



ADSORPTION CHARACTERISTICS OF DICHLORVOS ONTO HYDROUS TITANIUM DIOXIDE SURFACE

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(First received October 1994; accepted in revised form January 1996)

Abstract—Adsorption of dichlorvos (2,2-dichlorovinyl-*o,o*-dimethyl phosphate) onto hydrous TiO₂ from water was evaluated in the laboratory using a batch reactor. The presence of organic solvents resulted in a decreasing dichlorvos adsorption on TiO₂ surface. These data were used to assess a cosolvent model. Decreased adsorption of dichlorvos was observed at an initial pH of 4 with increasing ionic strength. The inhibitory adsorption is attributed to the blockade of surface sites by electrolytes. In addition, electrolytes play an important role on the pH-dependent dichlorvos adsorption. It is suggested that at pH < p*H*_{pzc} (point of zero charge), dichlorvos adsorption is inhibited because electrolytes compete with dichlorvos for surface sites. At pH > p*H*_{pzc}, the adsorption density of dichlorvos decreases with increasing solution pH due to the decrease of surface group, TiOH, on the TiO₂ surface. The variation of adsorption density with temperature over the range 10°–40°C has been investigated. Results show that the reaction is controlled by enthalpy. The adsorption of dichlorvos onto the TiO₂ surface is primarily brought about by hydrogen bonding. Copyright © 1996 Elsevier Science Ltd

Key words—titanium dioxide, adsorption, dichlorvos, photocatalytic oxidation, hydrogen bonding, cosolvent effect

INTRODUCTION

The increasingly intensive and widespread use of pesticides has resulted in significant contamination of surface and ground water by these chemicals. The purification of water contaminated by pesticides has become an important environmental protection task, however, traditional water purification processes are unable to remove many organic chemical contaminants. Among known treatment techniques biodegradation is probably the most frequently used, however, toxic compounds are often lethal to microorganisms which renders the biological method unapplicable (Dillon, 1981; Moore *et al.*, 1989; Bahnemann *et al.*, 1991). A number of recent publications have addressed the destruction of pesticides by photocatalytic degradation using a semiconductor as a photocatalyst, and have shown that photocatalytic degradation is a promising method for the removal of toxic chemicals (Pelizzetti *et al.*, 1989; Terzian *et al.*, 1991; Tseng *et al.*, 1991; Lu *et al.*, 1993).

Dichlorvos or DDVP (2,2-dichlorovinyl-*o,o*-dimethyl phosphate) was commercially manufactured in 1961 and used as an insecticide to protect stored

product and crops (WHO, 1989). The insecticide may be released into the environment during its application and disposal, and biological processes hardly degrade this insecticide. Recently, several authors have reported that dichlorvos can be degraded with UV-illuminated TiO₂ suspensions with a first-order rate behavior. The final degradation products are Cl⁻, PO₄³⁻, H⁺ and CO₂ (Harada *et al.*, 1990; Lu *et al.*, 1993). With regard to the degradation pathways of organic pollutants, several mechanisms have been proposed to account for the initial steps of semiconductor mediated photodegradation of aliphatic and aromatic organics. Direct charge transfer from the semi-conductor to the dissolved molecule has been proposed as one of the important reaction steps (Davis and Huang, 1990a,b; Minero *et al.*, 1992).

In a previous study, the photodegradation of dichlorvos by UV-illuminated TiO₂. Lu *et al.* (1993) have reported that the rate of dichlorvos oxidation follows a Langmuir–Hinshelwood expression. This prompted us to study the adsorption characteristics of dichlorvos onto TiO₂. Similar results have been reported on the importance of adsorption reaction to photocatalytic oxidation process (Davis and Huang, 1990a,b; Minero *et al.*, 1992). Moreover, information on the adsorption of dichlorvos adsorption is not

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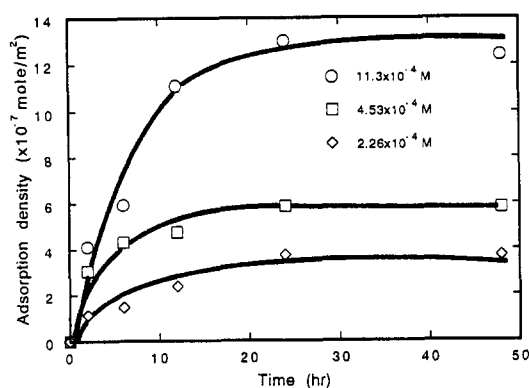


