.0 ml, $1.88 \times 10^{-2} \text{ mol dm}^{-3}$) was slowly added to standard solution of potassium permanganate (10.0 ml, 0.1 mol dm^{-3}) and the reaction mixture was then diluted to 1 dm^3 in a standard flask. In this way the solution prepared was dark brown transparent and remained stable for over a month. The stock solutions of methomyl (0.1 mol dm^{-3}) and HClO_4 (0.1 mol dm^{-3}) were prepared by dissolving in water.

Kinetic Measurements

Kinetic experiments were performed by taking requisite quantity of aqueous solution of methomyl in a reaction vessel kept in a thermostated water bath. The reaction vessel was allowed to remain in the water bath for sufficient time to attain the desired temperature with an accuracy of $\pm 0.5 \text{ }^\circ\text{C}$. The kinetic studies were carried out by adding the calculated amount of colloidal solution of MnO_2 and HClO_4 . The progress of the reaction was monitored spectrophotometrically. The absorbance of

unreacted MnO_2 in the reaction mixture was taken by UV-Visible spectrophotometer (Perkin Elmer, Model – lambda 25) at an optimized wavelength of 360 nm (i.e. $\lambda_{\text{max}} = 360 \text{ nm}$). The fulfillment of Beer's law was checked and found to be validated in experimental concentration range ($6.0 \times 10^{-5} - 2.0 \times 10^{-4} \text{ mol dm}^{-3}$) of MnO_2 . The measurements were taken under the varying of concentration of reactants (methomyl, MnO_2 and HClO_4) and temperature ($20 - 45 \text{ }^\circ\text{C}$).

Results and Discussion

General Consideration

All the measurements were formulated under the pseudo-first-order reaction conditions in which concentrations of methomyl and HClO_4 were taken in large excess over MnO_2 . The pseudo-first-order rate constants were calculated from the slope of log (absorbance) versus time plot. The plot of log (absorbance) versus time at a typical fixed concentrations of methomyl ($5.0 \times 10^{-3} \text{ mol dm}^{-3}$), MnO_2 ($6.0 \times 10^{-5} \text{ mol dm}^{-3}$) and HClO_4 ($6.0 \times 10^{-4} \text{ mol dm}^{-3}$) at $25 \text{ }^\circ\text{C}$ shown in **Figure 1** is represented by straight line with $r^2 = 0.994$. Thus the reaction is first order with respect to MnO_2 under the adopted reaction conditions.

Effect of Concentrations of Methomyl, MnO_2 and HClO_4 on the Reaction Rate

The dependence of the rate of reaction on the concentration of methomyl has been studied by conducting the kinetic measurements at the varying concentration of methomyl ($1.0 \times 10^{-3} - 1.0 \times 10^{-2} \text{ mol dm}^{-3}$) keeping the concentrations of MnO_2 ($6.0 \times 10^{-5} \text{ mol dm}^{-3}$) and HClO_4 ($6.0 \times 10^{-4} \text{ mol dm}^{-3}$) constant at a typical temperature of $25 \text{ }^\circ\text{C}$. Under the said conditions, the values of observed rate constant (k_{obs}) so obtained are plotted against the concentration of methomyl in **Figure 2**. This figure clearly indicates that the variation is nonlinear and the rate constant increases with increasing concentration of methomyl throughout the entire range as shown in **Figure 2**. The plot between log k_{obs} and log [methomyl] is linear (**Figure 3**) with a slope of 0.426 ($r^2 = 0.981$) indicating the fractional order with respect to methomyl. This result is in conformity with the observation of fractional order for the oxidative degradation of a number of compounds such as D-fructose [28], glycyl-glycine [29], glycyl-leucine [36], glycolic acid [38] etc. by colloidal MnO_2 in HClO_4 medium.

In order to understand the nature of reaction with respect to variation in concentration of MnO_2 , the rate constants have been determined at different initial concentration of MnO_2 ranging from 6.0×10^{-5} to $2.0 \times 10^{-4} \text{ mol dm}^{-3}$. The concentrations of methomyl ($5.0 \times 10^{-3} \text{ mol dm}^{-3}$) and HClO_4 ($6.0 \times 10^{-4} \text{ mol dm}^{-3}$), and temperature ($25 \text{ }^\circ\text{C}$) have been kept constants.

