

## THE SURFACE PROPERTIES OF HUMIC ACIDS EXTRACTED FROM CHERNOZEM AND GREY-BROWN PODZOLIC SOILS

*M. Flis-Bujak*<sup>1</sup>, *A. Księżopolska*<sup>2</sup>, *J. Stawiński*<sup>2</sup>, *R. Turcki*<sup>1</sup>

<sup>1</sup> Institute of Soil Science and Environment Management, University of Agriculture  
Kr. Leszczyńskiego 7, 20-069 Lublin, Poland

<sup>2</sup> Institute of Agrophysics, Polish Academy of Science, Doświadczalna 4, 20-236 Lublin, Poland

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**A b s t r a c t.** The authors characterized selected surface properties of humic acid preparations extracted from three types of Polish soils (degraded chernozem developed from loess, grey-brown podzolic soil developed from loam, grey-brown podzolic soil developed from loess). Based on the isotherms of water vapour adsorption, the specific surface area and the molar energy of adsorption were calculated; the effect of agrotechnical measures in multi-year cultivation on the surface properties of the humic acids under study was determined, and the effect of contamination of humic acids on the form of the isotherms of water vapour adsorption was analyzed.

**K e y w o r d s:** adsorption, specific surface area, molar energy of adsorption

### INTRODUCTION

The specific chemical structure of humic acids and the content of function groups cause in all the processes occurring in the soil, and they affect its physical, chemical and biological properties. They are the most important component of humus, as they have 'spongy' structures of a high capacity for ionic exchange and strong complex-forming properties [1].

From the view point of soil science, the surface properties are a very important physico-chemical feature of humic acids, so far little known and infrequently determined. As follows from the literature, few authors took an interest in the surface properties of humic acids, and especially in the isotherm of adsorption and desorption of water vapour [5].

According to the authors, the isotherm of adsorption is the fundamental characteristic of all adsorbents, humic acids included. It permits the determination of such important parameters as the value of the specific surface area and the distribution of macropores [2-4].

The knowledge of adsorption isotherms at several temperature levels permits the calculation of the adsorption energy of the adsorbate. Due to the specific properties of humic acids, water vapour is the best adsorbate characterizing their surface properties. The level of adsorption of polar substances, such as water vapour, is closely correlated with their exchange capacity with relation to cations.

The objective of this study was to characterize the surface properties of humic acids extracted from various types of Polish soils, and to determine whether agrotechnical treatments used in multi-year cultivation have a modifying effect on those properties.

### MATERIAL AND METHOD

The study was concerned with humic acids extracted from the following types of soils: degraded chernozem developed from loess, grey-brown podzolic soil developed from light boulder loam, and grey-brown podzolic soil developed from loess. Soil samples for the

study of humic acids were taken from under sixteen years crop rotations of differentiated cereal participation - 50 % and 100 %.

Samples of the chernozem were taken at differentiated levels of mineral fertilization: a - 240 kg/ha NPK, b - 360 kg/ha NPK, average yearly dosage for the crop rotations. Likewise, on the grey-brown podzolic soil developed from loam: a - 180 kg/ha NPK, b - 360 kg/ha NPK, average yearly dosage for the crop rotations. On the grey-brown podzolic soil developed from loess, samples were taken in the following variants: a - without herbicides, b - with herbicides. Mineral fertilization on this soil, average yearly dosage for the crop rotation, was from 220 to 240 kg/ha NPK.

Humic acids were extracted by means of the mixture of 0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$  + 0.1 M NaOH, according to the method of Kononowa-Bielczkova (cited in [1]). In the humic acid preparations the authors determined the elemental composition of C, H, O, N, and ash content (Table 1) and performed the following physico-chemical determinations (Table 2):

1. Adsorption isotherms were determined at three temperature levels (20, 33 and 43° C);
2. Specific surface area was determined according to the method of water vapour adsorption, calculating the monolayer capacity according to the BET method [2];
3. The value of the molar energy of water adsorption (for the monolayer) was deter-

mined on the basis of adsorption isotherms at three temperature levels;

4. Micropore distribution was determined in samples of different ash content, differing in the shape of the isotherms (gray-brown podzolic soil developed from loam), using the method of mercury porometry.

