

Adsorption and interaction of oxamyl with kaolinites

O P BANSAL, MAHESH PRASAD and S N SRIVASTAVA*

Chemical Laboratories, D.S. College, Aligarh 202 001, India

* Chemistry Department, Agra College, Agra, 282 002, India

MS received 29 August 1979 ; revised 2 May 1980

Abstract. The adsorptive behaviour of oxamyl with H-, Na- and Ca-kaolinites was studied. The effect of time on adsorption showed that the process was diffusion controlled. Kinetic studies showed that reaction was of first order. Maximum adsorption occurred at pH 6.5 (in the vicinity of pK value). The adsorption isotherms, Freundlich constants K , $1/n$ and desorption experiments provided evidence for a partly chemical adsorption and partly physical adsorption of oxamyl on clay surface, inferences on the protonation of the carbonyl oxygen of the oxamyl molecule by H^+ ions of kaolinite surface and/or the coordination of the metallic cations of kaolinite to the carbonyl oxygen of amide group found support from adsorption isotherm, x-ray and IR studies.

Keywords. Kaolinite ; adsorption isotherm ; oxamyl ; pesticide ; Freundlich isotherm.

1. Introduction

Numerous organic chemicals with a wide range of biochemical, chemical and physical properties are being introduced as pesticides and plant growth regulators in modern agriculture. Recently the behaviour of pesticides in soil has been a subject of great deal of research (Bailey and White 1960). Effective pesticidal action of organic chemicals in soil is governed by a number of factors, one of which is adsorption on soil colloids. The nature of adsorption affects the ease of movement of pesticidal chemicals, the plant availability, their persistence, degradation and toxicity. The interaction and adsorption of ionic pesticides on clay surfaces has been extensively studied (Nearpass 1971) but relatively less work has been reported on the reaction mechanism of non-ionic pesticides on soil colloids.

Clay minerals constitute the most reactive portion of soil. Clays provide heterogeneous chemical spots in the form of sorbed water around cations (Swoboda and Kunze 1968), lattice surface oxygen (Schofield and Samson 1954), electron accepting sites (Solomon 1968) and transition metals in higher valency states. Thus

an organic chemical may be adsorbed on a clay surface by ion exchange, protonation, hydrogen bonding, coordination (Russel 1965), van der Waals forces, charge transfer complexes and hemisalt formation (Tahoun and Mortland 1966).

Oxamyl (methyl-2 (dimethylamino)-N [(methylamino) carbonyl] oxy]-2-oxoethanimidothioate), a formulation of DuPont de Nemours and Co. Wilmington, Delaware, USA is a recently introduced broad spectrum non-ionic pesticide (Timmer 1974). The main objective of this work was to investigate the mechanism of adsorption and interaction of oxamyl with acid and base saturated kaolinites in dilute suspensions. It was considered that such a study will be useful in the efficient utilisation of the chemical both as nematocide and fungicide in kaolinitic soils.

2. Experimental

Kaolinite used in these studies was from Bath, South Carolina and was a monomineralic standard of Project No. 49 of the American Petroleum Institute. Less than 2 μm clay fraction was purified by sedimentation and centrifugation. Sodium and hydrogen-clays were prepared by Aldrich and Buchanan's (1958) method. The clay suspension was treated with NaCl and dil. HCl till the concentration of the supernatant liquid was 2N with respect to NaCl and 0.1 N with respect to HCl. This treatment was repeated and the sodium clay suspension was then washed with distilled water till no chloride was detected (with AgNO_3) and the conductivity of the suspension became constant. This suspension was stored in pyrex glassware. Hydrogen saturated kaolinite was freshly prepared from the sodium-kaolinite suspension by passing it through a column of H-Dowex-50W-X8 cation exchange resin. Calcium-kaolinite was prepared from sodium-kaolinite suspension by CaCl_2 using ion exchange technique. The clays were used for experiments immediately after preparation. The concentration of all the suspensions varied from 14.0 to 15.7 g/l. The cation exchange capacity (CEC) as determined by Ganguli's (1951) method was 106 u eq./g clay.