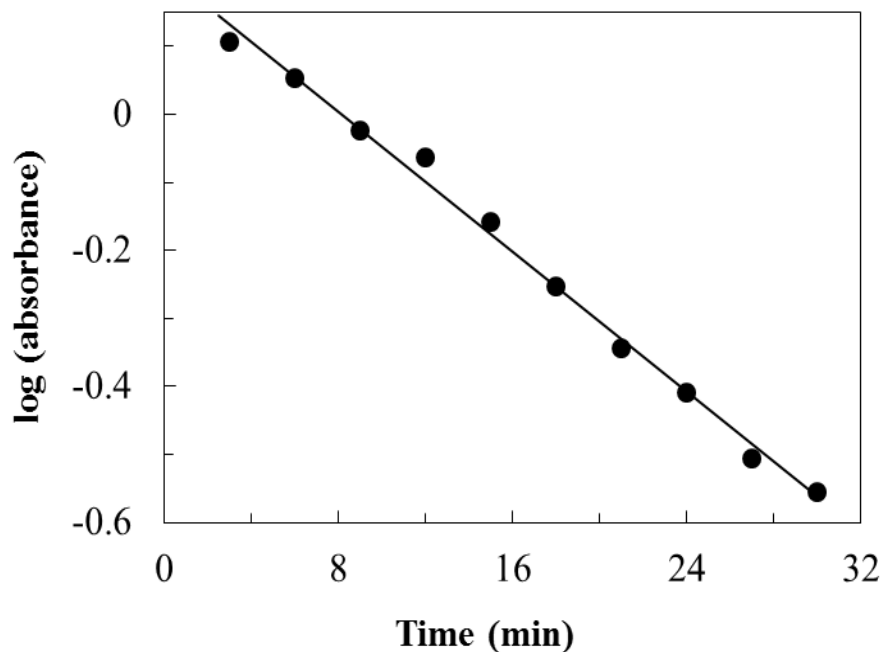


Figure 1 Plot of log (absorbance) versus time for the degradation of methomyl by colloidal MnO_2 (Reaction conditions: $[\text{methomyl}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{MnO}_2] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$, temperature = 25°C)

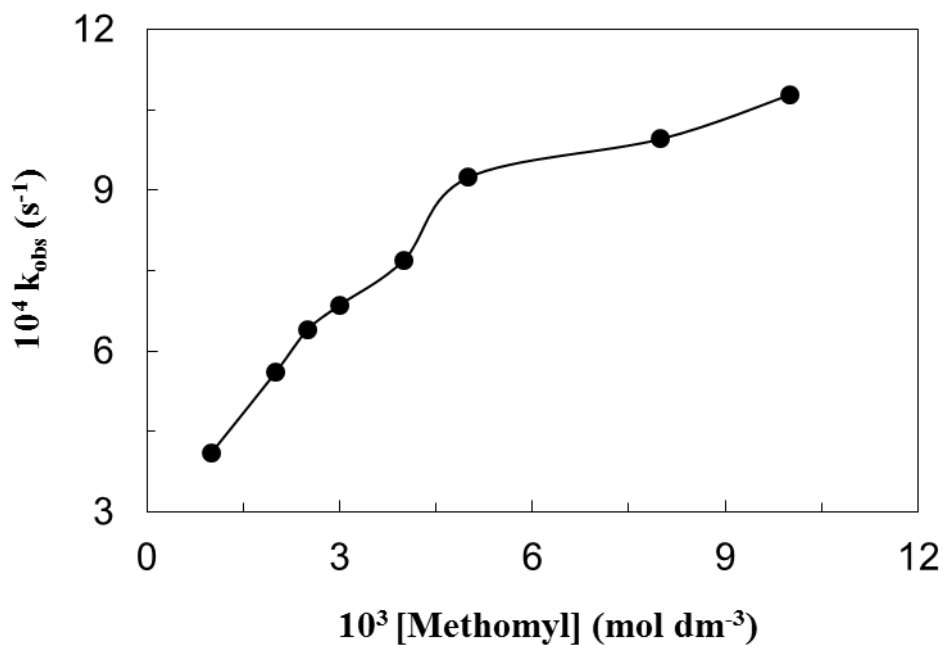


Figure 2 Effect of $[\text{methomyl}]$ on k_{obs} for the degradation of methomyl by colloidal MnO_2 (Reaction conditions: $[\text{MnO}_2] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$, temperature = 25°C)

