

## Research Article

# Kinetics of Reduction of Colloidal MnO<sub>2</sub> by Glyphosate in Aqueous and Micellar Media

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The kinetics of the reduction of colloidal MnO<sub>2</sub> by glyphosate has been investigated spectrophotometrically in an aqueous and micellar (cetyltrimethylammonium bromide, sodium lauryl sulfate) media. The reaction follows first-order kinetics with respect to colloidal MnO<sub>2</sub> in both the aqueous and micellar media. The rate of oxidation increases with increase in [glyphosate] in the lower concentration range but becomes independent at its higher concentrations. The addition of both the anionic (NaLS) and cationic (CTAB) micelles increased the rate of reduction of colloidal MnO<sub>2</sub> by glyphosate while the nonionic TX-100 micelles did not influence the rate of reaction. In both aqueous and micellar media, the oxidation of glyphosate occurs through its adsorption over colloidal MnO<sub>2</sub> surface. The reaction in micellar media was treated by considering the pseudophase model. The values of reaction rates and binding constants in the presence of micelles were determined.

## 1. Introduction

Manganese is the eleventh most abundant element in the earth crust and is among the important micronutrients for all micro-organisms. Manganese (III, IV) oxide minerals are thermodynamically stable in the oxygenated environments. These oxide particles in earth crust and in natural water are susceptible for reduction by humic acid and organics [1–4]. Thus, the humic and organic compounds are degraded into simpler molecules through the abiotic mechanisms. The oxidising and catalytic properties of manganese oxide have been limited due to its insolubility under ordinary conditions. However, in recent years, water-soluble perfectly transparent manganese dioxide has been prepared, by the reduction of alkaline potassium permanganate solution through  $\gamma$ -irradiation and also, by the reduction of neutral or slightly acidic potassium permanganate solution by sodium thiosulphate [5–11].

Glyphosate (N-phosphonomethylglycine) is an amino-phosphonic analogue of the natural amino acid, glycine. It is a postemergence nonselective broad spectrum herbicide extensively used in agriculture for the control of many

annual and perennial weeds [12]. Glyphosate is less toxic than a number of other herbicides and pesticides, such as those from the organochlorine family. It is essentially non-toxic to mammals and birds, but fish and invertebrates are more sensitive to this herbicide. Glyphosate degrades rapidly in soils under most conditions [13, 14]. In view of the significance of manganese dioxide and glyphosate, kinetic studies on the degradation of glyphosate by colloidal MnO<sub>2</sub> has been carried out. The influence of ionic (cetyl trimethyl ammonium bromide and sodium dodecyl sulphate) and nonionic (triton X-100) surfactants has also been studied. Surfactants are used in pesticide formulations [15–17] to increase the solubility of pesticide, to stabilize, to control evaporation or decomposition, and to enhance the effectiveness of pesticides by providing fine spray. The surfactant also acts as wetting, dispersing and emulsifying agent. Surfactants aggregates mimic enzyme structurally and functionally, and, therefore, the study in CTAB and SDS micelles will be helpful in understanding the mechanism of degradation of herbicide in humic and biological media. The observed data will also be helpful in the determination and interpretation of the fate of herbicide after its dispersal in the environment.

## 2. Experimental

**2.1. Materials.** Glyphosate, N-phosphonomethylglycine (Excelcropcarelimited, Mumbai), potassium permanganate (Qualigens, India), and sodium thiosulphate (Qualigens, India), cetyltrimethyl ammonium bromide (99.9% CDH, India), sodium lauryl sulphate (98% CDH, India), Triton X-100 (98% CDH, India), H<sub>2</sub>SO<sub>4</sub> (98% CDH, India), acetic acid (Qualigens, India) sodium acetate (Qualigens, India) were used as received. Doubly distilled water was used throughout the experimental work.

Stock solutions of glyphosate ( $= 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ), cetyltrimethyl ammonium bromide, sodium lauryl sulphate and Triton X-100 ( $= 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ) were prepared in doubly distilled water. All the other required solutions were also prepared in deionized water. Colloidal MnO<sub>2</sub> was prepared by mixing the standardized solutions of potassium permanganate (10 mL,  $0.1 \text{ mol dm}^{-3}$ ) and sodium thiosulphate (20 mL,  $1.88 \times 10^{-2} \text{ mol dm}^{-3}$ ) as given in the literature [9]. The resulting brown solution was transparent and obeyed Beer-Lamberts law within the concentration range of present studies. pH of the solution was adjusted using sulphuric acid solution and its measurement was made using Elico LI-120 pH meter.