The effect of time on adsorption was studied by taking 10 ml of appropriate clay suspensions in their H-, Na- and Ca-forms in several glass stoppered tubes and treating with 5.0 and 15.0 ml of oxamyl solution (1000 $\mu\text{g}/\text{ml}$). The total volume was made 25 ml after adding distilled water. The samples were continuously stirred for various periods ranging between 3 to 72 hr, then centrifuged and the oxamyl in the supernatant liquid was estimated spectrophotometrically at 435 nm (Singhal *et al* 1977). The amount of oxamyl adsorbed at various intervals of time (table 1) was obtained from the amount of oxamyl added minus the oxamyl which remained in the supernatants.

The effect of the equilibrium pH on adsorption was investigated at 8 pH values ranging between 2 and 12 by adding 0.1 N HCl or 0.1 N NaOH as required. Ten ml of H-, Na- and Ca- saturated kaolinite suspensions and 5.0 and 15.0 ml of oxamyl solution (1000 $\mu\text{g}/\text{ml}$) were shaken in glass stoppered tubes for 33 hr after making the volume to 25 ml by adding distilled water. The samples were then centrifuged and oxamyl adsorbed calculated as above.

The adsorption experiments were conducted by taking 10 ml of H-, Na- and Ca-saturated kaolinite suspensions in a large number of glass-stoppered tubes adding

various amounts (0 to 15 ml) of standard oxamyl solution (1000 $\mu\text{g/ml}$), (amount of oxamyl added was 3 times of CEC), making the volume to 25 ml by adding distilled water and shaking for 33 hr at 30° and 60° C. Oxamyl in the clear centrifuged supernatant was estimated as before.

In the desorption experiment 10 ml of oxamyl complexed clays were treated with water, 1 ml of 0.1M KCl and 1 ml of 0.1 M BaCl_2 respectively, the volume made to 25 ml by adding distilled water and the samples were shaken for 33 hr, the oxamyl estimated as above. The results are shown in table 2.

For x-ray analysis the acid saturated, base saturated and complexed samples of kaolinite were oriented on glass microslides and allowed to dry at room temperature. The x-ray patterns were recorded on Philips diffraction unit at 2θ 0.4°/min, filtered CuK_α radiation being used.

For IR analysis thin self supporting films of sample were prepared by drying the kaolinite suspensions (hydrogen, sodium and calcium forms) and their complexed suspensions at room temperature on polythene sheets. The spectra of samples and of oxamyl (pure) were recorded on a Beckman IR-20 double beam spectrophotometer in the range of 4000-400 cm^{-1} .

All experiments were conducted in triplicate with suitable blanks.

Table 1. Effect of time on the reaction of oxamyl with H-, Na- and Ca- saturated kaolinites at 30° C.

Form of clay	m moles of oxamyl added per 100 g clay	Rate constant $k \times 10^4$ (min^{-1})	Half life period ($t_{1/2}$) of adsorption in hours
H-kaolinite	16.3	1.43	80.7
	48.9	1.40	82.5
Na-kaolinite	14.6	1.47	78.5
	43.8	1.46	79.1
Ca-kaolinite	15.2	1.38	83.7
	45.6	1.27	90.9

Table 2. Desorption of oxamyl by different electrolytes from the H-, Na- and Ca saturated kaolinite oxamyl complexes.

Form of clay	Oxamyl adsorbed (m mol/100 g clay)	Oxamyl desorbed (m mol/100 g clay)		
		H_2O	KCl	BaCl_2
H-kaolinite	13.4	3.3	6.2	6.2
Na-kaolinite	13.8	4.7	8.6	8.3
Ca-kaolinite	12.5	3.7	8.1	8.1

3. Results and discussion

The adsorption of oxamyl by H-, Na- and Ca-saturated kaolinites increased with time upto an asymptotic maximum after 33 hr (figure 1). Such a slow rate of attaining equilibrium indicates that the process is at least partly of chemical nature (Levi-Minzi *et al* 1976). First order rate constants (table 1) fitted to the results showed that the half time of adsorption ($t_{1/2}$) increased with increasing oxamyl concentration, suggesting a diffusion-controlled process (Bunzl *et al* 1976).