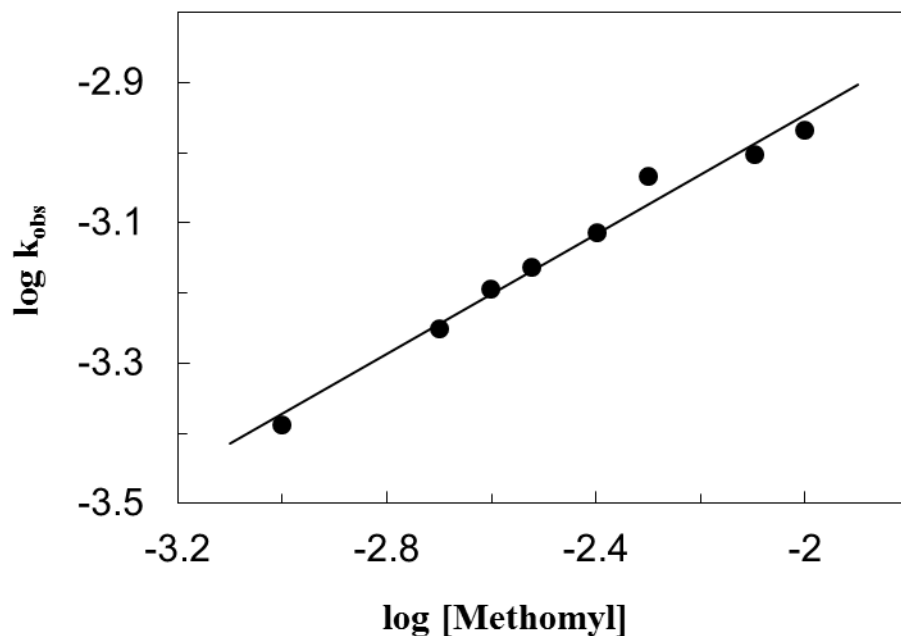


Figure 3 Effect of log [methomyl] on log k_{obs} for the degradation of methomyl by colloidal MnO_2 (Reaction conditions: $[MnO_2] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[HClO_4] = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$, temperature = 25 °C)

