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Sorption of Humic Substances on a Weakly Basic Anion-Exchange Resin: Relationship with the Adsorbate Structure

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Abstract—Adsorption of a broad range of humic substances (HS) of different origins and fractional compositions on a macroporous weakly basic anion-exchange resin is studied. It is found that the nature of the HS has a substantial effect on both the efficiency of sorption and the mechanism of interaction with the adsorbent. The dependence of the determined thermodynamic parameters of sorption on the HS origin, composition, and structure is shown for a broad range of HS. It is concluded that the results can be used to predict the sorption properties of weakly basic anion-exchange resins with respect to HS of known origin and structural group composition.

Keywords: humic substances, sorption, natural polyelectrolytes, structural group composition, anion-exchange resins

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INTRODUCTION

Humic substances (HS) are natural hyperbranched polyelectrolytes in which the aromatic skeleton is replaced with both oxygen-containing functional groups—mostly carboxyl (–COOH) and hydroxyl groups (–OH) [1]—and nitrogen-containing groups [2]. In addition to a hydrophobic aromatic skeleton, HS consist of hydrophilic polysaccharide and peptide moieties [3]. Owing to this composition, HS are capable of participating in ionic, donor–acceptor, and hydrophobic interactions, and are therefore highly active in sorption processes [4, 5]. These properties are responsible for the key role of HS in the surface modification of clay minerals, which is fundamental to the formation of soil structure because humic films form hydrophobic regions on the surfaces of hydrophilic clay minerals [6–8]. It was shown in [9] that the surface morphology of the adsorbed layers of silanized HS at a water–glass interface is largely determined by the molecular structure of the adsorbate, i.e., the presence or absence of bulk polysaccharide moieties in the adsorbate’s structure [9]. This relationship allows us to predict the properties of silanized HS films. At the same time, it is important to determine the relationship between the structure and sorption properties of native humic preparations without preliminarily modifying them with organosilanes in order to substantially deepen our understanding of the driving forces that determine HS adsorption on different solid substrates [8, 10, 11].

The aim of this work was to examine the sorption properties of HS of different origins on a weakly basic anion-exchange resin and determine a relationship between these properties and the adsorbate’s structure. A weakly basic anion-exchange resin was selected as a model substrate to study the sorption of HS not preliminarily modified.

EXPERIMENTAL

Both commercial humic preparations and HS moieties isolated and prepared under laboratory conditions were used as samples of HS of different origins. The following commercial preparations were used: Sakhalinskii potassium humate (OOO Biomir-2000, Moscow, Russia), which is produced via the alkaline extraction of lignite (below, CHS); Powhumus potassium humate (Humintech, Düsseldorf, Germany), which is produced via the alkaline extraction of leonardite, a product of lignite oxidation [12] (below, CHP); and sodium lignohumate (OOO NPO RET, St. Petersburg, Russia), which is produced via the oxidation of lignin sulfonate and therefore contains strongly acidic sulfonic groups (below, LH). In addition, desalted preparations of CHS (CHA-SH) and LH (LHA) were used (referred to below as desalted). These samples were prepared via the precipitation of humic acids from solutions of the original humates by bringing the solutions to a pH of 1 with hydrochloric

Table 1. Data on the elemental, structural group, and molecular weight composition of the studied HS preparations

Parameter		CHS	CHA-SH	CHP	LH	LHA	PHF	PHA	
Ash-free content of elements, wt %	C	50.79	52.66	53.40	49.65	43.31	50.59	50.79	
	H	4.71	4.25	5.15	6.21	4.67	5.11	4.71	
	N	0.00	1.96	1.31	0.00	0.37	5.45	0.00	
	O	44.50	41.13	40.14	44.14	51.65	38.85	44.50	
Weight fraction of ash (ω , %)		32.0	6.8	21.6	21.1	2.6	8.8	17.9	
Distribution over structural fragments, % of total C content	C=O	6.0		7.0	4.3		8.1	5.3	
	COO	19.4		14.2	4.3		15.2	15.8	
	ΣC_{Ar}	$C_{Ar}O$	10.5		10.5	15.0		10.5	8.2
		C_{Ar}	41.8		41.1	36.7		26.2	25.0
	ΣC_{Alk}	OCO	4.5		5.4	4.5		5.8	5.4
		$C_{Alk}O$	6.4		6.5	26.9		21.8	18.8
	CH_n	11.4		15.4	8.3		12.5	21.4	
Molecular weight, kDa		6–11			3		18–20		

acid. The resulting precipitates were dialyzed and dried using a rotary evaporator.