To determine the isotherms of water vapour adsorption, weighing trays with approximately 5 g samples of air dry adsorbent were placed in a vacuum drier over solutions of sulphuric acid of such a concentration which ensured suitable water vapour pressure. For the adsorption balance to stabilize, the samples were kept in the drier for 48 h; then they were weighed. When the solid mass settled, the solution was changed for a fresh one and the procedure was repeated for subsequent measurement points. The dry mass of a sample was determined by drying it at a temperature of 105 °C.

The adsorption isotherms are a source of data for the determination of the specific surface area of the humic acids under study, using the BET method [2]. In this method the authors used only four water solutions of  $\text{H}_2\text{SO}_4$ , their concentration being such that the water vapour pressure over the solution of the highest concentration did not exceed 0.35 of saturated water vapour pressure (range of applicability of the BET equation [2]).

Using the graphs of adsorption isotherms at three temperatures (293, 306, 316 K), the

**Table 1.** Basic composition and ash content of humic acids in %

Sample	Crop rotation % of cereals	C	H	O	N	C/H	Ash
Chernozem from loess (Werbkowice)							
1a	50 %	52.74	3.90	39.84	3.52	13.52	5.74
1b	50 %	52.58	3.84	40.07	3.51	13.69	3.75
4a	100 %	51.35	3.85	41.67	3.13	13.34	5.29
4b	100 %	53.16	3.94	39.53	3.37	13.49	5.28
Podzolic from loam (Grabów)							
6b	50 %	52.13	4.74	38.87	4.26	10.99	4.31
10a	100 %	51.81	5.02	38.83	4.24	10.32	5.40
10b	100 %	52.40	4.96	38.37	4.27	10.56	5.13
Podzolic from loess (Czesławice)							
1a	50 %	53.91	4.60	36.99	4.50	11.72	4.29
13a	100 %	50.75	4.63	40.19	4.43	10.96	3.97
13b	100 %	50.81	4.54	40.44	4.21	11.19	5.57

authors determined the values of molar energy of adsorption (for the monolayer), in kJ/k mole. The following data were necessary for the calculations:

- values of  $P_o = f(T)$  H<sub>2</sub>O, for the three temperatures respectively: 293 K = 17.535 mm Hg, 306 K = 37.729 mm Hg, 316 K = 64.800 mm Hg;
- absolute temperatures  $1/T$  (0.00341, 0.00327, 0.00316);
- values of  $A_m$  (monolayer capacity) for the humic acids under study;
- values of  $P/P_o$  - taken from the isotherm graphs;
- values of  $P$  and  $\log P$  - calculated;
- $(\log P \text{ to } 1/T) \text{ tg } \alpha$  relation - taken from the graph.

The molar energy of adsorption for the monolayers ( $m$ ) was calculated according to the formula for molar enthalpy ( $H^s$ ) [2]:

$$\Delta_a H_m^s = 2.303 R_o \text{ tg } \alpha$$

where  $R_o$  - gas constant =  $8.3143 \cdot 10^7$  erg/k mole.

Data from the calculations were compared with the value of molar enthalpy of evaporation  $L = \Delta H^o_{373} = 40.72$  kJ/mole.

The values of the molar energy of adsorption (for the monolayer) of particular fractions of humic acids are in agreement with the theory, i.e., they are always higher than the values of molar heat of evaporation (condensation) [2].

