



Adsorption and desorption of three carbamate pesticides by illite, kaolinite and humic acid-clay complexes

O.P. Bansal

Chemistry Department, D.S. College, Aligarh-202001 (U.P.), India

E-mail: drop1955@gmail.com

ABSTRACT

In soils organic matter and clay minerals are often so associated that it is not clear that how the presence of organic matter influences the sorptive process of clay minerals. So, in order to factor and quantify component contributions of mineral fractions and humic acid phase to the sorption of pesticides on clay minerals, adsorption and desorption of three carbamate pesticides oxamyl (I), S-Ethyl-N-(methyl carbamoyl)-oxythio acetimidate (II) and N-Phenyl (ethyl cabamoyl) propylcarbamate (III) by Na^+ , Ca^{2+} saturated illite, kaolinite and humic acid-clay complexes were investigated by batch experiments. The adsorption was more on illite than kaolinite and followed the order pesticide III > I > II, adsorption on Na-saturated clay samples was more than Ca-saturated. The presence of humic acid enhances the pesticide adsorption. A composite model for estimating pesticide adsorption, which assumes mineral and organic matter fraction individually as adsorbent phases, predicted sorption within a factor of 0.75-1.4 times the measured value. The desorption data indicated that humic acid retains more pesticide than clay mineral. XRD patterns showed that humic acid is restricted to the external surfaces of clay tactoids, denoting that clay mineral fractions in soils including those with organic coatings play an important role in the retention of polar carbamate pesticides.

Key words: Clay minerals; Freundlich isotherms; organic matter; oxamyl; pesticides

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INTRODUCTION

Carbamate pesticides, a new horizon, agrochemicals are widely used as insecticides and herbicides in home, garden and agriculture, as they are less persistent, possess less mammalian toxicity and may be used against those pests which have acquired immunity against organochlorine and organophosphate pesticides. Clay mineral can strongly adsorb certain aqueous phase organic compounds containing polar functional groups, suggesting the potential contributions of clay minerals to the retention of organic contaminants and pesticides in soils and sub soils [1-3]. Previous studies [4-7] have showed that polar carbamate pesticides were adsorbed on clay surfaces via protonation and/or coordination between exchangeable cations of clay and oxygen of $>C=O$ group of pesticides, hydrogen bonding and dipole association or vander Waal's forces with or without water bridges of water molecules surrounding cations. Bansal [8] reported that adsorption of oxamyl on montmorillonites saturated with different cations decreased in the order $Al > Fe > Li > Na > K > Cs$. Organic amendments are frequently added to soils as economic and environmentally acceptable means of promoting soil health, nutrition and fertility. The addition of organic amendments in soil might also lead to an increase in pesticide adsorption [9], thus decreasing the pesticide leaching [10]. Several previous Studies [11,12] have attempted to identify the critical ratio of clay minerals/ soil organic matter at which sorption by clay mineral phase plays an important role. A survey of literature indicates that no such attempt has been made so far for carbamate pesticides. Organic matter and clay minerals are the two most important soil components which affects retention of soil applied pesticides [13-14]. The potential contributions of these components have been measured individually, however in soils organic matter and clay minerals are associated. The influence of soil organic matter on the sorptive properties of the clay minerals is not fully understood. The objectives of this work is to study the influence of soil organic matter on the sorptive properties (e.g. availability) of the clay minerals and to evaluate relative contribution of the mineral fraction and humic acid phase to sorption and desorption of three polar carbamate pesticides, oxamyl{methyl-2-(dimethylamine)-N-[(methylamino)carbonyloxy]-2-oxoethanimidothioate} (I); {S-ethyl-N-ethyl(carbamoyl)oxy} thioacetimidate; $CH_3NHCON=C(CH_3)(SC_2H_5)$ (II) and {N-Phenyl (ethylcarbamoyl)propylcarbamate: $C_6H_5NHCOOCH(CH_3)CONHC_3H_7$ } (III) on Na^+ and Ca^{2+} saturated illite, kaolinite and the corresponding humic acid-clay complexes.

The studies were made during Sep 13 to dec 13 in the research laboratory of D.S.College, Aligarh (India)

MATERIALS AND METHODS

The $<2 \mu m$ fraction of illite (from Morris, Illinois) and kaolinite (from Bath South Carolina) were purified by sedimentation and centrifugation. The sodium form of these clay minerals was obtained by washing three times with 1M NaCl followed by washing five times with deionized water. Homoionic Ca^{2+} saturated clay samples were prepared from the Na-form by ion exchange techniques. The humic acid (HA) was obtained from Aldrich Chemical Co. Inc. HA-clay samples were prepared by dissolving 2 g humic acid in 1L of 0.5M NaCl or $CaCl_2$ solution (pH 6.0-6.2), followed by mixing with 1L of Na^+ or Ca^{2+} illite or kaolinite for 1 week, followed by centrifugation. The humic acid-clay complexes obtained by centrifugation were mixed with 0.5M NaCl and $CaCl_2$ solution (three to four times) separately to saturate the cation exchange sites in humic acid, and washed several times with double distilled water until neither light brown colored humic substances in supernatants nor humic acid particulates accumulating on the top of clay fractions after centrifugation were visualized. The humic acid-clay complexes were analyzed for organic C-contents by Walkley and Black method [15]. The pH of the suspensions were 6.3-6.4 for Na^+ and Ca^{2+} saturated illite and 6.2-6.4 for kaolinite and 5.2-5.3 for humic acid-clay complexes. The concentration of suspensions varied from 15.0 to 12.5 $g L^{-1}$. The CEC of clay was 24 C mol $(p^+) kg^{-1}$ for illite and 10.6 for kaolinite. The totalsurface area was 300-330 m^2/g for Na- and Ca-saturated illite and 170-190 m^2/g for kaolinite. The surface area was 320 and 350 m^2/g^{-1} for Na-humic acid-illite and Ca- humic acid-illite complexes and 180 and 200 m^2/g for Na and Ca-humic acid kaolinites.