In all the cases oxamyl adsorption increased with pH upto a value of pH 6.5 and beyond this the adsorption has a tendency to decrease (figure 2). The pK value of oxamyl in distilled water, determined by the conductivity method, was 6.2. Its potentiometric titration with 0.001 M HCl and 0.001 M NaOH showed that oxamyl behaves as an ampholyte, with pK_a value 4 and pK_b 8 (figure 3). As expected, in the vicinity of pK (6.2) value maximum adsorption of oxamyl occurs. It appears that at pH value < 6.5, H⁺ oxamyl and pH > 6.5 Na⁺ oxamyl may be formed by interaction with H⁺ (from 0.1 M HCl) and Na⁺ (from 0.1 M NaOH) ions. These ion complexes are not adsorbed by the acid and base-saturated kaolinites. This proposal is supported by desorption studies. In the absence of competition from H⁺ or Na⁺ ions at pH 6.5, a direct association of the pesticide with the cations on the clay surface occurs giving maximum adsorption (Singhal *et al* 1978; Singhal and Singh 1978).

Adsorption of oxamyl on H-, Na- and Ca- saturated kaolinite suspensions (1.40–1.57% w/v) in the equilibrium concentration 0 to 2.2 mM at 30° C and 60° C yielded isotherms as given in figure 4. An examination of adsorption isotherms revealed that they were similar to class 'L' as defined by Giles *et al* (1960). Such types of isotherms have been observed where adsorption was either concentration-dependent or factors other than those related to the structural forms of the clay-water system were involved. According to Giles *et al* (1960) such types of isotherms indicate that oxamyl molecule met no strong competition from solvent for adsorption on the kaolinites. The change in orientation of convex curves pointed to the gradual saturation of adsorption sites (Giles *et al* 1974). Adsorption followed the order Na⁻ > H⁻ > Ca⁻ kaolinite. Further, with increase in temperature from 30° to 60° C there is decrease in adsorption, which may be due to increased desorption by increasing the thermal energy of adsorbate. Figure 4 also showed that change in temperature only influences the number of adsorption sites and/or affinity for oxamyl.

The results of desorption (*vide* table 2) indicate that part of the oxamyl adsorbed on the acid and base saturated kaolinites can be desorbed by water or solutions of inorganic salts, indicating a partly physical adsorption of oxamyl.

The adsorption data followed the Freundlich equation,

$$X/m = KC^{1/n} \text{ or } \ln X/m = \ln K + 1/n \ln C, \quad (1)$$

where X/m was μg oxamyl adsorbed per g clay, C was equilibrium concentration ($\mu\text{g}/\text{ml}$), $1/n$ and K were constants representing the slopes and intercept of the isotherms. A plot of $\ln X/m$ against $\ln C$ gave linear curves in all cases at both the temperatures (figure 5). The values of $1/n$ and K ($C = 1.0 \mu\text{g}/\text{ml}$) were estimated from the Freundlich plots (figure 5) and are given in table 3.