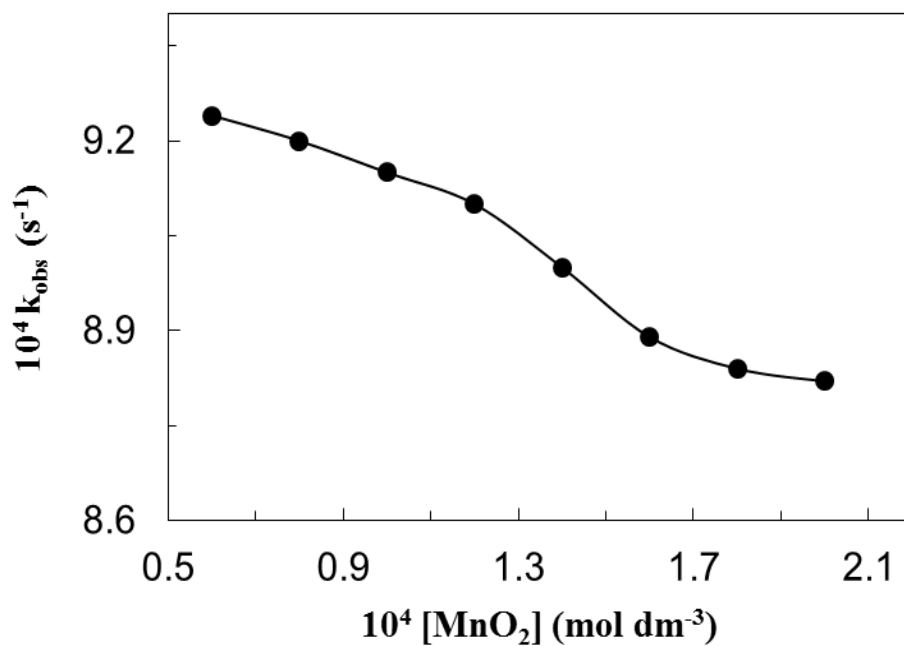


Figure 4 Effect of $[MnO_2]$ on k_{obs} for the degradation of methomyl by colloidal MnO_2 (Reaction conditions: [methomyl] = $5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[HClO_4] = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$, temperature = 25 °C)

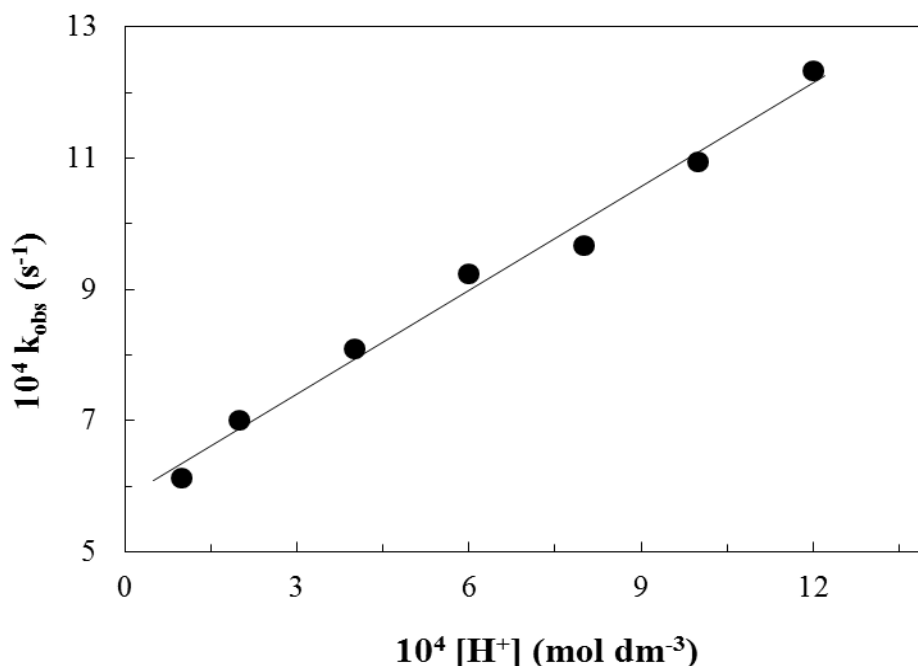


Figure 5 Effect of $[\text{H}^+]$ on k_{obs} for the degradation of methomyl by colloidal MnO_2 (Reaction conditions: [methomyl] = $5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{MnO}_2] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$, temperature = 25°C)

The pseudo-first-order rate constant obtained at different concentration of MnO_2 are plotted in **Figure 4**. This figure clearly shows that the rate constant decrease with increasing concentration of MnO_2 . The similar observation of decrease of rate constant with increasing concentration of MnO_2 under pseudo-first-order reaction conditions has also been reported for the oxidative degradation of a number of compounds such as aspartic acid [25], oxalic acid [26,27], glycyl-glycine [29], glycyl-leucine [36], glycolic acid [38], DL-malic acid [39], glyphosate [40] and L-methionine [41]. The continuous and regular decrease of rate constant with increasing concentration of MnO_2 is due to possible coagulation (flocculation) of its particles.