Fig. 1. Rate of dichlorvos adsorption. Experimental conditions: ionic strength, 0.1 M NaClO₄; temperature, 30°C; TiO₂, 10 g/l; initial pH, 4.0.

available. The objects of this research are: (1) to investigate the adsorption of dichlorvos onto TiO₂ surface, (2) to demonstrate the effects of pH, cosolvent, temperature, and ionic strength on the adsorption of dichlorvos onto hydrous TiO₂ surface, and (3) to propose adsorption mechanisms for dichlorvos onto hydrous TiO₂.

MATERIALS AND METHODS

All solutions and suspensions were prepared from 18 ΩM/cm resistivity water (Millipore Corp.). TiO₂ was obtained from the Degussa A. G. (Frankfurt, Germany). According to the information provided by the manufacturer, this semiconductor has a specific surface of 50 ± 15 m²/g and is mostly in the anatase form. The TiO₂ was allowed to equilibrate for 1 week in water in order to assure complete hydrolysis before adsorption experiments. Dichlorvos (96.33% purity, Bayer Japan Ltd) was used without further purification. The dichlorvos solution was prepared by stirring in water at room temperature. The solution was then filtered and standardized by a gas chromatograph. Sodium perchlorate (Merck, >99%) was used for ionic strength adjustment since perchlorate ion exhibits less effect on dichlorvos adsorption and photodegradation (Abdullah *et al.*, 1990; Lu *et al.*, 1993). The following reagents were purchased from Merck A. G., and used as received: methanol (>99.8%), acetone (>99.5%), sodium chloride (>99.5%), perchloric acid (70%), acetic acid (>99.8%), sodium acetic acid (99.5%), sodium bicarbonate (>99.5%).

Zeta potential measurements of TiO₂ were carried out by a Zeta-Meter System 3.0 zeta meter (Zeta-Meter Inc., New York). In determining the pH_{pzc} (point of zero charge) of TiO₂, 10 g/l of TiO₂ powder was dispersed in 1 l NaClO₄ solution at the desired concentration. While the suspensions were being stirred with continuous bubbling of N₂ gas to remove O₂, the initial pH was measured and recorded. The solution pH was then adjusted with HClO₄ or NaOH to cover a range from pH 3 to 10. The zeta potential of the TiO₂ surface with or without being adsorbed was carried out after equilibrating the TiO₂ in the corresponding solution by shaking for 24 h. Adsorption experiments were conducted in polypropylene flasks with screw covers using 10 g/l TiO₂ in a total of 100 ml solution. Caution was exercised to prevent any light impingement on the flasks so as to minimize any photocatalytic degradation reactions. For studying the effect of pH, buffer solutions were used. A series of buffers, CH₃COONa/CH₃COOH and NaHCO₃/

HClO₄, were used to maintain constant pH; the ionic strength of buffers was 0.1 M. In a separate experiment, the pH was also adjusted by NaOH and HClO₄ in the NaClO₄ solution to investigate the influence of pH on dichlorvos adsorption. pH values were measured with a Sontex 3000A pH meter equipped with a glass electrode and reference electrode against NBS pH buffers. Except for investigating the effect of ionic strength on dichlorvos adsorption, an ionic strength of 0.1 M (NaClO₄) was used. To obtain the adsorption isotherm, samples were allowed to equilibrate by shaking overnight for *ca* 24 h on a shaker. At the end of a 24 h period, the equilibrium pH was recorded. For adsorption kinetics, the experimental procedures were essentially the same as described, except that samples were taken periodically. The amount of dichlorvos adsorbed was determined by the concentration difference between the final and the blank. Before measurement, suspensions were filtered with Gelman 0.2 μm microfilters to collect the filtrates. Dichlorvos was extracted by adding 5 ml each of the filtrate and hexane to a 20 ml test tube then mixed vigorously for 3 min. The water layer containing the insecticide was extracted twice more. The extracts were dried and combined by passing through anhydrous sodium sulfate. The concentration of dichlorvos was determined with a gas chromatograph (Hewlett Packard 5890 II) equipped with an electron capture detector and a 15 m × 0.53 mm PTE-5 (Supelco Corp.) column.