#### RESULTS AND DISCUSSION

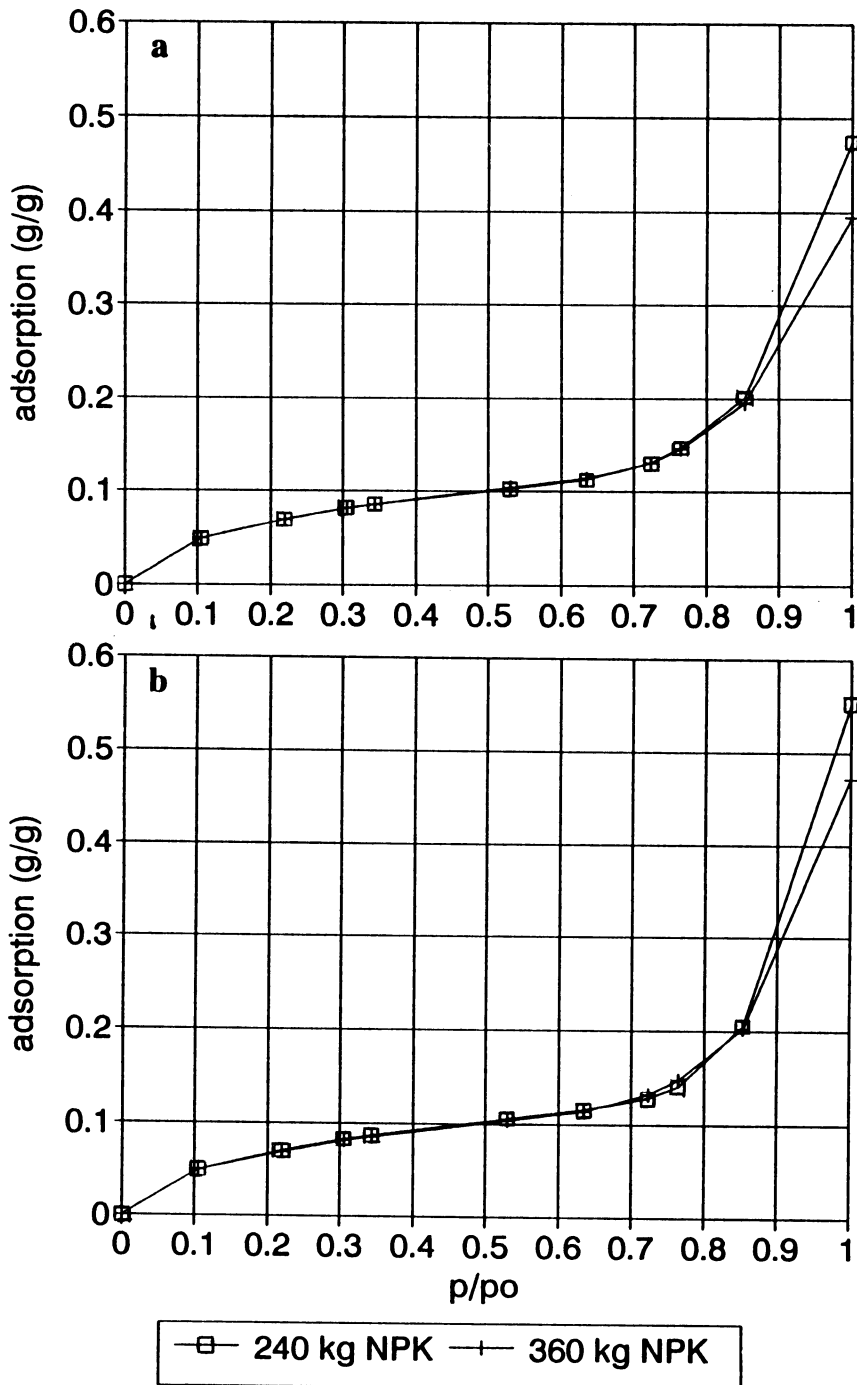
The results of the study are presented in graphs and tables. Figure 1 presents the water vapour adsorption isotherms for humic acids from the degraded chernozem developed from loess. Figure 1a depicts the isotherm for rotations with 50 % cereal participation at two different levels of fertilization, i.e., 240 and 360 kg/ha NPK, while Fig. 1b presents the shape of isotherms for crop rotations with 100 % cereal composition, for the same levels of fertilization. As follows from the graphs, for water vapour pressures < 0.85 the isotherms are

identical. Their shape begins to vary at higher water vapour pressures. Lower levels of fertilization are accompanied by higher values of water vapour adsorption, irrespective of the cereal percentage in the crop rotations. Such a form of adsorption isotherms may indicate a decrease in the microporosity of the samples due to an increase in NPK fertilization dosage per hectare.

