

MODEL STUDIES ON THE ADSORPTION OF PESTICIDES ON HUMIC ACID

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Introduction

In the adsorption of pesticides on soil components, besides clay minerals, polymeric substances of high surface area, such as humic acid and humates play the most important role. In soils of high organic content due to adsorption an overdose of pesticide is necessary in order to achieve the required effect. This effect is an obvious disadvantage both from the economic and environmental points of view.

The objective of the present study was to investigate — with possible practical applications in mind — the adsorption of a set of typical pesticides on humic acid and to determine the main factors affecting this adsorption.

Since pesticide formulations such as wettable powders, emulsifiable concentrates, mostly contain surfactants, our investigations have also been extended to the simultaneous adsorption of pesticides and surfactants on humic acid. Humic acids are alkali soluble components of soils. Their molecular weight is high but variable. According to their alkali solubility three main types of humic acids may be distinguished: humatomelanic acid, brown and grey humic acid. Their molecular weight and sensitivity to electrolytes and oxidation is increasing in this order. Other physical and chemical characteristics of humic acids are shown in Table I.

Acidic character and ion exchange properties of humic acid originate from their content of carboxyl and phenolic groups. Chemical degradation, mainly oxidation with agents of different redox potentials [7—14] has demonstrated the presence of mono- and diphenols, aromatic aldehydes, polycarboxylic acids, further the combinations and derivatives of these functional groups. Nitrogen content is present as heterocycles, as imino groups linking the subunits, and finally as aminosugars and amino acids associated with the carboxyl groups. Humic acids are therefore essentially polymeric substances containing polynuclear units substituted with amino, carboxyl, phenolic and alkyl groups, inclusive their derivatives.

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Table I
Characteristics of humic acids (literary data)

Features		References
Denomination	Numerical value	
Mol. weight	$50 \cdot 10^3 - 300 \cdot 10^3$	1
Average composition	C 43.00 — 61.99 H 1.99 — 7.34 O 29.80 — 47.80 N 3.11 — 6.48	2
Form of molecule	asymmetrical axis ratio 1 : 6 — 1 : 12	1
Length of molecule	30—50 Å	1
Surface structure	loose spongy structure with a high number of voids	3
Free radicals	≈ 10 mol%	4,5
Degree of dissociation	pH = 6.5 complete pH < 6.5 partial	6

Experiments

Physical characteristics of the humic acid sample used in our experiments have been determined as shown in Table II.

Table II
Characteristics of humic acid (measurement values)

Features	
Denomination	Numerical value
Elementary composition	C: 51.58 H: 3.88 N: 1.02 O: 53.22
Ashes %	10.17
Density g/cm ³	1.554
—COOH equivalent mval/g	3.79
Salt splitting capacity mval/g	0.48
Solubility in water at 25 °C mg/l	<10
pH of 1% suspension in water	4.5

In adsorption experiments, it is first necessary to know the structure and area of the adsorbent surface. Both have been determined in one step according to the method of SCHAY and NAGY [15, 16], by taking the surface excess isotherms of liquid mixtures. In these experiments, solvent pairs of known composition have been adsorbed on humic acid of known grain size. After equilibrium had been established, equilibrium concentrations of the components were determined by measuring the refraction indices. From the data obtained, surface excess values were calculated and plotted as a function of equilibrium concentrations (cf. Figs 1—3). With all three mixtures the isotherms changed sign, i.e., they were of the so-called type IV. From the central linear section of the isotherms the intercepts were determined by the method of least squares. Surface excess values obtained in this way provided the monolayer adsorption capacity. Specific surface areas were calculated by multiplying adsorption capacities by the surface requirement