In addition to the commercial humates, we studied the properties of HS isolated from peat: unfractionated HS of sedge peat (Ivanovo oblast, Russia) and humic acids of reed–sedge peat (Tver oblast, Russia), referred to below as PHF and PHA, respectively. The peat humic preparations were isolated via alkaline extraction as described in [13] after exposing the crushed peat to a benzene–ethanol mixture. The alkaline extracts were desalted by passing them through a cation-exchange resin, acidified, and decanted; the isolated precipitate was purified using dialysis membranes. The resulting preparations were dried on a rotary evaporator [2].

The HS were characterized via elemental analysis and ^{13}C NMR spectroscopy (Table 1). The C, H, and N content was determined in the laboratory of microanalysis at the Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences. The elemental composition of the HS was converted to ash-free organic matter. The oxygen content was calculated as $[O], \% = 100 - ([C] + [H] + [N])$.

The composition of structural groups was studied on a Bruker Avance 400 ^{13}C NMR spectrometer with an operating frequency of 100 MHz. A ~40 mg weighed portion of an HS was dissolved in 0.6 mL of 0.3 M NaOD/D₂O and placed into a 5 mm NMR tube. Quantitative spectra were recorded using a CPMG pulse sequence; the broadband proton decoupling was turned off during the registration of free induction decay signal in order to eliminate the nuclear Overhauser effect (the INVGATE pulse technique). To ensure the complete relaxation of all ^{13}C nuclei, the relaxation delay was 7.8 s [14].

The molecular weight distribution was determined via size exclusion chromatography. Fractionation was conducted using an Abimed chromatography system comprising a HPLC pump, an autosampler, a glass column ($\varnothing 15$ mm, $L = 25$ cm), a UV spectrophotometric detector, and a recording computer. The column was packed with Toyopearl TSK HW-55S gel (Toso-Haas, Japan) with a fractionation range of 1–200 kDa in respect to polydextrans. A phosphate buffer (0.03 M, a pH 6.8) was used as the mobile phase. Conditions of analysis were the same as described in [15].

An ANS macroporous weakly basic anion-exchange resin (GP Smoly, Dneprodzerzhinsk, Ukraine) was used as our ion-exchange resin. Since the resin was supplied in a mixed chloride–hydroxide (up to 60%) form, it was converted to the chloride form by exposing it to 1 M HCl (special purity grade) and subsequently washing it with bidistilled water until a neutral reaction was obtained [16]. The prepared anion-exchange resin was dried in a vacuum oven at a temperature of 60°C for 1 day and then stored in a sealed container. The bulk weight of the sample, which was determined as described in [17], was 0.45 g/mL; the mass fraction of moisture was 4.4% [18].

The sorption isotherms of the HS were recorded using a set of 0.05 g weighed portions of the anion-exchange resin immersed into 45 mL of an HS solution with a concentration of 20–1000 mg/L. The resulting solutions were placed in centrifuge tubes and stirred by overturning the tubes at a frequency of 45 rpm for 20 h. The tubes were then left to stand for 1 h, and the HS content in the solutions was determined spectrophotometrically (according to absorbance at 254 nm).

Excess (Gibbs) adsorption was determined according to the formula [19]

$$\Gamma = (C_0 - C_{eq})V/m,$$

Table 2. Parameters of the Langmuir and Freundlich equations for the sorption of the studied HS preparations on an ANS weakly basic anion-exchange resin and the standard deviations of residuals for the proposed models