The effect of concentration of HClO_4 (in range of $1.0 \times 10^{-4} - 1.2 \times 10^{-3} \text{ mol dm}^{-3}$) was studied by conducting a series of kinetic measurements at the fixed concentration of methomyl ($5.0 \times 10^{-3} \text{ mol dm}^{-3}$) and MnO_2 ($6.0 \times 10^{-5} \text{ mol dm}^{-3}$) at a constant temperature of 25°C . The plot of k_{obs} against $[\text{H}^+]$ shown in **Figure 5** gives a positive intercept on k_{obs} axis. Thus the degradation of methomyl by MnO_2 comprises with acid independent and acid dependent paths. It is also clear from this figure that the rate constant increases with increase in $[\text{HClO}_4]$ throughout the entire concentration range. The slope of linear plot of $\log k_{\text{obs}}$ versus $\log [\text{H}^+]$ has been calculated

to be 0.266 ($r^2 = 0.960$). Thus there is fractional order dependence of methomyl degradation with respect to $[\text{H}^+]$ in acid dependent path. On the basis of above observations and findings the rate (v) of the degradation of methomyl under pseudo-first-order reaction conditions with respect to MnO_2 may be given in term of the following rate law equation:

$$v = -d[\text{MnO}_2]/dt = (K_1 + k_D [\text{H}^+]^{0.266}) [\text{methomyl}]^{0.426} [\text{MnO}_2] \quad (2)$$

where, k_1 and k_D are rate constants for hydrogen ion concentration in acid independent and dependent paths, respectively.

Effect of Temperature on Rate Constant and Determination of Activation Parameters

A series of kinetic experiments were performed at different temperatures in the range of $20 - 45^\circ\text{C}$ at the fixed concentrations of methomyl ($5.0 \times 10^{-3} \text{ mol dm}^{-3}$), MnO_2 ($6.0 \times 10^{-5} \text{ mol dm}^{-3}$) and HClO_4 ($6.0 \times 10^{-4} \text{ mol dm}^{-3}$). The values of rate constant so obtained at different temperatures are used to calculate the activation energy of the process. The variation of $\log k_{\text{obs}}$ against $1/T$ has been observed to obey the following linear

relationship which indicates that the system obeys Arrhenius relationship:

$$\log k_{\text{obs}} = -1029.5/T + 0.4225 \quad (r^2 = 0.987) \quad (3)$$

The value of activation energy (E_a) as calculated from the slope of the above equation is listed in **Table 1**. In order to realize whether the reaction mechanism is associative or dissociative, the entropy of activation is necessarily required. The values of entropy of activation (ΔS^\ddagger) along with other thermodynamic activation parameters such as enthalpy of activation (ΔH^\ddagger) and free energy of activation (ΔG^\ddagger) as calculated from following Eyring equation are also presented in **Table 1**.

$$\log (k_{\text{obs}}/T) = -(\Delta H^\ddagger/2.303RT) + \log (k_B/h) + (\Delta S^\ddagger/2.303R) \quad (4)$$

Table 1 Activation parameters for the degradation of methomyl by colloidal MnO_2 (Reaction conditions: [methomyl] = 5.0×10^{-3} mol dm^{-3} , $[\text{MnO}_2]$ = 6.0×10^{-5} mol dm^{-3} , $[\text{HClO}_4]$ = 6.0×10^{-4} mol dm^{-3})

Activation parameters	Values
E_a (kJ mol^{-1})	19.7
ΔH^\ddagger (kJ mol^{-1})	17.2
ΔS^\ddagger (J K^{-1} mol^{-1})	-245.4
ΔG^\ddagger (kJ mol^{-1})	92.0

In the above equation k_B , R and h represent Boltzman, gas and Plank's constants, respectively. A large negative value of entropy of activation points out the formation of highly ordered associative transition state complex during the degradation process of methomyl by colloidal MnO_2 . Moreover, the activation parameters as listed in

Table 1 also highlight that the entropy factor plays dominating role over enthalpy factor.

Conclusions

The kinetic studies for the oxidative degradation of methomyl by colloidal MnO_2 in acidic medium have successfully been performed over wide concentration ranges of the reactants. The rate constants have been determined as function of the concentrations of methomyl, MnO_2 and HClO_4 under the pseudo-first-order reaction conditions. The order of the reaction has been observed to be first order in MnO_2 and fractional order in both methomyl and HClO_4 . On the basis of variation of the rate constant following rate law equation has been developed:

$$v = (K_I + k_D [\text{H}^+]^{0.266}) [\text{methomyl}]^{0.426} [\text{MnO}_2] \quad (5)$$

The kinetic results have also been used to generate various activation parameters associated with the degradation of methomyl by colloidal MnO_2 in presence of HClO_4 .

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