RESULTS

Rate of adsorption

Figure 1 shows the rate of dichlorvos adsorption onto hydrous TiO₂ surface. Generally, adsorption is rapid. After *ca* 24 h, an equilibrium adsorption is reached. It is also noteworthy that the solution pH varies as a function of equilibrium time and is proportional to the amount of dichlorvos adsorbed (Fig. 2).

Adsorption from solvent-water system

All experiments were performed at a total ionic strength of 0.1 M (as NaClO₄) with or without methanol or acetone at 30°C. Methanol is a protic solvent with hydrogen bonding character. Acetone, less polar than methanol, is a dipolar aprotic solvent that cannot act as a hydrogen bond donor (Loudon, 1988; Zachara *et al.*, 1988). The presence of organic

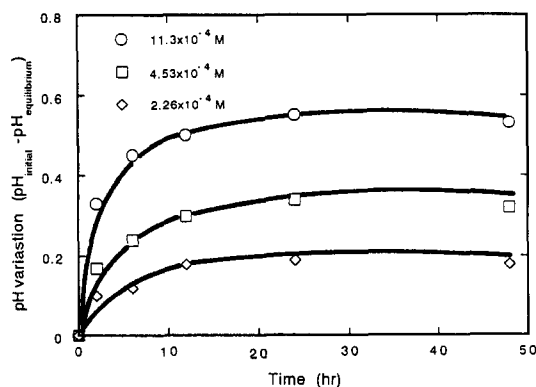


Fig. 2. Changes in pH during dichlorvos adsorption. Experimental conditions: ionic strength, 0.1 M NaClO₄; temperature, 30°C; TiO₂, 10 g/l; initial pH, 4.0.

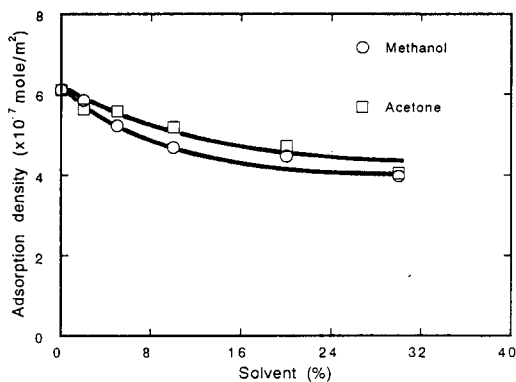


Fig. 3. Adsorption of dichlorvos onto TiO_2 in the presence of cosolvent. Experimental conditions: initial [dichlorvos] = 4.53×10^{-4} M; ionic strength, 0.1 M NaClO_4 ; temperature, 30°C; TiO_2 , 10 g/l; initial pH, 4.0.

solvents (methanol and acetone) decreases dichlorvos adsorption on hydrous TiO_2 surface (Fig. 3). Results also indicate that methanol appears to inhibit dichlorvos adsorption to an extent slightly greater than acetone.

Effect of temperature

Temperature is an important factor in controlling dichlorvos adsorption onto hydrous TiO_2 . The electrostatic characteristics of the solid-liquid interface are a function of temperature (Fokkink *et al.*, 1990). The adsorption isotherm for dichlorvos onto hydrous TiO_2 was measured as a function of temperature (10°, 20°, 30° and 40°C). Figure 4 shows that the amount of dichlorvos adsorbed increases with increasing temperature.