**2.2. Kinetic Measurements.** Kinetic experiments were carried out by taking the requisite amounts of aqueous solutions of glyphosate, colloidal manganese dioxide and surfactant in a three-necked reaction vessel. The reaction vessel was fitted with a double surface condenser to prevent any evaporation. The reaction vessel was kept in a thermostated water bath at the desired temperature ( $\pm 0.5^\circ\text{C}$ ). The reaction vessel containing the reactants was kept in the water bath for sufficient time to attain the temperature of bath. The reaction was started with the addition of colloidal MnO<sub>2</sub>. The absorbance was measured by means of a Spectronic 20D+ Thermoscientific UV-V is Spectrometer using 1 cm path length quartz cuvette. The progress of the reaction was monitored by measuring the absorbance at  $\lambda_{\text{max}}$  ( $= 365$ ) because the colloidal manganese dioxide showed strong absorption at this wave length while the absorbance by the complexes of manganese (II) and manganese (III) was negligible at this wave length. All the kinetic experiments were run under the first-order reaction condition in which the concentrations of surfactant and glyphosate were kept in large excess over [MnO<sub>2</sub>]. Kinetic experiments were performed under the varying conditions of temperature and concentrations of reactants, surfactants and sulphuric acid. The pseudo first-order rate constants for the oxidation of glyphosate were calculated from the slope of the  $\ln(\text{absorbance})$  versus time.

## 3. Result and Discussion

Barrett and McBride [1] reported that glyphosate is degraded in dilute aqueous suspensions of birnessite [MnO<sub>2</sub>], a manganese oxide common in soil, to yield phosphate ion in solution. The abiotic degradation of glyphosate involves the C-P bond cleavage at the manganese oxide surface. A similar degradation was observed when colloidal MnO<sub>2</sub> was

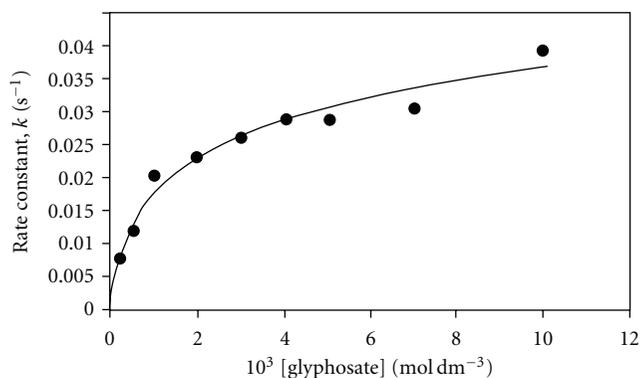


FIGURE 1: Plot of dependence of rate constant on [glyphosate] at [MnO<sub>2</sub>] ( $= 2 \times 10^{-4} \text{ mol dm}^{-3}$ ), temperature =  $30^\circ\text{C}$ , and pH = 6.

added to glyphosate solution. The brown colour of colloidal MnO<sub>2</sub> faded away slowly giving glycine and phosphate at the end of reaction. The presence of glycine and phosphate was tested using ninhydrin reagent and ammonium molybdate solution, respectively.

The order of reaction in [MnO<sub>2</sub>] was determined by measuring the rate of reaction at different initial concentrations of colloidal MnO<sub>2</sub> in the concentration range from  $0.5 \times 10^{-4}$  to  $2.5 \times 10^{-4} \text{ mol dm}^{-3}$  at a fixed concentration of glyphosate ( $= 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) at pH 6 and temperature  $30^\circ\text{C}$ . It was observed that the rate constant decreases with increase in concentration of colloidal manganese dioxide. This decrease in rate constant may be due to the flocculation of the colloidal MnO<sub>2</sub> particles. As the MnO<sub>2</sub> concentration further increases, the rate constants become independent of the initial MnO<sub>2</sub> concentration. It was observed that the rate constant values were also independent of the initial concentrations of glyphosate, when the initial concentration of glyphosate was taken excess (tenfolds or more) over [MnO<sub>2</sub>] and, therefore, the kinetic experiments were carried out at lower concentrations of glyphosate also. The dependence of rate constant on [glyphosate] were carried out in the concentration range  $2 \times 10^{-4}$ –  $1 \times 10^{-2} \text{ mol dm}^{-3}$  at  $2 \times 10^{-4} \text{ mol dm}^{-3}$  MnO<sub>2</sub> concentration. It was observed that the reaction followed zero order kinetics in [glyphosate] at higher concentration and fractional order at lower concentrations as depicted in Figure 1.