Adsorption experiments were conducted using 10 mL of the appropriate clay suspensions (with no initial amount of carbamate pesticides) in a large number of glass stoppered tubes, adding various amounts of standard pesticide solution (0-15 mL of 2500 $\mu g mL^{-1}$ for illite and 1000 $\mu g mL^{-1}$ for kaolinite), and making up the volume to 25 mL with water. After shaking for 30 h at $25 \pm 1^\circ C$ (preliminary studies indicated that equilibrium was attained in $<27h$) the suspensions were centrifuged for 15 min at 13000rpm and aliquots were taken for estimation. The supernatants were estimated spectrophotometrically at 435 nm as copper dithiocarbamate [16] using systronics spectrophotometer. The detection limits were 10 $\mu mole L^{-1}$. The amount of pesticide adsorbed was obtained from the amount added minus that remaining in the supernatants.

In the desorption experiments 10 mL of pesticide-complexed clay suspensions were treated with water, 1 mL of 0.1M KCl and 0.05M $BaCl_2$. The volume was adjusted to 25 mL with water and the sample was shaken for 30 h. the pesticide in solution was estimated as cited above.

For X-ray analysis, the samples collected after adsorption were oriented on glass slides and allowed to dry at room temperature. The X-ray patterns were recorded on a General Electric XRD6 diffraction unit at 2θ $0.4^\circ/min$, Ni-filtered CuK_α radiation being used.



RESULTS AND DISCUSSION

The empirical Freundlich relationship can be used to describe the carbamate pesticide adsorption results on clay samples. The linear form of this equation is $\log X/m = \log K + 1/n \log C_e$. Where X/m is the amount (mg kg^{-1}) of pesticide adsorbed by clay or humic acid-clay complexes, C_e is the equilibrium concentration in solution (mg L^{-1}), K ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{kg}^{-1}$), K is the Freundlich adsorption coefficient and $1/n$ is a descriptor of isotherm curvature. The results from Freundlich equation fittings are given in Table 1. The value of $1/n$ during adsorption of three carbamate pesticides on Na- and Ca-saturated illite and kaolinite were less than unity indicating a convex or 'L' type of isotherm [17,18] [Fig 1a and 1b] and were higher for illite than kaolinite. This kind of isotherm may arise because of minimum competition of solvent for sites on the adsorbing surface. The slope of the isotherm steadily decreases with the rise in solute concentration, because vacant sites become less accessible with the progressive covering of the surface. The Fig. 1 denotes that adsorption of all the studied carbamate pesticides on illite surface was more than kaolinite surface. The curvilinear isotherm suggests that the number of available sites for the adsorption become a limiting factor. The constants K and $1/n$ provide rough estimates of the adsorbent capacity and intensity of adsorption [19] respectively. The values of $1/n$ and K (Table 1) also indicate that the intensity of the carbamate pesticides adsorption was in the order pesticide III > I > II. The adsorption of all the three carbamate pesticides on both the clay surfaces follows the order Na-clay > Ca-clay which may be due to larger enthalpy of hydration of Ca^{2+} (as compared with Na^+) which inhibits direct interactions between pesticide functional group and the exchangeable cation [20, 21] also larger hydration sphere around Ca^{2+} reduces hydrophobic interactions between the surface and pesticide. The values of Freundlich constant K also support the order of adsorption was illite > kaolinite.

The nature of pesticide adsorption isotherms for clay and humic acid-clay complexes are given in Figs. 1. The isotherms were non-linear. The adsorption of carbamate pesticides on clay HA samples were more than on clays. It may be due to the interaction of pesticides with organic matter via multiple bonding mechanisms [22, 23].

Clay minerals and organic matter both contribute to the sorption of soil-applied pesticides. The potential contributions of these components have been measured individually. However in soils, organic matter and clays are often associated.

A common procedure for factoring individual sorption contributions in complicated systems like soil involves sequential removal of various components and subsequent sorption measurements. A commonly held viewpoint was that the mineral fraction of most soils was not available for pesticide sorption due to blockage by organic carbon and/or reduction in organic carbon availability when incorporated into soil.