Effect of NaClO_4 and $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$

The adsorption experiments were conducted in distilled water and NaClO_4 solution at different concentrations ranging from 0.0 to 0.25 M. Figure 5 shows the extent of dichlorvos adsorption as a func-

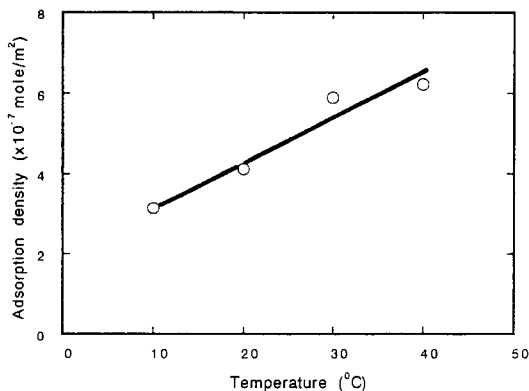


Fig. 4. Effect of temperature on dichlorvos adsorption. Experimental conditions: initial [dichlorvos] = 4.53×10^{-4} M; ionic strength, 0.1 M NaClO_4 ; TiO_2 , 10 g/l; initial pH, 4.0.

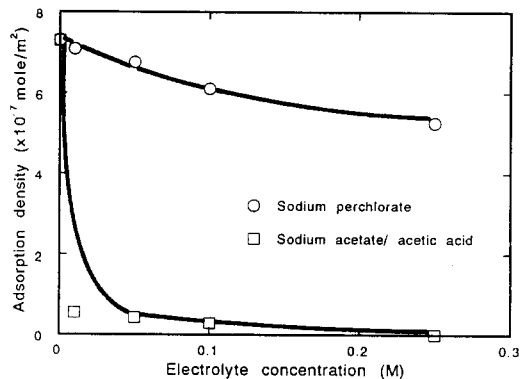


Fig. 5. Effect of electrolytes on dichlorvos adsorption. Experimental conditions: initial [dichlorvos] = 4.53×10^{-4} M; temperature, 30°C; TiO_2 , 10 g/l; initial pH, 4.0.

tion of ionic strength at initial pH of 4.0. As the concentration of NaClO_4 increases from 0 to 0.25 M, the extent of adsorption decreases by 26%. In order to study the effect of buffer on dichlorvos adsorption, $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ was chosen. Dichlorvos adsorption is almost negligible at a buffer concentration of 0.25 M (Fig. 5). The amount of dichlorvos adsorbed is diminished by as much as 70–100% in the presence of $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ at concentrations from 0.01 to 0.25 M. Results indicate that ClO_4^- is indeed more inert than CH_3COO^- as dichlorvos adsorption is less inhibited in NaClO_4 than in CH_3COONa solution. Many researchers have also reported the effect of inorganic electrolytes on photocatalytic degradation (Abdullah *et al.*, 1990; Tseng *et al.*, 1991; Lu *et al.*, 1993). Little change in oxidation rates was observed in the presence of ClO_4^- . It is generally accepted that ClO_4^- has the least effect in blockading the active surfaces of TiO_2 .

Effect of pH

According to the electrical double layer theory, the relation between potential at the distance x from the surface, ψ , and surface potential (ψ_0) is

$$\ln \left[\tanh \left(\frac{zF\Psi}{4RT} \right) \right] = \ln \left[\tanh \left(\frac{zF\Psi_0}{4RT} \right) \right] - \kappa x, \quad (1)$$

where z is the sign and magnitude of ionic charge; F is the Faraday constant; ψ is the electrical potential at distance x ; R is the gas law constant; T is the absolute temperature; ψ_0 is the surface potential; κ is the Debye-Hückel parameter; x is the distance from the surface of the colloid. The electrolyte concentration is present through its effect on the parameter κ (nm^{-1}), which can be written:

$$\kappa = 3.092I^{1/2} \quad (2)$$

for water at 30°C. Here I is the ionic strength (M). From equation (2), it is possible to calculate the surface potential at different pH values. The equations describing distribution of charge and potential for the Gouy-Chapman model are

$$\sigma_d = -0.1174C^{1/2} \sinh\left(\frac{zF\Psi_0}{2RT}\right) \quad (3)$$

$$\sigma_0 + \sigma_d = 0, \quad (4)$$

where σ_d is the charge density of the diffuse layer; C is the electrolyte concentration; σ_0 is the surface charge density. From equations (4) and (5), surface charge density is obtained. Besides, the surface concentration of proton $\{H^+\}$ is related to its bulk phase quantity, $[H^+]$, by the Boltzmann equation:

$$\{H^+\} = [H^+] \exp\left(\frac{-F\Psi_0}{RT}\right), \quad (5)$$

where F , ψ_0 , R and T are the Faraday constant, surface potential, gas constant and absolute temperature, respectively. According to Huang's approach (1981), the following acidity equation can be obtained:

$$\frac{1}{\{H^+\}} = \frac{N_t}{K_{a1}^{int}} \frac{1}{\sigma_+} - \frac{1}{K_{a1}^{int}}; \text{ at } \text{pH} < \text{pH}_{\text{pzc}} \quad (6)$$

$$\{H^+\} = N_t K_{a2}^{int} \frac{1}{\sigma_-} - K_{a2}^{int}; \text{ at } \text{pH} > \text{pH}_{\text{pzc}}, \quad (7)$$

where N_t is the total number of ionizable sites; K_{a1}^{int} and K_{a2}^{int} are the intrinsic constants; σ_+ and σ_- denote the surface charge density of positively and negatively charged surface, respectively. A plot of $1/\{H^+\}$ vs $1/\sigma_+$ or $\{H^+\}$ vs $1/\sigma_-$ yields intercepts and slopes from which K_{a1}^{int} , K_{a2}^{int} and N_t can be calculated. At 0.1 M NaClO₄, the K_{a1}^{int} and K_{a2}^{int} and N_t values for TiO₂ are $10^{-5.3}$, $10^{-7.5}$, 1.24×10^{14} sites/cm², respectively. From K_{a1}^{int} and K_{a2}^{int} , the pH_{pzc} of TiO₂ can also be obtained. The pH_{pzc} of TiO₂ is 6.4 based on the $\text{p}K_{a1}^{int}$ and $\text{p}K_{a2}^{int}$ values.

Buffers were used to maintain the constant pH during adsorption experiments while keeping the solution of ionic strength at 0.1 M. Figures 6 and 7 show dichlorvos adsorption as a function of pH. The adsorption density is small at acidic pH, increases to a maximum value at pH 5.5, and then decreases to an

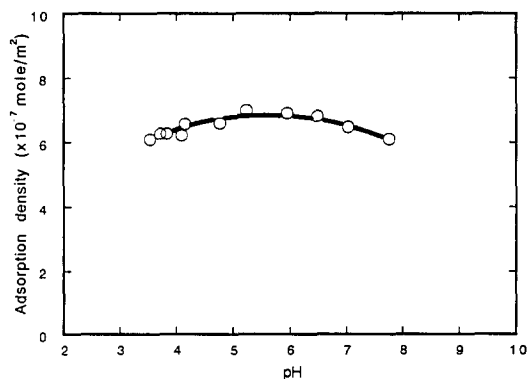


Fig. 6. Effect of pH on dichlorvos adsorption in 0.1 M NaClO₄ solution. Experimental conditions: initial [dichlorvos] = 4.53×10^{-4} M; temperature, 30°C; TiO₂, 10 g/l.

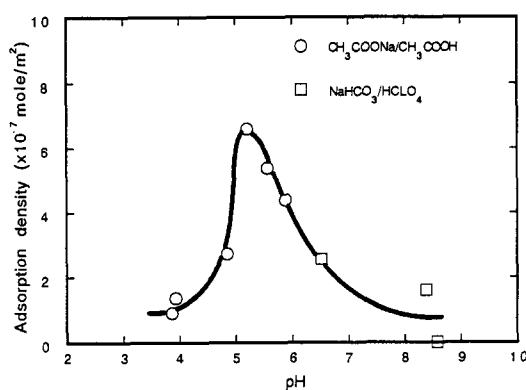


Fig. 7. Effect of pH on dichlorvos adsorption in 0.1 M buffer solution. Experimental conditions: initial [dichlorvos] = 4.53×10^{-4} M; temperature, 30°C; TiO₂, 10 g/l.

undetectable level in the alkaline pH region. This pH of maximum adsorption density is lower than the pH_{pzc} of TiO₂, 6.4.

The zeta potential of the TiO₂ surface on which dichlorvos is adsorbed and desorbed were measured for comparison (Figs 8 and 9). It is evident that dichlorvos adsorption can decrease the zeta potential of the TiO₂ surface. Generally, the suppression of zeta potential is larger in CH₃COOH/CH₃COONa solution than in NaClO₄. This means that ClO₄⁻ is more inert than CH₃COO⁻ towards the TiO₂ surface.