The study on the variation of pH from 4 to 6 at  $30^\circ\text{C}$  shows that the reaction rate is independent of the pH in this range. However, the rate of reaction increased linearly with the increase in [H<sub>2</sub>SO<sub>4</sub>] as shown in Figure 2. The reaction between the colloidal MnO<sub>2</sub> and glyphosate takes place at the surface of colloidal manganese dioxide after the adsorption of glyphosate over the MnO<sub>2</sub> surface. The reaction follows two independent paths namely; path I, which is hydrogen ion independent and path II is hydrogen ion dependent. The overall reaction rate may be presented through Scheme 1 as follows.

The rate of oxidation of adsorbed glyphosate at the MnO<sub>2</sub> surface is given by

$$V = k\theta[\text{MnO}_2], \quad (1)$$

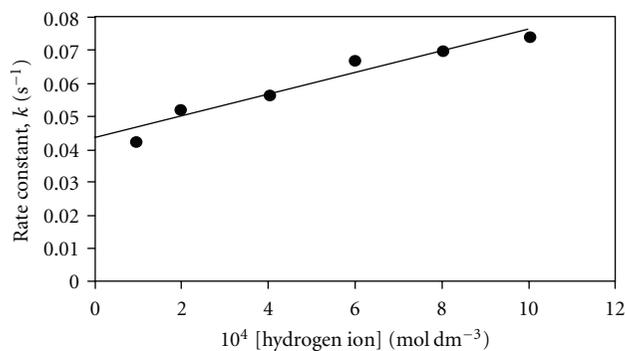


FIGURE 2: Plot of rate constant versus  $[H^+]$  at [glyphosate] ( $= 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ),  $[MnO_2]$  ( $= 2 \times 10^{-4} \text{ mol dm}^{-3}$ ) and Temperature  $= 30^\circ\text{C}$ .

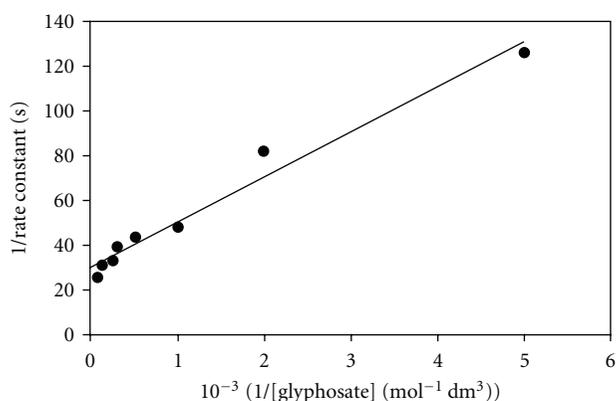


FIGURE 3: Plot of  $1/k_{\text{obs}}$  versus  $1/[\text{glyphosate}]$  for  $[MnO_2]$  ( $= 2 \times 10^{-4} \text{ mol dm}^{-3}$ ), temperature  $= 30^\circ\text{C}$ , and  $\text{pH} = 6$ .

where  $k$  is the overall rate constant and  $\theta$  is the extent of adsorption of glyphosate over  $MnO_2$  surface and in terms of equilibrium constant  $K_{\text{ad}}$ , it is given by

$$\theta = \frac{K_{\text{ad}}[\text{Glyphosate}]}{(1 + K_{\text{ad}}[\text{Glyphosate}])}. \quad (2)$$

On putting the value of  $\theta$ , corresponding to the above Scheme, the rate of reaction is given by

$$V = \frac{(k_1 + k_2[H_3O^+])K_{\text{ad}}[\text{Glyphosate}][MnO_2]}{(1 + K_{\text{ad}}[\text{Glyphosate}])}, \quad (3)$$

where  $k_1$  is rate constant for the hydrogen ion concentration independent path and  $k_2$  is the rate constant for the hydrogen ion concentration dependent path. At low hydrogen ion concentration, the reaction proceeds through path I and reaction occurring through path II is negligible. Equation (3) can be rewritten in terms of observed rate constant as

$$k_{\text{obs}} = \frac{k_1 K_{\text{ad}}[\text{Glyphosate}]}{(1 + K_{\text{ad}}[\text{Glyphosate}])}, \quad (4)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_1} + \frac{1}{(k_1 K_{\text{ad}}[\text{Glyphosate}])}. \quad (5)$$

TABLE 1: Values of rate constants, adsorption constant, and binding constant for the oxidation of glyphosate by colloidal manganese dioxide.