Figure 2 presents the isotherms of water vapour adsorption on humic acids extracted from the grey-brown podzolic soil developed from loess. As follows from the graphs, the shape of the isotherms gets differentiated for water vapour pressures above 0.77, the values of water vapour adsorption being higher for the variant with no herbicides of the crop rotation with 50 % cereals. An opposite relationship was observed in Fig. 2b for the crop rotation with 100 % cereals. Clarification of this ambiguous relationship requires more detailed studies on the effect of herbicides on the surface properties of humic acids extracted from soil.

Figure 3 presents water vapour adsorption isotherms for humic acids extracted from the grey-brown podzolic soil developed from boulder loam, with 100 % and 50 % cereal participation in the crop rotation and with two different levels of NPK fertilization, i.e., 180 and 360 kg/ha. As can be seen in the graph, the isotherms are nearly identical.

Figure 4 presents adsorption isotherms for the mean values of humic acids of the soil types studied. As follows from the graph, the shapes of isotherms for water vapour pressure values < 0.73 are nearly identical. This suggests that irrespective of the type of soil the shapes of isotherms for soil samples fairly thoroughly purified of contaminants are similar to one another. This indicates a uniform chemical character of the surface of all the preparations under study. The isotherms get differentiated at water vapour pressures above 0.73. These changes are probably correlated with the different ash content levels in the preparations. In order to clarify this relationship in humic acid preparations from the grey-brown



**Fig. 1.** Isotherms of water vapour adsorption for humic acids from the degraded chemozem developed from loess (Werbkowice) at two different levels of fertilization with 50 % (a) and 100 % (b) cereal participation in the crop rotation.