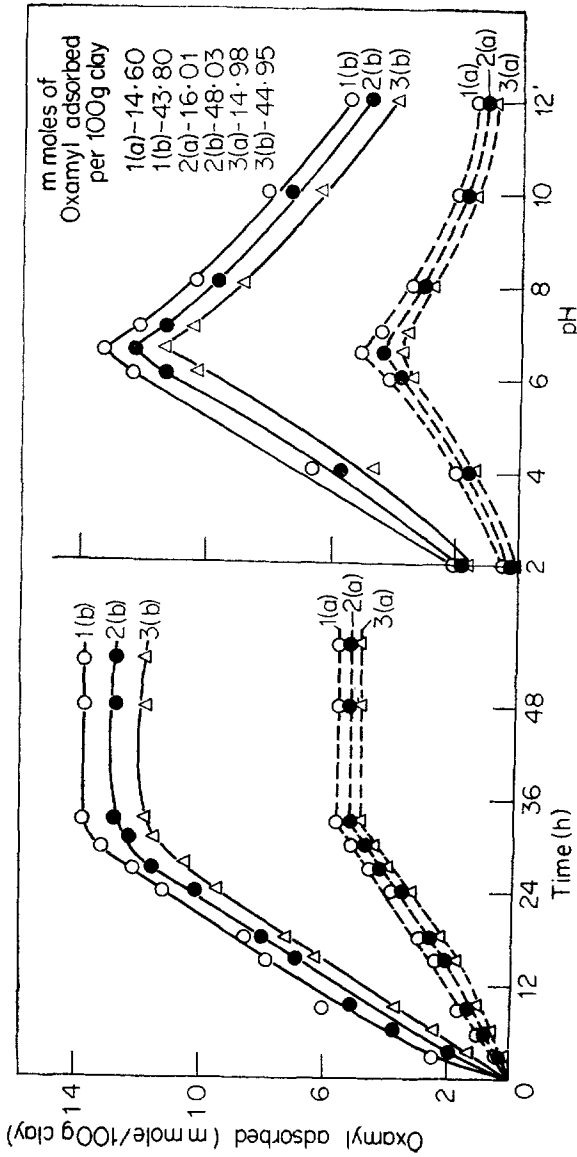


Figure 1.

Figure 1. Effect of time on the adsorption of oxamyl by kaolinites (●) hydrogen form, (○) sodium form, (△) calcium form, oxamyl added per 100 g of clay.

Figure 2. Effect of pH on the adsorption of oxamyl on kaolinites, (●) hydrogen form, (○) sodium form, (△) calcium form, oxamyl added per 100 g of clay.

Figure 2.

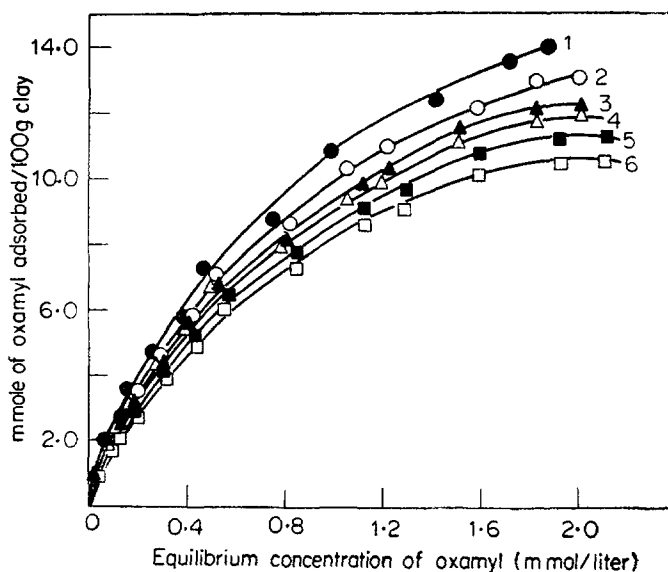


Figure 3. Adsorption isotherms of oxamyl on H(X), Na (●), Ca (○) at 30° and on H (■), Na (Δ) and Ca (□) kaolinities at 60° C.

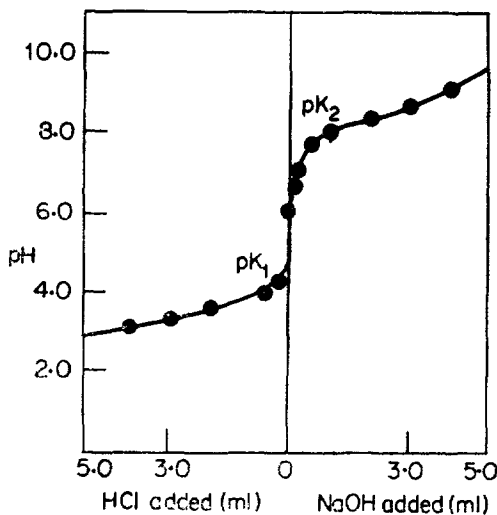


Figure 4. Variation of pH during treatment of oxamyl with acid or alkali.