Rate constant/adsorption constant/binding constant	Aqueous medium	Micellar medium	
		CTAB	SDS
$k_1$ ( $s^{-1}$ )	0.0328	—	—
$k_2$ ( $s^{-1}$ ) $10^2$	32.248	—	—
$k_m$ ( $\text{mol dm}^{-3} s^{-1}$ )	—	$1.88 \pm 0.37$	$15.80 \pm 0.07$
$K_n$ ( $\text{mol dm}^{-3}$ )	—	12	8
$K_s$ ( $\text{mol dm}^{-3}$ )	—	400	40
$K_{\text{ad}}$ ( $\text{mol dm}^{-3}$ )	1509.455	—	—

According to (5), a straight-line plot for  $1/k_{\text{obs}}$  versus  $1/[\text{Glyphosate}]$  should be obtained. The observed results as given in Figure 3 support the proposed mechanism for the plot of  $1/k_{\text{obs}}$  versus  $1/[\text{Glyphosate}]$ . The values of  $k_1$  and  $K_{\text{ad}}$  were obtained from the slope and intercept of the plot, respectively and are given in Table 1.

The rate of reaction at higher hydrogen ion concentrations mainly occurs via path II in which the adsorbed glyphosate interacts with hydrogen ion and the contribution of hydrogen ion independent path becomes negligible. Thus in presence of sulphuric acid equation (3) can be rewritten as:

$$k_{\text{obs}} = k_2[H_3O^+], \quad (6)$$

where it is assumed that  $K_{\text{ad}}[\text{Glyphosate}] \geq 1$ .

Thus, according to (6) a straight-line plot should be obtained for  $k_{\text{obs}}$  versus  $[H_3O^+]$  and the value of  $k_2$  (Table 1) can be obtained from the slope.

The effect of variation of surfactant concentration on the rate of degradation of glyphosate by colloidal manganese dioxide was studied at  $30^\circ\text{C}$  by keeping the concentrations of  $MnO_2$ , glyphosate constant at  $2.0 \times 10^{-4} \text{ mol dm}^{-3}$  and  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ , respectively. The increase in CTAB concentrations resulted in an increase in rate of reaction but the rate decreased on further increase in [CTAB] as shown in Figure 4. The maximum value of rate constant was found to be  $0.212 s^{-1}$  at  $[SDS] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ . The addition of SDS also increased the rate of reaction for the degradation of glyphosate by colloidal manganese dioxide (Figure 4). The addition of TX-100 did not influence the rate of reaction.

The variation of rate constant on  $[MnO_2]$  and  $[\text{Glyphosate}]$  in the presence of surfactants showed a similar behaviour as was observed in aqueous medium. These observations indicate that the same mechanism is being followed in both aqueous medium and micellar medium. The increased rate of reaction in the presence of CTAB and SDS may be explained on the basis of pseudophase model of micelles in which reactions are considered to occur both in aqueous and micellar pseudophases with varying rate constants [18–22]. Scheme 2 has been proposed for reactions occurring in aqueous and micellar media as follows.

In this scheme, “G” denotes glyphosate “ $D_n$ ” the micellized surfactant and  $K_s$  the binding constant between surfactant and glyphosate and  $K_n$  is the binding constant



