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Adsorption of Herbicide Acetochlor Onto Kaolin-Humic Acids Complexes

Introduction

Adsorption is an important factor affecting the fate and biological activity of herbicides released into soil. Acetochlor belongs to the group of acetanilide herbicides and is used on a large scale in Europe and USA as a weed-control agent. Soil organic matter and humic acids (HA) in particular, determine to a great extent adsorption of acetochlor onto soil particles (Qiquan et al., 1999; Weiping et al., 2000). To predict adsorption affinity of acetochlor for different soils, quantitative relationships are to be established between structural characteristics of HA and partition coefficients of acetochlor. The objective of this study was to estimate partition coefficients of acetochlor onto model kaolin-HA complexes and establish their relationship to the properties of complexes.

Material and Methods

Kaolin clay (Kaolin CF 70) was provided by the Caminauer Kaolinwerk GmbH (Caminau, Germany) and saturated with calcium using 0.1 M $CaCl_2$ as described in (Balcke et al., 2002).

Ten **humic acids** (HA) samples used in this study were isolated from soil, peat, and brown coal. Soil HA were isolated from seven soils: three sod-podzolic soils (SHA-Pw98, SHA-Pp96, SHA-Pg98), two grey-wooded soils (SHA-Gw98, SHA-GpS00), alluvial soil (SHA-Am98), and chernozem (SHA-CtL00). The HA were isolated using 0.1 M NaOH extraction according to (Orlov and Grishina, 1981). Peat HA were isolated from highland (PHA-T7H98) and lowland (THA-T10L98) bog peat according to (Lowe, 1992). Coal HA (CHA-AGK) was a commercial preparation of brown coal (Specboitech Ltd., Russia). All HA samples used in the study were characterized using elemental analysis and ^{13}C NMR spectroscopy.

Kaolin-HA complexes were synthesized as described in (Balcke et al., 2002) and characterized with organic carbon content and surface area according to (Kutilek, 1962).

Adsorption experiments were conducted using herbicide Harnes (acetochlor 90 %) (Monsato, EU). A weight of 0.2 g of kaolin-HA complex was dispersed in 25 mL of herbicide solution in 0.1 M KCl (pH 5.5) in a centrifuge vial with lid. Adsorption isotherms were recorded for initial acetochlor concentrations ranging from 0.05 to 45.5 mM/L. The samples were equilibrated for 24 h. The equilibrium concentration of acetochlor was determined by polarisation fluorescent immune analysis (PFIA). Adsorption affinity of acetochlor for kaolin-HA complexes was characterized with partition coefficients K_d and K_{OC}.

Results and Discussion

Obtained kaolin-HA complexes differed significantly in OC contents: from 0.41 to 1.17 % (Table 1). Surface area values laid in the range of 34.1-117.0 m^2/g. The highest OC content and surface area were observed for kaolin complex with coal HA, whereas the lowest values were observed for bare kaolin clay. This can be indicative of the governing role of HA in formation of surface area.

Calculated K_d values for acetochlor varied from 5.2 to 29.9 L/kg and increase along with an increase in the surface area of kaolin-HA complexes ($r = 0.87$). There was no relationship found between K_d and OC values. Nonetheless, the values of acetochlor K_d for kaolin-HA complexes were higher than those for bare kaolin clay. This finding demonstrates that both quantity and quality of HS forming the surface of kaolin-HA complexes contribute into their affinity for acetochlor. Indeed, the statistically significant relationship was established between K_{OC} and content of aromatic carbon (^{13}C-NMR data) of HA adsorbed onto kaolin clay

Table 1. Properties of kaolin-HA complexes and the determined partition coefficients of acetochlor

HA in complex	OC content, %	Surface area, m^2/g	K_d, L/kg	K_{OC}, L/kg OC
SHA-Pw98	1.00	34.1	5.2	523
Sha-pg98	0.86	47.6	6.4	738
SHA-Pp96	0.57	76.3	12.1	2129
SHA-Gw98	0.57	59.1	29.9	5252
SHA-Gps00	0.97	33.4	10.7	1102
SHA-Am98	0.53	65.7	30.6	5765
SHA-Ctl00	0.41	94.3	30.7	7487
PHA-T7H98	0.58	51.4	19.1	3297
PHA-T10L98	0.54	40.9	10.5	1939
CHA-AGK	1.17	117.0	57.7	4955
Kaolin clay	0.12	31.0	2.3	-

($r = 0.72$). Given that the amount of aromatic structures is an indicator of HA hydrophobicity, the observed relationship shows a substantial contribution of hydrophobic interactions in adsorption of acetochlor on the HA-kaolin complexes.

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