Parameter		CHS	CHA-SH	CHP	LH	LHA	PHF	PHA
Langmuir equation*	Γ_{\max} , mg/g	(59.3)	146.0	78.8	117.4	122.7	21.2 (14.8)	6.4 (9.1)
	$K \times 10^3$, L/mg	(9.0)	1.5	2.6	2.5	1.3	14.4 (24.1)	43.6 (23.6)
	R^2	(0.982)	0.987	0.995	0.996	0.997	0.963(0.996)	0.811(0.996)
Freundlich equation*	β	(1.23)	1.25	1.06	0.94	0.40	1.64	2.01
	$1/n$	(0.63)	0.63	0.60	0.68	0.77	0.40	0.18
	R^2	(0.997)	0.997	0.994	0.990	0.999	0.868	0.630
Langmuir equation**	$\Gamma_{\max}^{\text{cor}}$, mg/g	(40.3)	136.0	61.8	92.6	119.5	19.3 (13.5)	5.2 (7.4)
	$K^{\text{cor}} \times 10^3$, L/mg	(13.2)	1.6	3.3	3.2	1.3	15.8 (26.4)	53.1 (28.7)
	$\Delta G + RT \ln M$, kJ/mol	(10.72)	15.98	14.18	14.27	16.46	10.27 (9.01)	7.27 (8.80)
Freundlich equation**	β^{cor}	(1.07)	1.22	0.96	0.87	0.40	1.55	1.71
	$1/n^{\text{cor}}$	(0.63)	0.63	0.60	0.68	0.77	0.40	0.18
$C_{\text{eq}} = 0-333$ mg/L	s_L , mg/g	3.0	4.9	1.8	13.1	3.9	3.6	3.7
	s_F , mg/g	2.4	2.5	2.8	19.7	14.9	8.6	3.0
	s_{LF} , mg/g	2.2	4.7	1.0	16.4	10.8	6.4	3.6
$C_{\text{eq}} = 0-1000$ mg/L	s_L , mg/g	—	10.6	3.0	23.3	28.3	3.3	3.8
	s_F , mg/g	—	2.6	2.8	31.5	38.3	7.1	3.3
	s_{LF} , mg/g	—	5.0	1.8	27.4	33.2	5.0	3.5

Values in parentheses are data for the initial portion of the isotherm.

* Without allowance for the ash content in the HS.

** With allowance for the ash content in the HS.

where C_0 and C_{eq} are the initial and equilibrium concentrations (mg/L) of the substance in the solution with volume V (L) over weighed portion m (g) of the sorbent.

Parameters of the Langmuir [20] and Freundlich equations [21] were determined via the linearization of experimental data in inverted or logarithmic coordinates. Table 2 lists the respective parameters determined with and without allowance for the data on the ash content in the initial preparations obtained by the method described above (Table 1). The Gibbs energies for adsorption reactions were calculated from equilibrium constants. Table 2 lists these values per adsorbate weight with allowance for ash content. To estimate and compare the energy effects of HS adsorption on an anion-exchange resin, the term $\sim 2.5 \ln M$, where M is the molecular weight of a given HS (Table 1), must be subtracted from the ΔG value listed in Table 2.

RESULTS AND DISCUSSION

The quantitative characteristics of sorption of HS of different origins on the anion-exchange resin were determined by the static method. The results obtained by this method characterize the thermodynamic properties of the studied systems and allow the determina-

tion of relative changes in adsorption interactions for single-type adsorbates. The recorded sorption isotherms (Fig. 1) show the dependence of the sorption interaction pattern on the nature of the HS. Most of the isotherms, particularly in the initial portion of equilibrium concentrations, can be adequately described by the Langmuir and Freundlich equations (Table 2) and are consistent with the BET classification's type IVa isotherms [22], which are characteristic of sorbents with mixed pore structures.

An exception is HS of peat origin; one preparation, PHA, exhibited the lowest sorption efficiency in the studied range of concentrations (Fig. 1, curve 7), and the lowest Gibbs energy (Table 2). The PHF preparation was characterized by the presence of a weakly pronounced adsorption peak at average equilibrium concentrations (Fig. 1, curve 6), due apparently to it containing both humic and fulvic acids.

The sorption isotherm of the CHS sample has a pronounced step-like pattern (Fig. 1, curve 1), so the excess adsorption of potassium humate grows abruptly at an equilibrium concentration of ~ 400 mg/L. These changes in sorption isotherms are generally associated with the possible occurrence of multilayer sorption. Descriptive parameters in terms of the BET model of polymolecular sorption from solutions were addition-