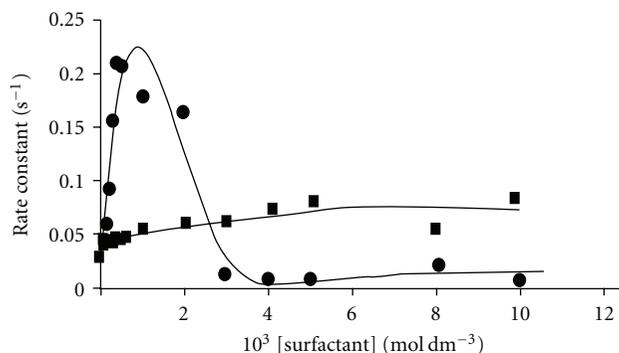
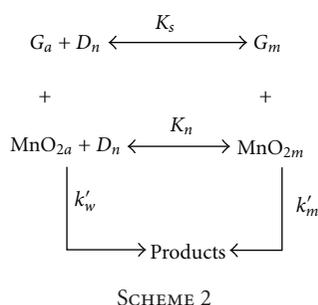


FIGURE 4: Plot for the dependence of rate constant on [CTAB] (•) and [SDS] (■) at  $[\text{MnO}_2] = 2 \times 10^{-4} \text{ mol dm}^{-3}$ , [glyphosate] ( $= 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ), temperature =  $30^\circ\text{C}$ , and pH = 6.



between surfactant and  $\text{MnO}_2$ . Subscript  $a$  and  $m$  denote aqueous and micellar pseudophase, respectively.

The overall rate can be expressed as

$$\begin{aligned}
 v &= k_\Psi [G_T] = k [G_T] [\text{MnO}_{2T}] \\
 &= k'_w [G_w] [\text{MnO}_{2w}] + k'_m [G_m] [\text{MnO}_{2m}],
 \end{aligned}
 \quad (7)$$

where

$$[G_T] = [G_w] + [G_m], \quad (8)$$

$$[\text{MnO}_{2T}] = [\text{MnO}_{2w}] + [\text{MnO}_{2m}],$$

$$k_\Psi = \frac{k'_w + k'_m K_s [D_n]}{1 + K_s [D_n]}. \quad (9)$$

The pseudofirst-order rate constants in aqueous ( $k'_w$ ) and micellar ( $k'_m$ ) pseudophase are given by

$$\begin{aligned}
 k'_w &= k_w [G_w], \\
 k'_m &= \frac{k_m [G_m]}{[D_n]} = k_m m_G,
 \end{aligned}
 \quad (10)$$

where  $m_G$  is mole ratio of micellar bound glyphosate to surfactant headgroup  $k_m$  and  $k_w$  are second order rate constants for reactions occurring in micellar and aqueous pseudophase, respectively.

Equation (9) can now be expressed in terms of second order rate constants as

$$k_\Psi = \frac{k_w [G_T] + (k_m K_n - k_w) m_G [D_n]}{1 + K_n [D_n]}. \quad (11)$$

The values of  $m_G (= [G_m]/[D_n])$  were determined by applying the mass action model for the distribution of glyphosate in the aqueous and micellar pseudophases using the following relationship [18]:

$$K_S [G_m]^2 - (K_S [D_n] + K_S [G_T] + 1) [G_m] + K_S [D_n] [G_T] = 0. \quad (12)$$

The fitting values of  $k_m$ ,  $K_n$ , and  $K_S$  were obtained from the computer program by minimizing the deviation between the simulation and the observed values for  $k_\Psi$ -[CTAB] and  $k_\Psi$ -[SDS] profiles. The values of these parameters are given in Table 1.

The observed higher rate in CTAB and SDS could be attributed to the binding of both glyphosate and colloidal manganese dioxide on to the micellar surface. It is evident from the higher  $K_n$  values that the colloidal manganese dioxide is adsorbed strongly to both the CTAB and SDS micelles. The binding of colloidal manganese dioxide is to the cationic micellar surfaces of  $\text{CTA}^+$  may probably through the oxygen atom. The strong adsorption of colloidal manganese dioxide to  $\text{SD}^-$  may occur via electropositive manganese atom. In the presence of surfactants, the reactions mainly occur in the Stern layer of the micelles. With the increase in [CTAB] and [SDS] the local molarities of colloidal manganese dioxide and glyphosate in the micellar pseudophase increase and, therefore, the rate of oxidation of glyphosate by colloidal manganese dioxide increases. The decrease in rate of oxidation at higher CTAB concentrations may be due to the increase in CTAB concentration results into the formation of increased number of micelles and causes in the dilution of micellar bound colloidal manganese dioxide. It, therefore, results into decrease in concentrations of colloidal manganese dioxide in the micellar pseudophase and thus, the reduction rate for colloidal manganese dioxide is decreased.

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