In order to factor and quantify component contributions of mineral fractions and humic acid phase to the sorption of pesticides following relationship was used (assuming that mineral and humic acid phases contribute independently to pesticide sorption) by modifying empirical Freundlich equation with the help of Karickhoff [24] concept.

$$C = C_{\text{clay}} + C_{\text{om}} = f_{\text{clay}} K_{\text{clay}} C_e^{1/n_{\text{clay}}} + f_{\text{om}} K_{\text{om}} C_e^{1/n_{\text{om}}}$$

where C , C_e , K and $1/n$ are the same parameters defined in Freundlich equation, f (g g^{-1}) is the mineral or organic fraction in the humic acid clay complexes, and $f_{\text{clay}} + f_{\text{om}} = 1$. The subscripts of clay and om refer to the reference clay and the associated humic acid phase. The Freundlich equation parameters for clays humic acid (obtained by preliminary studies) and HA-clay complexes are given in Table 1. The humic acid phase (f_{om}) was estimated by dividing the measured organic C content by the fractional C content of humic acid, for our studies f_{om} calculated was 0.435 the remaining mass was assumed to be the clay mineral fraction (f_{clay}). The predicted values are within a factor of 0.75 to 1.4 of the measured values for all the three pesticides on both the clay surfaces, indicating that in general adsorption by humic acid-clay complexes can be reasonably estimated by summing up their individual contributions to pesticide sorption.

Desorption results (Table 2) indicate that part of the pesticide adsorbed can be desorbed by water or solutions of inorganic salts. Desorption was in the order pesticide II > I > III. More of the pesticide was desorbed by salt solution than by the distilled water as well expected [25, 26]. Desorption in humic acid-clay complex was less than in clay only indicating that humic acid phase retains more pesticide. Retention of pesticides was significantly correlated ($r = 0.960$) with organic matter content.

X-ray diffraction analysis indicate basal expansions of 0.20 to 0.32 nm for Na- and Ca-saturated unmodified illite and kaolinite and 0.33 to 0.39 nm for Na-, Ca-saturated humic acid modified clay for all the three studied pesticides. These results indicate a flat orientation of the intercalated pesticides in monomolecular layers with formation of complexes at basal surfaces [27].

CONCLUSIONS

From these studies it may be concluded that studied carbamate pesticides sorption occurred primarily in clay interlayer and was not diminished substantially by humic acids association with the external surfaces of clay tactoids and also suggested that humic acids are restricted to external surfaces of clay tactoids. From these results it may also be inferred that Karickhoff composite model can be successfully used to study the composite effect of clay minerals and soil organic matter on the sorption of polar pesticides in soils.

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Table 1. Freundlich adsorption isotherm constants of carbamate pesticide adsorption on illite, kaolinite, humic acid and humic-acid clay complexes saturated with Na and Ca-cations.

Sorbent	Pesticide I			Pesticide II			Pesticide III		
	K	1/n	r ²	K	1/n	r ²	K	1/n	r ²
Na-illite	345	0.795	0.92	310	0.770	0.93	365	0.815	0.98
Ca-illite	320	0.755	0.90	302	0.735	0.96	335	0.780	0.98
Na-Humic acid	605	0.910	0.96	590	0.890	0.96	635	0.940	0.97
Ca-Humic acid	570	0.880	0.96	540	0.860	0.96	600	0.905	0.97
Na-Humic acid-illite	455	0.815	0.95	430	0.800	0.92	475	0.845	0.94
Ca-Humic acid-illite	425	0.785	0.95	400	0.765	0.95	445	0.825	0.94
Na-kaolinite	295	0.760	0.95	275	0.740	0.96	315	0.780	0.95
Ca-kaolinite	280	0.740	0.93	262	0.720	0.95	295	0.755	0.94
Na-Humic acid-kaolinite	400	0.775	0.96	380	0.765	0.95	430	0.800	0.95
Ca-Humic acid-kaolinite	380	0.755	0.92	365	0.745	0.93	405	0.775	0.96

K=Freundlich adsorption constant; 1/n isotherm curvature; r²= correlation coefficient

Table 2. Desorption of three carbamate pesticides-clay complexes and pesticide-humic acid clay complexes in $\mu\text{moles g}^{-1}$ clay by water, 0.1M KCl and 0.05M BaCl₂

Sorbent	Pesticide I				Pesticide II				Pesticide III			
	Amount adsorbed	Amount desorbed			Amount adsorbed	Amount desorbed			Amount adsorbed	Amount desorbed		
		Water	0.1M KCl	0.05M BaCl ₂		Water	0.1M KCl	0.05M BaCl ₂		Water	0.1M KCl	0.05M BaCl ₂
Na-illite	265	76	140	145	248	89	161	162	291	70	130	134
Ca-illite	244	70	122	126	232	78	144	146	266	64	116	120
Na-HA illite	333	64	126	121	309	77	136	138	363	60	114	116
Ca-HA illite	301	56	103	108	286	69	121	123	321	54	94	96
Na-kaolinite	134	47	86	83	120	52	92	92	145	42	82	80
Ca-kaolinite	125	37	81	81	112	43	84	86	132	35	74	76
Na-HA-kaolinite	178	40	74	75	168	46	81	82	190	36	70	70
Ca-HA kaolinite	167	33	68	70	158	38	75	74	178	31	65	66