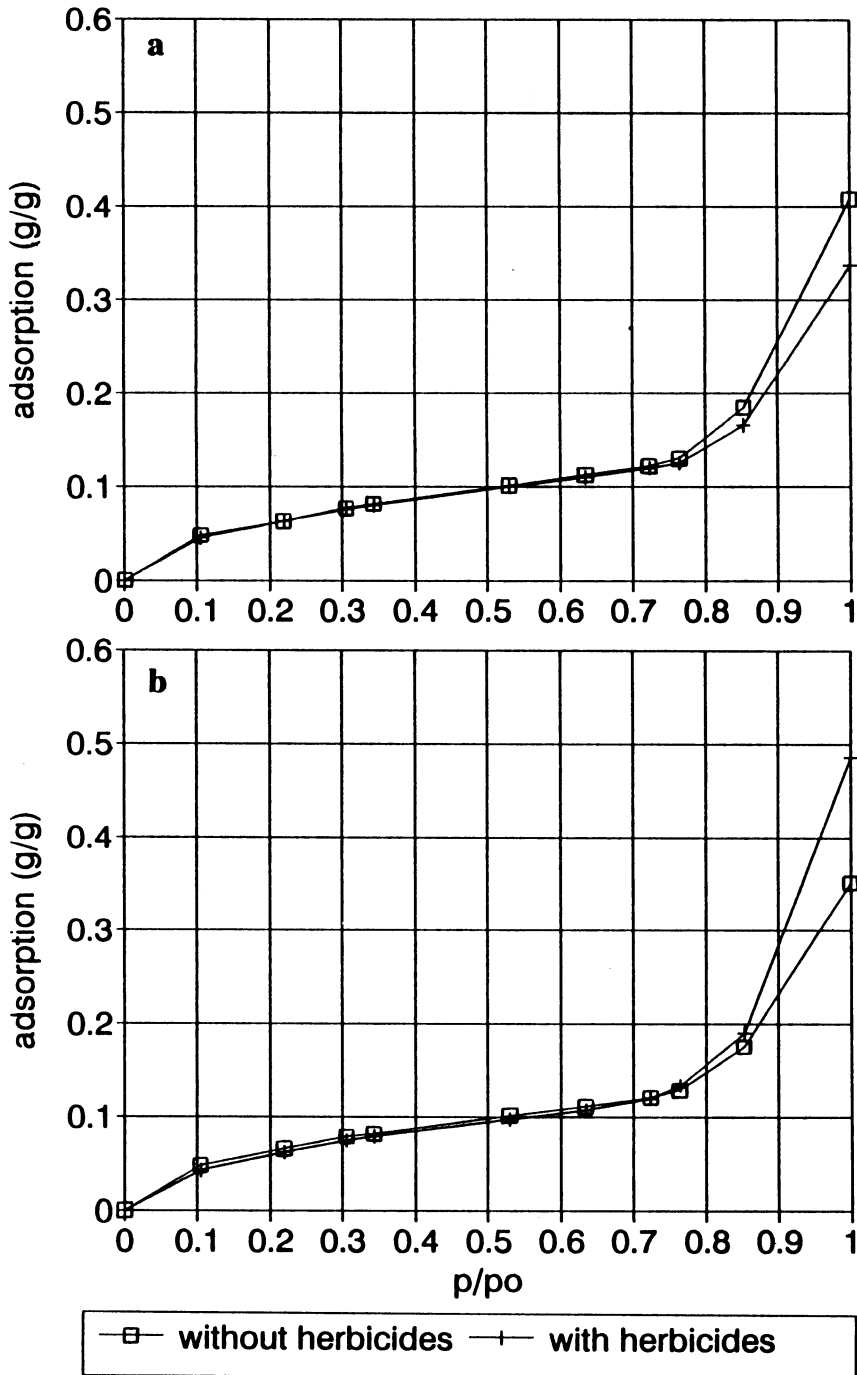


Fig. 2. Isotherms of water vapour adsorption for humic acids from the grey-brown podzolic soil developed from loess (Czesławice) for variants with and without herbicides with 50 % (a) and 100 % (b) cereal participation in the crop rotation.

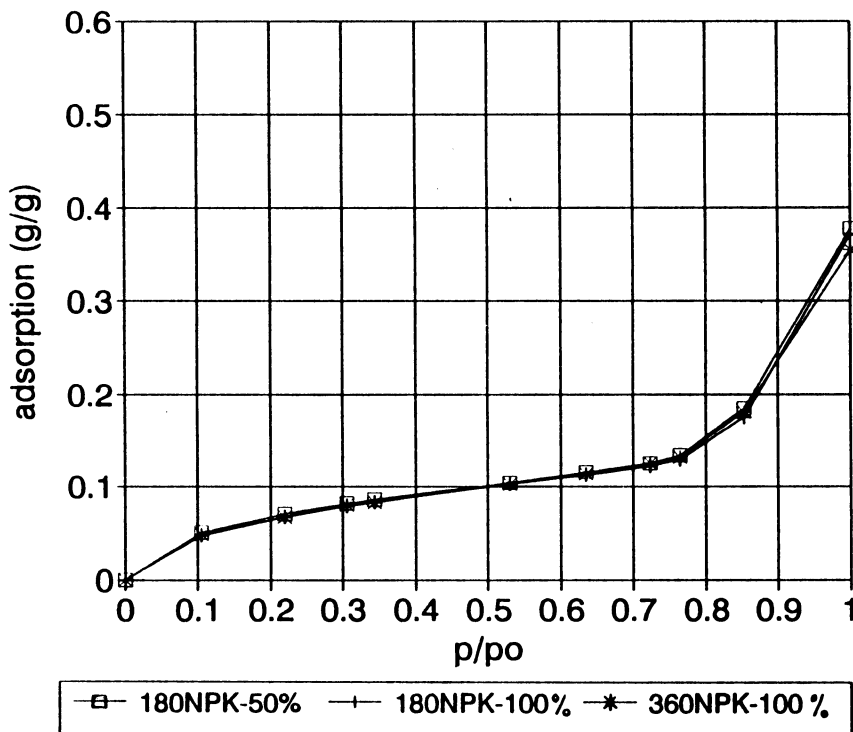


Fig. 3. Isotherms of water vapour adsorption for humic acids from the grey-brown podzolic soil developed from boulder loam (Grabów).

podzolic soil developed from boulder loam, varied considerably with respect to their ash content, porosimetric determinations were performed, following the method of mercury porosimetry. The results of the porosimetric analyses are presented in Table 2. As follows from the data in the table, in sample Nos 6 and 8 exist a linear correlation between ash content and average pore diameter. This indicates that contamination affected the shape of the isotherm through a change in the microporosity of the preparations. Increase in the number of larger radius particles caused an increase in water ad-

sorption within the range of relative water vapour pressure values corresponding to capillary condensation. The shape of adsorption isotherms for those preparations is presented in Fig. 5. Contaminated samples display distinctly higher values of water vapour adsorption within the range above  $0.63 P/P_0$ .