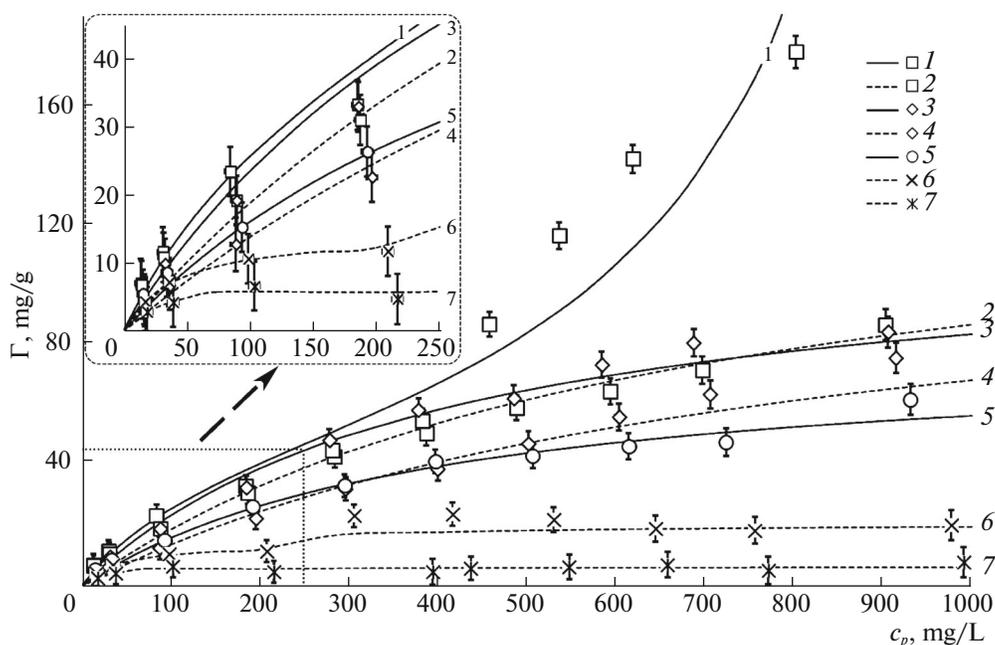


Fig. 1. Experimental data on the sorption of HS on ANS anion-exchange resin and respective theoretical isotherms in terms of (1) the BET and (2–7) Langmuir models: (solid lines) commercial preparations (1) CHS, (3) LH, and (5) CHP and (dashed lines) desalted samples (2) CHA-SH, (4) LHA, (6) PHF, and (7) PHA.

ally determined for this isotherm [23] (Fig. 1, curve 1). The limiting adsorption ($\Gamma_{\max} = 50.0$ mg/g) and sorption equilibrium constants ($K_L = 7.8 \times 10^{-3}$ L/mg) determined for this model were in good agreement with the parameters obtained for the initial portion of sorption in terms of the Langmuir model (Table 2). The sorption equilibrium constant for one polymolecular layer is $K_S = 9.52 \times 10^{-4}$ L/mg.

Note that the sorption isotherm of the desalted sample of this HS preparation (CHA-SH) repeats the isotherm of the purified commercial sample in the initial portion and continues to grow monotonically in the second portion (Fig. 1, curve 2). The sorption isotherm of the CHA-SH preparation in the Langmuir model is characterized by extremely high limiting sorption and a negligible adsorption constant (Table 2).

The sorption isotherm curves of the original LH sample and its desalted product (LHA) vary monotonically in the investigated range of concentrations (Fig. 1, curves 3 and 4, respectively). The Langmuir equation parameters determined for these preparations (Table 2) suggest that even though this group of preparations exhibits the highest $\Gamma_{\max}^{\text{cor}}$ values, it is characterized by the lowest adsorption equilibrium constants. These features result in the pronounced linearity of the respective isotherms (Table 2, the $1/n^{\text{cor}}$ parameter of the Freundlich equation); LHA is characterized by a more rectilinear isotherm and lower

adsorption values over the investigated range of concentrations.

CHP exhibits the lowest sorption of all the commercial preparations in the region of high concentrations (Fig. 1, curve 5).

Analysis of the recorded sorption isotherms thus suggests that purifying humates via dialysis leads either to a slight reduction in the efficiency of sorbate–sorbent interaction (as in the case of the LH/LHA samples) or to a change in the mechanism of this interaction (CHS/CHA-SH). The HS of peat origin exhibit weaker adsorption on this anion-exchange resin.

The sorption isotherm analysis data can be analytically described in terms of a particular conventional sorption model (Table 2). Analysis of the formal parameters derived in terms of the Langmuir sorption model shows that the limiting sorption capacity values for the studied HS samples are inversely proportional to the sorption equilibrium constants (Fig. 2a). The data on the HS of the same origin are grouped in particular portions of the respective dependence. The HS of peat origin are thus characterized by the lowest $\Gamma_{\max}^{\text{cor}}$ values and the highest K^{cor} values (Fig. 2a), while the lignohumate preparations have high limiting adsorption values and the lowest adsorption constants. For the HS of coal origin, the determined limiting sorption and equilibrium constants generally had average values.