DISCUSSION

For adsorption onto a solid surface, the free energy ΔG_{ads}^0 is a summation of various adsorption energy components (Curtis *et al.*, 1986):

$$\Delta G_{\text{ads}} = \Delta G_e + \Delta G_i + \Delta G_c + \Delta G_{\text{id}} + \Delta G_{\text{hb}} + \Delta G_{\text{hp}}. \quad (8)$$

The subscripts e, i, c, id, hb and hp represent contribution of electrostatic interaction, ion exchange, coordination by surface metal cations, ion-dipole interactions, hydrogen bonding, and hydrophobic interactions, respectively. Since dichlorvos is an

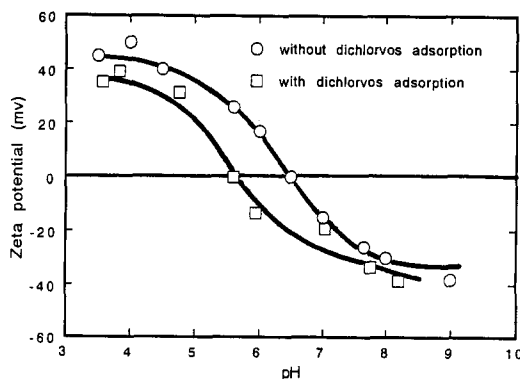


Fig. 8. Zeta potential of TiO₂ surface with or without dichlorvos adsorption in 0.1 M NaClO₄ solution. Experimental conditions: initial [dichlorvos] = 4.53×10^{-4} M; temperature, 30°C; TiO₂, 10 g/l.

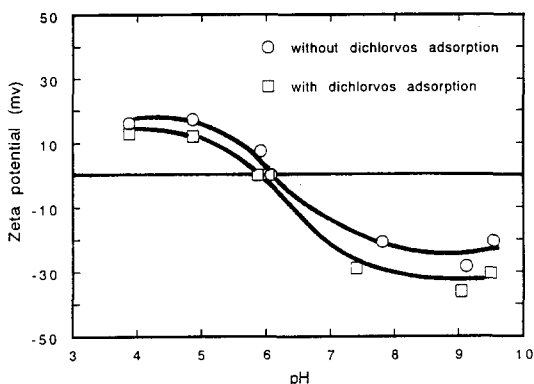


Fig. 9. Zeta potential of TiO_2 surface with or without dichlorvos adsorption in 0.1 M buffer solution. Experimental conditions: initial $[\text{dichlorvos}] = 4.53 \times 10^{-4}$ M; temperature, 30°C ; TiO_2 , 10 g/l.

unionizable compound, the first and second of these mechanisms are negligible. The ion-dipole interactions between the charged surface and the non-ionic adsorbate are also expected to be negligible in this solution. Coordination by exchanged and structural metal cations is important only when the organic ligand is a good electron donor (Lewis base) relative to water (Curtis *et al.*, 1986). Thus, the adsorption energy is contributed by hydrophobic interaction and hydrogen bonding.

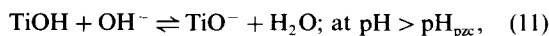
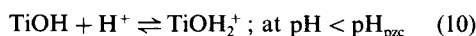
The addition of organic solvent to water enhances the interaction between the dichlorvos and the solvent resulting in a decrease in adsorption density. This may be attributed to the difference in proton affinity and solvation of these solvents. Thus, adsorption may be favorable in less polar solution due to the hydrophobic driving force. However, results show that although acetone is less polar than methanol, the inhibitory effect in acetone solution for dichlorvos adsorption is greater than that in methanol solution. The adsorption behavior in solvent can be explained by the cosolvent theory of hydrophobic compounds partitioning onto surfaces. The cosolvent reduces the adsorption of dichlorvos onto hydrous TiO_2 by enhancing solute-solvent interaction. In other words, increasing dichlorvos solubility in the mixed solvent results in a reduced driving force for adsorption. The cosolvent theory predicts a log-linear relationship between the mole-based partition coefficient (K_m) and volume fraction (f_s) in equilibrium adsorption. The basic expression for the phenomenon is:

$$\log\left(\frac{K_{m,i}}{K_{m,w}}\right) = -\alpha\sigma_s f_s, \quad (9)$$

where $K_{m,i}$ and $K_{m,w}$ are mole based partition coefficients for water/solvent mixture and solvent-free water, respectively; the coefficient α and σ_s refer to solvent-solute and solute-surface interactions, respectively (Walter and Guiseppi-Elie, 1988). Linear plots of $\log(K_{m,i}/K_{m,w})$ vs f_s , and $\alpha\sigma_s$ were obtained (Table 1). Table 1 shows that acetone has a larger $\alpha\sigma_s$

than methanol. In other words, methanol interacts with dichlorvos less strongly than acetone. In addition, the $\alpha\sigma_s$ values of methanol and acetone in the adsorption of dichlorvos on TiO_2 are smaller than that of hydrophobic organic adsorption on soil (Walter and Guiseppi-Elie, 1988), and phenols adsorption on hydrous CdS (Davis *et al.*, 1990a,b). Consequently, the hydrophobic adsorption of dichlorvos onto hydrous TiO_2 may be insignificant.

Dichlorvos is an unionizable compound. Therefore, it is assumed that the effect of pH on the adsorption of dichlorvos on TiO_2 must result from a modification of the TiO_2 surface. It is well established that upon hydration, the TiO_2 surface develops hydroxo groups which can undergo a proton association or dissociation reaction:



where TiOH_2^+ , TiOH and TiO^- are positive, neutral and negative hydrous TiO_2 surface functional groups, respectively. In NaClO_4 and $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ solution, the density of dichlorvos adsorption decreases with increasing electrolyte concentration (Figs 6 and 7). The effect of CH_3COO^- on dichlorvos adsorption is greater than that of ClO_4^- . This means that both electrolytes compete with dichlorvos molecules for adsorption sites, and CH_3COO^- is more active than ClO_4^- in competing with dichlorvos in adsorption. Figure 6 depicts the pH dependence of dichlorvos adsorption in the presence of NaClO_4 . In this situation, dichlorvos adsorption is more pronounced at $\text{pH} \sim 5.5$ than at pH values lower or higher than 5.5. A similar tendency was observed in the $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ solution (Fig. 7). However, the adsorption of dichlorvos onto the TiO_2 surface in $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ solution is inhibited more than in NaClO_4 solution. It is noteworthy that the maximum adsorption in these two solutions occurs at $ca 7.0 \times 10^{-7}$ mol/m². In another experiment, the adsorption of dichlorvos at an initial pH of 4 onto TiO_2 without background electrolyte was carried out to compare with adsorption in the presence of NaClO_4 and $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$. It is clear that the adsorption density in the absence of background electrolyte under the above experimental conditions is almost the same as that in the presence of electrolyte, namely with a maximum of 7.3×10^{-7} mol/m². In other words, the adsorption density of dichlorvos on TiO_2 surface will be maximum under the following conditions: (1) there is no electrolyte to inhibit the adsorption reaction, and (2) electrolytes do not affect

Table 1. Values for $\alpha\sigma_s$ in the cosolvent adsorption model

Adsorbate	Solvent	$\alpha\sigma_s$
dichlorvos	acetone	1.13
	methanol	0.95

Table 2. Thermodynamic parameters for the adsorption of dichlorvos on hydrous TiO₂

Temp. (°C)	ΔG_{ads} (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol)
283	-50.5	58.1	382
293	-53.7	58.1	382
303	-58.4	58.1	382
313	-61.7	58.1	382

the adsorption reaction at the pH_{pzc} of TiO₂. Therefore, it is suggested that the variation of adsorption density at different pHs is contributed by electrolytes at $\text{pH} < \text{pH}_{\text{pzc}}$. There is no significant difference between TiOH and TiOH_2^+ in adsorbing dichlorvos. At $\text{pH} > \text{pH}_{\text{pzc}}$, the decrease of dichlorvos adsorption is speculated to be the decrease of surface function group, TiOH , since hydrogen binding is the primary mechanism for dichlorvos adsorption.