The adsorption isotherms plotted for all the humic acid preparations under study served as a basis for the determination of such surface properties as the specific surface area, molar energy of adsorption in the monolayer, monolayer capacity  $A_m$ , and constant  $C$  from equation BET.

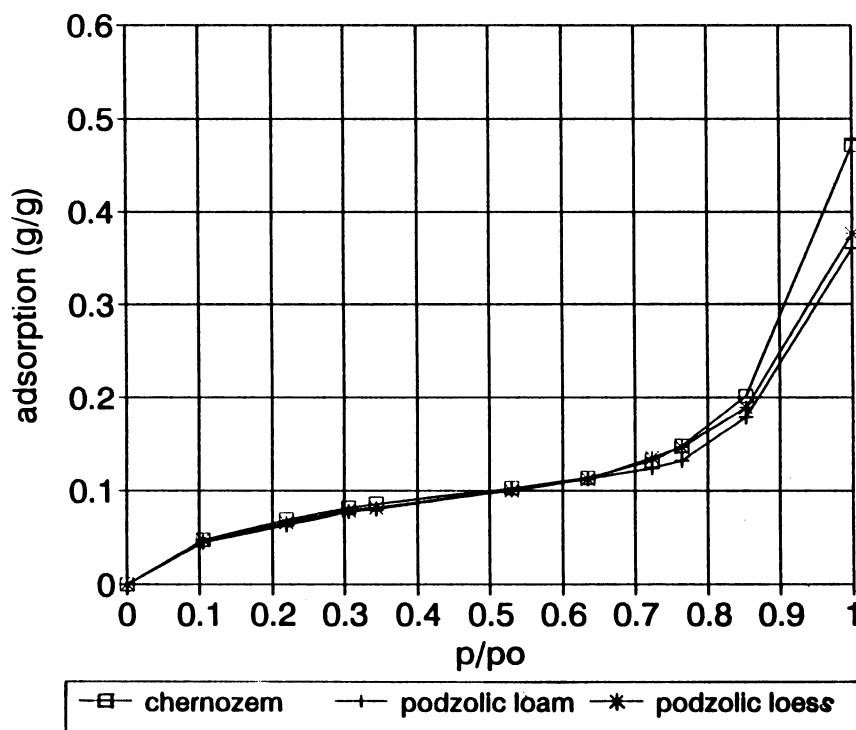
Table 2. Pore size distribution (mercury porosimetry) for humic acids of different ash content

Podzolic from loam	% ash	Average pore diameter ( $\mu$ )	Total pore volume (mm/g)
6a	10.27	4.50	304
6b	4.31	1.99	409
8a	6.81	3.83	199
8b	4.05	1.99	402

**Table 3.** Surface phenomena of humic acids

Sample	C (%)	Am (g/g)	S (m <sup>2</sup> /g)	Mean S	E ads. (kJ/kmol)	Mean E
Chemozem from loess						
1a	22.6	0.0607	219	221	58.98	58.8
1b	20.4	0.0613	221			
4a	20.0	0.0625	226			
4b	22.6	0.0607	219			
Podzolic from loam						
6b	25.8	0.0593	214	212	61.27	62.6
10a	23.0	0.0585	211			
10b	23.7	0.0588	212			
Podzolic from loess						
1a	23.3	0.0569	205	208	62.80	59.6
1b	17.6	0.0581	209			
13a	21.9	0.0582	210			
13b	15.8	0.0581	209			

C - organic carbon; Am - mono-layer capacity; S - specific surface area; E ads. - molar energy of adsorption for the mono-layer.