By analogy, it can be shown that the Freundlich model parameters determined from the experimental

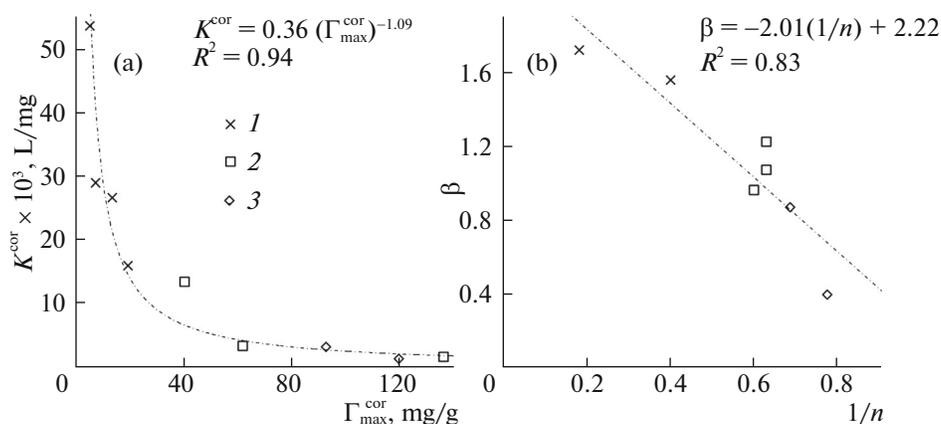


Fig. 2. Correlations between the parameters of (a) the Langmuir and (b) Freundlich equations describing the sorption of (1) peat HS, (2) coal HS, and (3) lignohumates on ANS.

data are linearly interrelated (Fig. 2b). The HS of peat origin are characterized by minimum $1/n$ and maximum β values; the lignohumate samples exhibit the maximum $1/n$ and minimum β values; the HS of coal origin are grouped in the central portion of the correlation line (Fig. 2b).

It is obvious that these relationships can be attributed to structural differences between the studied HS. A key structural feature of HS of different origin is their structural group composition (Table 1). Statistical analysis of the experimental data (Tables 1, 2) revealed correlations between some formal parameters of the sorption equations (K^{cor} , β , and $1/n$) and the $\Sigma C_{\text{Ar}}/\Sigma C_{\text{Alk}}$ ratio for HS of different nature (Fig. 3 for K^{cor} and $1/n$). The aromatic to aliphatic carbon content ratio ($\Sigma C_{\text{Ar}}/\Sigma C_{\text{Alk}}$) was calculated from ^{13}C NMR data and can be used to estimate the hydrophobic–hydrophilic balance of the molecular ensemble of HS [24], since it is the ratio between the content of hydrophobic aromatic moieties and hydrophilic aliphatic moieties, which mostly consist of carbohydrates and peptides. The HS of coal origin comprise a considerable fraction of the aromatic carbon skeleton, which can hinder the formation of bonds between the adsorbate and multiple adsorption sites of the adsorbent. This feature is responsible for the relatively low adsorption constants for the HS of coal origin (Fig. 3a). On the other hand, aromatic carbon determines the hydrophobic properties of HS, so additional hydrophobic adsorption sites for the analogous skeleton moieties of other adsorbate molecules form and ensure a relative increase in the limiting adsorption (Fig. 2a) and the occurrence of multilayer sorption (Fig. 1, curve 1). Conversely, HS of peat origin comprise a significant fraction of a branched carbohydrate periphery and are capable of simultaneously forming bonds with multiple sorption sites; the sorption constant therefore grows substantially (the entropy effect) (Fig. 3a). On the other hand, this feature leads to a

reduction in the ratio between the number of available sorption sites and the number of adsorbate molecules, and to a drop in limiting adsorption for the peat HS (Fig. 2a).

Figure 3b shows that lignohumates are not included in the correlations of the Freundlich adsorption model parameters for HS of natural origin. This can be attributed to both the different nature of aromatic carbon [25] and the fundamentally different pattern of interaction between the HS and the anion-exchange resin owing to strongly acidic sulfo groups. On the other hand, this also confirms the key role of carboxyl groups in the interaction between an HS of natural origin and a weakly basic anion-exchange resin.