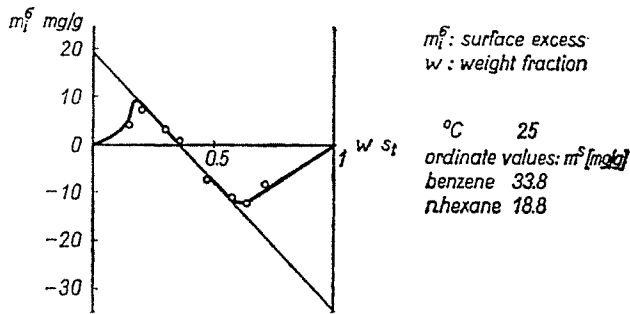


Fig. 1

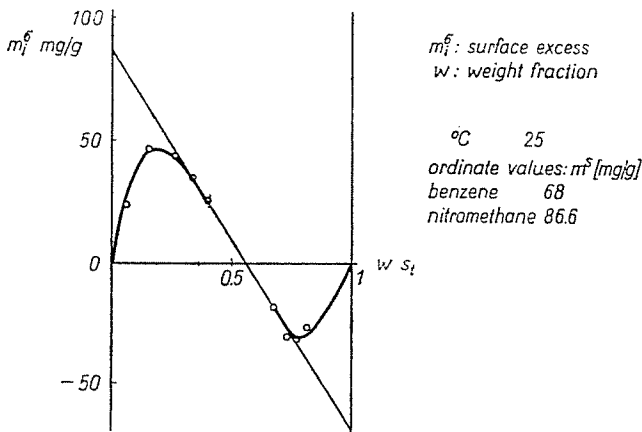


Fig. 2

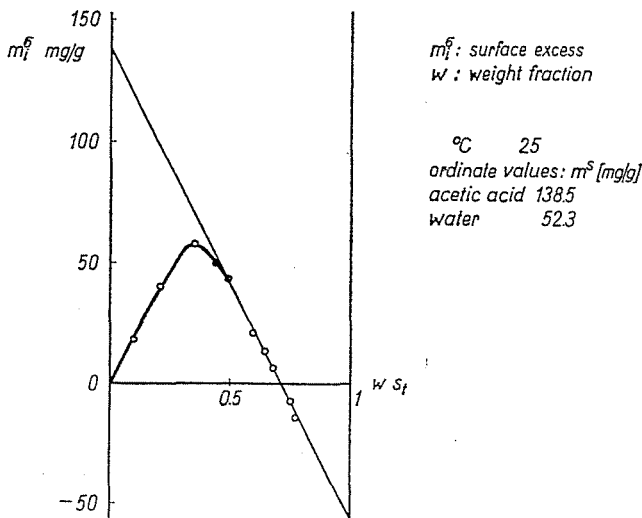


Fig. 3

of the substrate. These results as well as dielectric constants of the solvents are shown in Table III.

As it is apparent from the values shown, specific areas determined by liquid adsorption are much higher than BET areas determined on dry humic acid by nitrogen adsorption. Also the calculated areas increase with the polarity of the components of the mixture. These results also confirm that humic acid is a porous structure having polar groups on its surface and undergoing considerable swelling when solvated.

Table III

	Specific surface area of humic acid [m ² /g]	Dielectric constants of solvents [ϵ]
BET	<10	—
Benzene-n-hexane	105	2.27—20.4
Benzene-nitromethane	310	2.27—35.9
Acetic acid-water	450	6.17—78.4

Adsorption of the following types of pesticides or pesticide precursors on humic acid was studied in aqueous solution: phenylureas, trichlorophenoxy derivatives, *m*-dinitrophenol derivatives.

Equilibrium concentrations were determined by spectrophotometry. The surface excess values were calculated from the concentrations and their reciprocals plotted vs. the reciprocals of equilibrium concentrations. The adsorption process can be described by the *Langmuir* isotherm, as exemplified by the adsorption of trichlorophenoxy derivatives shown in Fig. 4.

From the *Langmuir* equation monolayer adsorption capacity m_p^s , and equilibrium constant K were determined by linear regression analysis. Calculated values are shown in Table IV. The following tentative, qualitative conclusions can be drawn from these experiments:

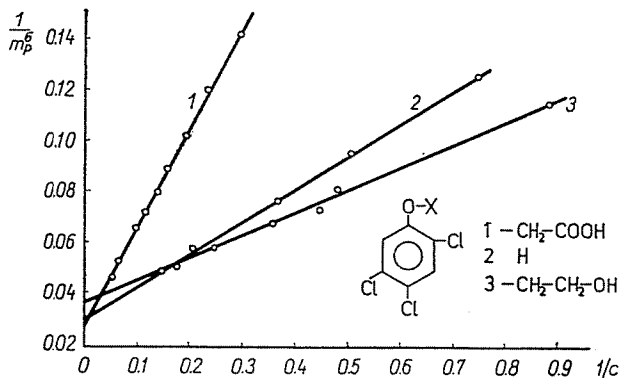


Fig. 4

Table IV

$$\frac{1}{m_p^s} = \frac{1}{m_p^g} + \frac{1}{m_p^g \cdot b} \cdot \frac{1}{c} \quad K = \frac{1}{b} = \frac{k \text{ adsorption}}{k \text{ desorption}}$$

Type	Structure of examined molecule	Mark	Gram-molecular volume [cm ³]	Apparent mono-layer capacity m_p^s [μ mol/g]	$K \cdot 10^2$
di-nitrophenol derivative		MDB	108	167	3.3
Phenyl-carbamid derivative		MKF-186	262	55	5.2
Phenoxy derivatives		TFA	204	134	7.6
		TF	111	166	24.0
		TFE	152	114	41.0

Adsorption and bonding force depend on the physicochemical nature of the substrate on its steric requirements and on the quality of its functional groups. Considering the fact that on the surface of the adsorbent there are various functional groups that may establish adsorptional links with the substrate, it is a reasonable assumption that in the binding of different substrates different functional groups of the adsorbent play a decisive role. This is supported by the fact that the range of the equilibrium constants K is limited by *m*-dinitro-benzene which is polar but lacks active functional groups and trichloro-phenoxy-ethanol, which is also polar, but has a free alcoholic hydroxy group too. K values range over one order of magnitude; for trichloro-phenoxy-ethanol 13 times higher than for *m*-dinitro-benzene. Increased adsorption may be attributed to the free hydroxy group of the substrate establishing hydrogen bonds with polar functional groups of the adsorbent, whereas with *m*-dinitro-benzene only dipole-dipole interactions are operative. With trichloro-phenoxy-acetic acid, which is of pronounced acid character, adsorption of dissociated molecules has to be considered as well. In this way hydrogen bonds can only be formed in part, dipole-dipole interactions, however, may be rather strong. With the phenylurea derivative, MKF-186, *m*-dinitro-benzene and trichloro-phenoxy-acetic acid, most probably polarity and polarizability of these compounds are important factors in establishing adsorptive bonding.

A comparison between adsorption capacities, m_p^s and molecular volumes of the substrates studied indicates that irrespective of the character of bonding, adsorption is limited by the steric requirement of the substrate. With increasing molecular volume, adsorption capacity, in general, decreases. These hypotheses need corroboration by further studies, first of all by adsorption experiments and dipole moment measurements. According to our original research scheme we also studied the adsorption of our model compounds in aqueous solution in the presence of sodium-lauryl-sulphate as a surfactant.

In order to obtain meaningful results we determined first the critical micellar concentration (C.M.C.) of sodium-lauryl-sulphate by conductometry, both with the pure surfactant and when C.M.C. was decreased by adding electrolytes. In the adsorption experiments its concentrations were measured by spectrophotometry in form of its methylene-blue complex. Concentration of the substrate was determined by UV spectrophotometry. Under standard conditions the following phenomena were investigated:

- a) adsorption of a pesticide at a given initial concentration in the presence of an electrolyte;
- b) adsorption isotherms of sodium-lauryl-sulphate solutions set to different C.M.C. values by adding electrolyte;

c) adsorption of pesticide in the presence of surfactant set to different C.M.C. values as a function of sodium-lauryl-sulphate concentration.

Whereas, as shown earlier, isotherms of pesticides are unequivocally all of the *Langmuir* type, in the concentration range covered, isotherms of the surfactant show maxima around the C.M.C. values. This phenomenon may be ascribed to the following factors:

- a) owing to their size, adsorption of micelles is insignificant;
- b) micelle formation reduces the concentration number of non-associated surfactant molecules capable to adsorption;
- c) an equilibrium is established between unassociated, associated and adsorbed concentrations of the surfactant.