**Fig. 4.** Isotherms of water vapour adsorption for the mean value of humic acids of studied soils.

The results are presented in Table 3. The values of the specific surface area of the humic acid preparations studied fell within the range from 205 to 225 m<sup>2</sup>/g, while the values of the molar energy of adsorption for the mono-layer formed a range from 56.0 to 67.4 kJ/kmole. As

follows from Table 3, neither the energy of water vapour adsorption nor the value of the specific surface area are much differentiated, which additionally confirms the similar spatial geometry of the humic acid preparations and their similar chemical character. With relation

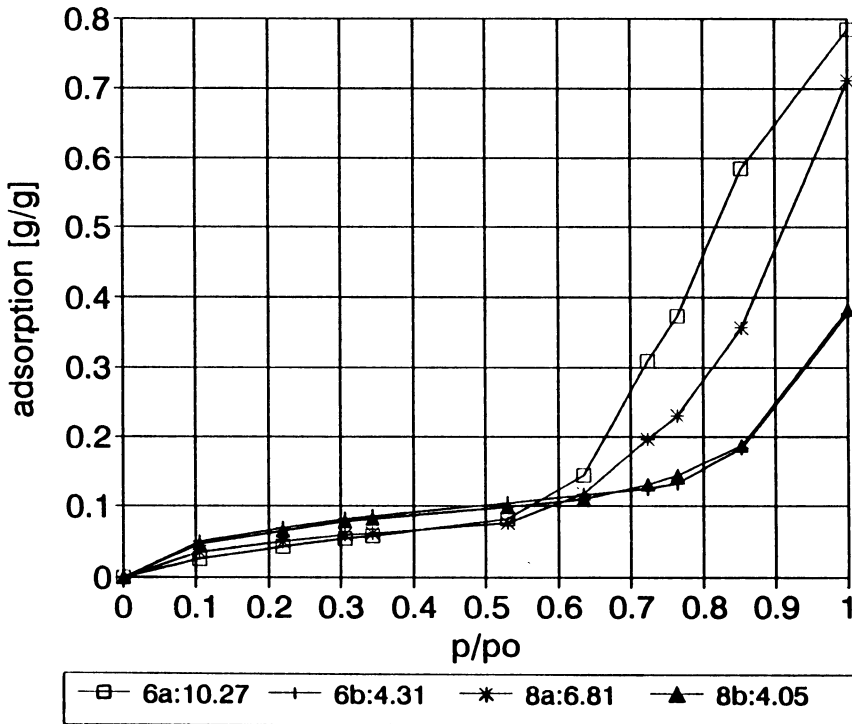


Fig. 5. Isotherms of water vapour adsorption for humic acids of different ash content.

to the above it remains a matter of discussion whether the nearly identical surface properties of the preparations studied result from their character, or whether the cause lies in the identical method of their extraction. It can be suspected that the extraction of humic acid preparations using the mixture of 0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$  and 0.1 M NaOH 'produces' so-called artifacts, i.e., that the properties of the humic acids are not necessarily the same as under natural conditions. The solution this problem, however, requires a separate study.

#### CONCLUSIONS

1. The isotherm of water vapour adsorption constitutes a good and accurate method for the characterization of the surface properties of humic acid preparations. It defines the chemical character of the surface as well as the microporosity of the preparations.

2. The effect of fertilization the shape of isotherms of water vapour adsorption differs

with relation to the type of soil. In the case of the chernozem, an increase in NPK fertilization caused a decrease in the microporosity of humic acids irrespective of the percentage of cereals in the crop rotation. In the case of the grey-brown podzolic soil developed from boulder loam, the shapes of the isotherms of adsorption are nearly identical for all the fertilization doses.

3. The effect of herbicides applied on the grey-brown podzolic soil developed from loess was manifested as a decrease in the porosity of humic acid preparations when the crop rotation was 50 % cereal, and an increase when the cereal participation was 100 %.

4. The degree of contamination of humic acid preparations affected the shape of the isotherms of water vapour adsorption. This was notable especially for relative water vapour pressures above 0.63. Increase in preparation contamination caused an increase in the average



radius of the micro-pores and a decrease in the total porosity.

5. The value of the specific surface area of the humic acids under study varied from 205 to 225 m<sup>2</sup>/g, and the molar energy of adsorption in the monolayer varied from 56.0 to 67.4 kJ/kmole.

6. The similar shapes of the isotherms of water vapour adsorption and the low variability of the specific surface area and the molar energy of adsorption (for preparations sufficiently purified) suggest that the surface properties of the preparations are affected primarily by the method of their extraction. Extraction by means of the mixture of 0.1 M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and 0.1 M NaOH may cause the formation of artifacts, which should be taken into consideration in further studies.

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