According to the above data and the correlations derived from them, we propose the following universal equations for describing the sorption of HS of natural origin with known relative contents of aromatic to aliphatic carbon ($\Sigma C_{\text{Ar}}/\Sigma C_{\text{Alk}}$) in terms of the Langmuir model:

$$\Gamma_{\text{L}} = (0.21 (\Sigma C_{\text{Ar}}/\Sigma C_{\text{Alk}}) - 0.11) C_{\text{eq}}^{\text{cor}} / ((\Sigma C_{\text{Ar}}/\Sigma C_{\text{Alk}}) + 4.4 \times 10^{-3} C_{\text{eq}}^{\text{cor}} - 0.6)$$

or, in terms of the Freundlich model,

$$\Gamma_{\text{F}} = (1.9 - 0.4 (\Sigma C_{\text{Ar}}/\Sigma C_{\text{Alk}})) \times C_{\text{eq}}^{\text{cor} \cdot (0.24 (\Sigma C_{\text{Ar}}/\Sigma C_{\text{Alk}}) + 0.1)}$$

where $C_{\text{eq}}^{\text{cor}} = C_{\text{eq}}(100 - \omega\%)/100$ is the equilibrium HS concentration corrected for the content of ash in the product.

A validation criterion for the proposed models is the standard deviation of residuals for the experimental data (Fig. 1) corrected for ash content:

$$s_{\text{m}} = ((\Sigma (\Gamma_{\text{i}}^{\text{cor}} - \Gamma_{\text{m}}(C_{\text{i}}^{\text{cor}}))^2) / (n - 1))^{1/2},$$

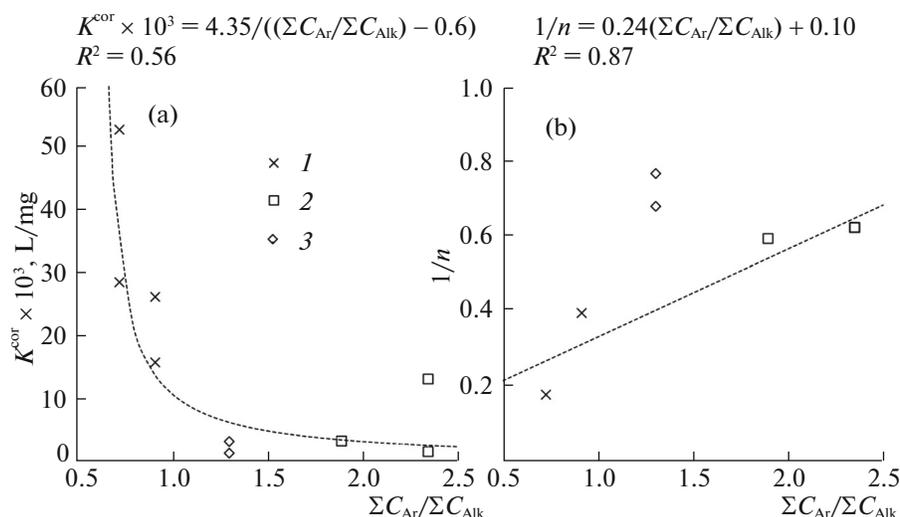


Fig. 3. Correlations between sorption characteristics and the structures of HS: (a) Langmuir and (b) Freundlich model parameters for (1) peat HS, (2) coal HS, and (3) lignohumates HS.

where Γ_i^{cor} is the experimental adsorption value for equilibrium concentration C_i^{cor} and $\Gamma_m(C_i^{\text{cor}})$ is the adsorption of an HS with concentration C_i^{cor} calculated for model M according to the above equations (Table 2). Since the error of the experimental determination of adsorption is 3.5–5.5 mg/g, we may state that the above equations can be used to adequately describe the sorption of HS of coal or peat origin over a wide range of concentrations. The slightest deviation of the results of the equation for Γ_L is observed for the peat HS, while the equation for Γ_F gives the results that are the closest to the experimental data for the coal HS. A more universal equation is the expression

$$\Gamma_{\text{LF}} = (\Gamma_L + \Gamma_F)/2,$$

which can be used to describe the sorption isotherms of HS in a wide range of $\Sigma C_{\text{Ar}} / \Sigma C_{\text{Alk}}$ values. The derived equations can be useful in predicting the sorption properties of weakly basic anion-exchange resins with respect to HS of known origin and structural group composition, e.g., in the manufacture of sorbents for water purification [26]. It is obvious that analogous expressions can be derived for sorbents of other natures.

CONCLUSIONS

Our study of the adsorption of HS of different origins and fractional compositions on an ANS macroporous weakly basic anion-exchange resin shows that the highest degree of sorption is observed for potassium humate produced from lignite. Analysis of the determined thermodynamic parameters of sorption for a broad range of HS showed that the parameters depend on the origin, composition, and structure of

an HS. Equations to relate the adsorption of HS on an anion-exchange resin and the relative content of aromatic to aliphatic carbon were proposed.

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