The values of the sorption intensity $1/n$ were in order Na- > H- > Ca- kaolinite and decreased with increase in temperature indicating that the intensity of oxamyl adsorption was in order Na- > H- > Ca- kaolinities. The values of $1/n$ at both the temperatures in all cases was less than unity, indicating a curvilinear type of isotherms. The curvilinear isotherms indicate an exponential decrease in the sorption energy as the proportion of adsorption sites saturated with oxamyl became larger

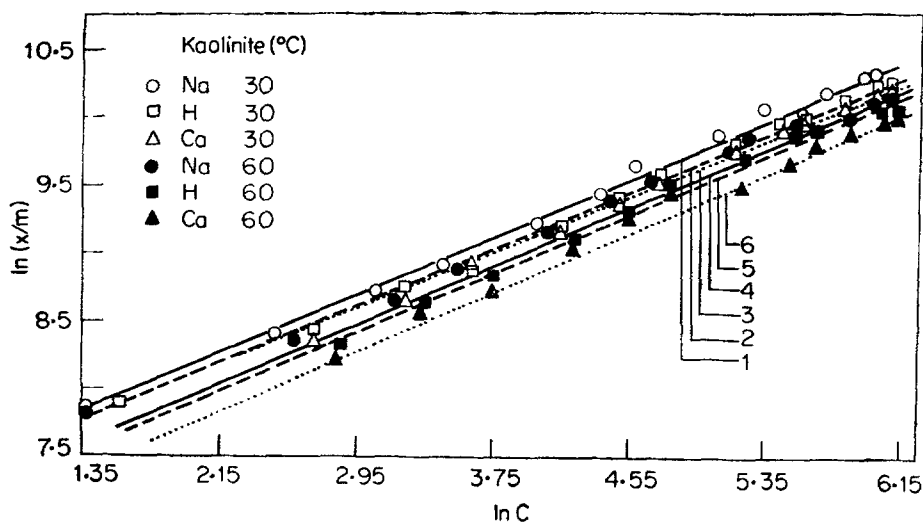


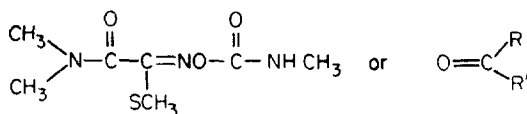
Figure 5. Freundlich isotherm of oxamyl adsorption on H(□), Na(O), Ca(Δ) at 30° C and on H(■), Na (●) and Ca (▲) kaolinites at 60° C.

Table 3. Freundlich constants for adsorption of oxamyl on H- and Ca- kaolinites at 30° and 60° C.

Nature of kaolinite	Temperature (° C)	Freundlich constants	
		K	1/n
Hydrogen	30	1096	0.54
	60	1079	0.50
Sodium	30	1140	0.56
	60	1129	0.52
Calcium	30	1042	0.52
	60	1005	0.48

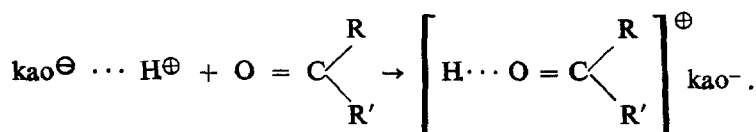
(Bache and Williams 1971). This found further confirmation from the values of *K*, the Freundlich constant. The higher value of *K* at 30° than at 60° C in all cases pointed to a decrease in the adsorption of the pesticide with rise in temperature i.e. the interaction of oxamyl with Na-, H- and Ca- kaolinites was of an exothermic nature and followed the order Na-kaolinite > H-kaolinite > Ca-kaolinite.

Oxamyl, is a non-ionic neutral molecule, possessing a slight polarity at the nitrogen and oxygens of amide group due to electromeric and resonance effects. These nitrogens and oxygens of amide groups may thus interact with suitable spots on



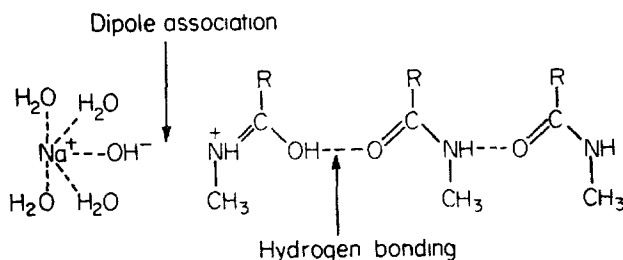
Scheme-I

the kaolinites. It appears that on H-saturated kaolinite oxamyl is adsorbed by protonation on the edges and basal planes as follows



The base saturated kaolinite carry exchangeable cations which provide excellent sites for linking of polar organic molecules through a direct coordination reaction (Tahoun and Mortland 1966), to the oxygen of the carbonyl group (Fraenkel and Franconi 1960) or *via* protonation due to dissociation of water molecule in contact with exchangeable cation (Mortland 1966; Fripiat *et al* 1965; Fraenkel 1974) as reported elsewhere (Bansal and Bansal 1980).