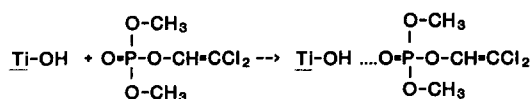
An attempt was made to calculate the change of free energy of adsorption by the following equation (Crisp, 1956):

$$\Delta G_{\text{ads}}^0 = -RT \ln \frac{K}{\tau}, \quad (12)$$

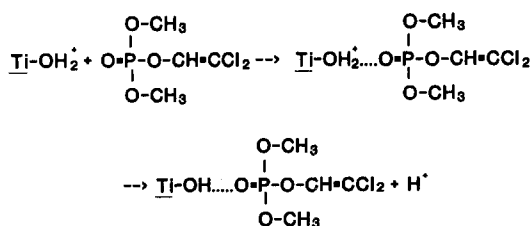
where R is the universal gas law constant, T is the absolute temperature, K is the partition constant, and τ , assumed to be 5.0×10^{-10} m, is the free space available in the direction perpendicular to the solid surface (Crisp, 1956). According to the Gibbs equation, the free energy of adsorption, ΔG_{ads} , is given by (Chattoraj and Birdi, 1984):

$$\Delta G_{\text{ads}} = \Delta H - T\Delta S, \quad (13)$$

where ΔH is enthalpy and ΔS is entropy. A plot of ΔG_{ads} vs T yields ΔH and ΔS (Table 2). The results show that dichlorvos adsorption is mostly controlled by enthalpy. Our findings agree with that reported by Mehrian who has studied the adsorption of tetrabutylammonium nitrate (TBAN) on AgI (Mehrian *et al.*, 1991). AgI is a hydrophobic substance and the adsorption of TBAN onto AgI surface is brought by electrostatic attraction and hydrophobic bonding. The contribution from hydrophobic bonding to adsorption takes place at a maximum temperature, T_{max} and T_{max} depends on the nature and the state, i.e. free or adsorbed, of the organic adsorbate. In the present experiment, the adsorption density of dichlorvos increases with increasing temperature. This may be attributed to the decrease in enthalpy as temperature increases due to increasing randomization of the water structure (Fokkink *et al.*, 1990). However, as discussed above, hydrophobic interaction is not responsive for dichlorvos adsorption. In addition, Zeltner *et al.* (1986) have shown that proton dissociation on oxide surface (i.e. $\text{MOH}_2^+ \rightleftharpoons \text{MOH} + \text{H}^+$) is an



Scheme 1.



Scheme 2.

endothermic reaction. It is seen that the amount of TiOH increases with increasing solution temperature. Since adsorption of dichlorvos onto hydrous TiO₂ surface is favorable at the TiOH sites, increasing solution temperature will promote the efficiency of the dichlorvos adsorption. Thus, the adsorption of dichlorvos onto TiO₂ surface can be proposed to be an enthalpy-driven process as proton dissociation on TiO₂ is endothermic.

It is, therefore, concluded that hydrogen bonding is the dominant mechanism for dichlorvos adsorption onto TiO₂. Since chloride can only form weak hydrogen bonds, the adsorption mechanism is as proposed in Scheme 1. Figure 2 shows that pH decreases upon dichlorvos adsorption with a tendency which is identical to that of dichlorvos adsorption rate. The zeta potentials of TiO₂ surface decreased upon dichlorvos adsorption at different pHs (Figs 8 and 9). These findings imply that H^+ is released from the surface following dichlorvos adsorption. In this case, the adsorption of dichlorvos onto TiO₂ surface may be hypothesized as shown in Scheme 2.

CONCLUSIONS

The presence of cosolvent, such as methanol and acetone, can affect the adsorption reaction by a cosolvent effect. The variation of adsorption density at different pHs is contributed to by electrolyte inhibition and the decrease of surface function group, TiOH . The extent of dichlorvos adsorption increases with temperature indicating that the adsorption is mostly controlled by enthalpy. The results demonstrate that hydrogen bonding formation is the primary force bringing about dichlorvos adsorption.

Acknowledgement—The research was supported by the National Science Council of the Republic of China (Grant NSC 82-0410-E-009-066).

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