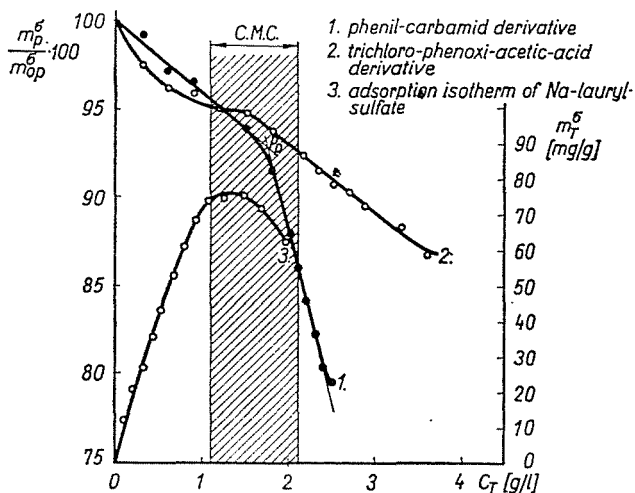


Fig. 5

Simultaneous adsorption experiments demonstrated that the adsorption of pesticides is significantly influenced by the presence of a surfactant. The result of such an experiment is shown in Fig. 5 as an example. Curve No. 3 is the adsorption isotherm of surfactant with a C.M.C. range of 1.1 to 2.1 g/l. Curves No. 1 and 2 represent the adsorption of pesticides of given constant initial concentration from surfactant solution of increasing concentration.

Substrate adsorption is given as percentage of values without surfactant. It is clear from the figure that whereas in dilute surfactant solutions adsorption of the pesticide only slightly decreases, in the C.M.C. range decrease becomes sharp. In the case of MKF-186, tangents drawn to the two ranges of differing slope intersect in a well defined point called the P_p value. Correlation of P_p

values and C.M.C. set to different values by the addition of electrolyte is given for constant initial concentration of the pesticide in Table V.

These experiments demonstrated that at low concentrations of the surfactant, i.e. before the C.M.C., adsorption of sodium-lauryl-sulphate molecules is preferred over that of pesticide molecules. This process may be the

Table V
Adsorption of "MKF-186" in presence of surfactant

CMC interval of Na-lauryl-sulfate [g/l]	Abscissa of point P_p [g/l]
0.3–1.3	1.22
1.1–2.1	1.71
2.4–3.4	2.43

reason for the slight decrease of pesticide adsorption, which continues as long as adsorption of the surfactant increases (Fig. 5). Around C.M.C., however, non-adsorbable micelles are forming which decreases the net adsorption of surfactant. Since in the same concentration interval also a sharp decrease of pesticide adsorption can be observed, it is justified to conclude on the solubilization of the pesticide molecules by the aggregating surfactant. Namely if all of the pesticide molecules could take part freely in the adsorption equilibrium process, their adsorption would be at least constant after having reached the C.M.C. range of the surfactant.

Our suggestion about the complicated equilibria established in such systems is demonstrated in the scheme of Fig. 6.

There is an equilibrium first between adsorbed, free and aggregated surfactants, second, between adsorbed, free and solubilized pesticides and third, between surfactant micelles and solubilized pesticides. As long as there are no micelles present in the system only equilibria labelled A exist and the two substrates are competing. State ($A + B$) is characteristic of the presence of micelles. The solubilizing effect of micells reduces the concentration of free pesticides hence also that of the adsorbed ones. Our interpretation summarized in Fig. 6 needs further experimental verification.

	A	B
I. Surfactant	$C_S \text{ adsorbed} \rightleftharpoons C_S \text{ free}$	$\rightleftharpoons C_S \text{ micella}$
II. Pesticide	$C_P \text{ adsorbed} \rightleftharpoons C_P \text{ free}$	$\rightleftharpoons C_P \text{ solubilized}$

Fig. 6

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Summary

A study of the adsorption of pesticides and pesticide-like compounds on humic acid suggested that substrates of different types established different types of bonds with the adsorbent. In the presence of a surfactant, adsorption of pesticides decreases sharply around the C.M.C. of the surfactant, a phenomenon interpreted by solubilization of the pesticide by the micelles.

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