The desorption data indicate that some physical adsorption also occurs. The physical adsorption may occur through formation of hydrogen bonds between the protonated molecules on the mineral surface and neutral oxamyl molecules (2) as postulated by Stutzmann and Siffert (1977).



Scheme II

X-ray diffraction analysis indicates basal expansion of 0.20, 0.18 and 0.22 nm during interaction of oxamyl with H-, Na- and Ca- saturated kaolinites respectively, which showed that only the external basal surfaces and the lateral edges and corner sites of kaolinites were available for interaction with oxamyl.

IR studies confirm the above propositions. A shift in the frequency from 1670 to 1655 cm^{-1} ($>\text{C}=\text{O}$ stretching) and from 1680 to 1685 cm^{-1} ($\text{C}=\text{N}$ stretching) during the interaction of kaolinite in the hydrogen form suggests protonation of the carbonyl oxygen. Spectral shifts from 1670 to 1650 cm^{-1} ($>\text{C}=\text{O}$ stretching) and from 1680 to 1690 cm^{-1} ($\text{C}=\text{N}$ stretching) during interaction of the sodium

and calcium forms of kaolinite with oxamyl support coordination and/or protonation of pesticide molecule to Na⁺ or Ca²⁺ ion through the oxygen of the carbonyl group.

Acknowledgement

Authors are thankful to Prof. S S Gupta for providing laboratory facilities and encouragement.

References

- Aldrich D G and Buchanan J R 1958 *Soil Sci. Soc. Am. Proc.* **22** 281
Bache B W and Williams E G 1971 *J. Soil Sci.* **22** 289
Bailey G W and White J L 1970 *Residue Rev.* **32** 29
Bansal O P and Bansal V 1980 *J. Agric. Sci.* **94** 557
Bunzl K, Schmidt W and Sansoni B 1976 *J. Soil Sci.* **27** 32
Fraenkel A and Franconi C 1960 *J. Am. Chem. Soc.* **82** 4478
Fraenkel M 1974 *Clays Clay Miner.* **22** 435
Fripiat J J, Jelli A, Poncelet G and Andre J 1965 *J. Phys. Chem.* **69** 2185
Ganguli A K 1951 *J. Phys. Coll. Chem.* **55** 1417
Giles C H, MacEwan T H, Nakhwa S N and Smith D 1960 *J. Chem. Soc.* p. 3973
Giles C H, Smith D and Huitson A 1974 *J. Colloid. Interface Sci.* **47** 735
Levi-Minzi R, Soldatini G F and Riffaldi R 1976 *J. Soil Sci.* **27** 10
Mortland M M 1966 *Clays Miner.* **6** 143
Nearpass D C 1971 *Soil Sci. Soc. Am. Proc.* **35** 64
Russel J D 1965 *Trans Faraday Soc.* **61** 2284
Schofield R K and Samson H R 1954 *Discuss. Faraday Soc.* **18** 135
Singhal J P, Khan S U and Bansal O P 1977 *J. Agric. Food Chem.* **25** 377
Singhal J P and Singh N 1978 *Soil Sci.* **123** 301
Singhal J P, Khan S U and Bansal O P 1978 *Aust. J. Chem.* **31** 2151
Solomon D H 1968 *Clays Clay Miner.* **16** 31
Stutzmann T H and Stiffert B 1977 *Clays Clay Miner.* **25** 392
Swoboda A R and Kunze G W 1968 *Soil Sci. Soc. Am. Proc.* **32** 806
Tahoun S and Mortland M M 1966 *Soil Sci.* **102** 248
Timmer L W 1974 *Plant Dis. Res.* **58** 882