

Adsorption of Humic Substances onto Kaolin Clay Related to Their Structural Features

Gerd U. Balcke,* Natalia A. Kulikova, Sebastian Hesse, Frank-Dieter Kopinke, Irina V. Perminova, and Fritz H. Frimmel

ABSTRACT

Eleven well characterized humic substances (HSs) were adsorbed from aqueous solution onto a Na-kaolin clay. The adsorption affinity (K_L), maximum adsorption capacity (b), a coefficient of desorption hysteresis (H), and the concentration of irreversibly adsorbed HS (IHS) were derived from adsorption-desorption isotherms. These parameters were correlated with structural features of the HS. The adsorption affinity was shown to correlate directly with the aromaticity of the HS and inversely with their polarity, expressed as the O/C atomic ratio. A dependency between polarity and maximum adsorption capacity was not confirmed. The parameters b , H , and IHS expose close correlation with the molecular weight (MW) and the partial negative charge of HS (Z) at the operating pH value. The following quantitative relationship was obtained: $b = 715 - 0.06 \times MW - 529 \times Z$ ($r = 0.92$). It allows a selection of HS with respect to the largest content of organic matter in HS-kaolin clay complexes. Among the HS studied the high molecular weight materials enriched with C- and H-substituted aromatics, such as coal and peat humic acids (HAs), are shown to be the most preferential materials for preparing stable HS-clay complexes.

INTERACTIONS OF HS with clays take place in various environmental compartments, such as soils, sediments, and aquifers. They may affect the extractability of humus and the rate of its decomposition. Adsorption of HS onto minerals is also important in relation to speciation and mobility of contaminants. Modern remediation strategies apply cationic or anionic surfactants immobilized onto mineral surfaces of aquifer materials for retardation of hydrophobic organic compounds (HOC) in ground water flows (Wagner et al., 1994; Hunter et al., 1996). An environmental friendly alternative to synthetic surfactants are naturally occurring materials. Thus, covering mineral and sediment surfaces with HS, that are natural surfactants, is of particular interest.

Adsorption of HS onto mineral surfaces has been intensively investigated over the decades (Davis, 1982; Baham and Sposito, 1994; Vermeer, 1998a,b; Specht et al., 2000). Despite that, the mechanisms governing the adsorption of HS are still not well understood.

Ligand exchange (carboxyl and hydroxyl groups of the HS versus surface hydroxyl groups of the minerals) has been frequently discussed as one mechanism for HS binding (Tipping, 1981; Spark, 1997; Totsche, 1998). Several authors have provided spectroscopic evidence

of specific interactions between metal oxide surface hydroxyl groups or adsorbed water and the oxygen of adsorbed carboxyl or hydroxyl groups of organic acids including HA (Parfitt, 1977; Yost et al., 1990; Biber and Stumm, 1994). Ligand exchange is highly affected by the pH value of the adjacent solution. As a rule, adsorption of HS onto metal oxide surfaces increases with decreasing pH value, passing a maximum at pH = 4.3 to 4.7, corresponding to pK_a values of most abundant carboxylic acids (Davis, 1981; Perdue, 1985; Murphy, 1990). The pH value determines the protonation state of the sorbate as well as of the surface hydroxyl groups. As a result, the surface complexation via ligand exchange becomes less favorable as soon as the pH value exceeds the point of zero net surface charge (pH_{zpc}) simply because of increasing electrostatic repulsion between the surface and the anionic humic ligands. Nonetheless, significant HS adsorption can be still observed at these high pH values, for example, about 30% of the maximum adsorption in a hematite system at pH = 9 (Vermeer et al., 1998a), and about 37% in a kaolin clay system (Kretzschmar et al., 1997). For pure polycarboxylic aromatic acids, Evanko and Dzombak (1998) reported no adsorption onto iron oxide surfaces at pH > pH_{zpc} . However, polyhydroxybenzenes particularly with hydroxyl groups in ortho-position could still attack electrophilic central metal ions of oxide surfaces at pH > pH_{zpc} . The authors addressed this effect to the formation of chelate surface complexes supported by hydroxyl groups in ortho-position.

Hydrophobic adsorption may be considered as a second mechanism contributing to HS binding onto mineral surfaces. It becomes more favorable at low pH values, when hydroxyl and carboxyl groups of HS are protonated. However, this mechanism cannot be distinguished from the electrostatic attraction at pH < pH_{zpc} . At higher pH values, hydrophobic adsorption can still occur in case it outweighs electrostatic repulsion (Lyklema, 1986). Similar to nonionogenic homopolymers (Day et al., 1994), this process will become the more important, the higher the molecular weight of HS is. As a consequence, fractionation of polydisperse polymers is to be expected. That is, the high molecular weight HS may sorb preferentially (Davis, 1981; Jardine, 1989; Baham and Sposito, 1994; Kaiser et al., 1997). Vermeer and Koopal showed that bigger HA molecules displace faster

G.U. Balcke, F.-D. Kopinke, Dep. of Remediation Res., Centre for Environm. Res., Leipzig-Halle GmbH, Permoserstr. 15, D-04318 Leipzig, Germany; N.A. Kulikova, Dep. of Soil Science and I.V. Perminova, Dep. of Chemistry, Lomonosov Moscow State Univ., Leninskie Gory, 119899 Moscow, Russia; S. Hesse, F.H. Frimmel, Univ. of Karlsruhe, Engler-Bunte Inst., Engler-Bunte-Ring 1, D-76131 Karlsruhe, Germany. Received 30 Aug. 2001. *Corresponding author (balcke@hdg.ufz.de).

Abbreviations: b , maximum sorption capacity; FA, fulvic acid; HA, humic acid; H , desorption hysteresis coefficient; HOC, hydrophobic organic compound; HS, humic substance; IHS, concentration of irreversibly adsorbed HS; K_L , adsorption coefficient; MW, weight averaged molecular weight; OC, organic C; P , error probability; QSAR, quantitative structure activity relationship; SEC, size-exclusion chromatography; TC, total C; zpc , zero point of surface charge

sorbing smaller fulvic acids (FAs) in a slow process (Vermeer and Koopal, 1998b).

To gain a deeper understanding about mechanisms governing HS adsorption onto mineral surfaces, quantitative structure-activity relationships (QSAR) can provide assistance. However, because complete molecular structures of HS cannot be determined yet, we approached a quantitative relationship between sorption parameters and some structural features of HS of different origin by means of an extended regression analysis. The following analytical methods have been applied: elemental analysis, size-exclusion chromatography, ^{13}C solution-state nuclear magnetic resonance (NMR) analysis, and potentiometric acid-base titration.

For a given mineral this allowed us to relate the HS structure to its adsorption-desorption parameters (sorption affinity, maximum adsorption capacity, adsorption-desorption hysteresis), thus getting close to what QSARs are capable of.

As far as we know, such an approach has not been applied yet for the problem under consideration. The objectives of this study were to (i) investigate the adsorption of HS from different sources onto Na-kaolin clay and (ii) reveal the structural features of HS that govern mineral adsorption.

MATERIALS AND METHODS

Kaolin Clay

Kaolin clay (Kaolin CF 70) was provided by the Caminauer Kaolinwerk GmbH (Caminau, Germany). The material has been characterized as shown in Table 1. The clay contains a significant portion of quartz which causes the unusual low pH_{zpc} . Nonetheless, local positive surface charges on kaolin particles can be expected at the operating pH value. Quartz and kaolinite could not become completely separated by size fractionation.

The kaolin clay sample was dispersed in 0.1 M NaClO₄ solution using an ultrasonic bath to saturate the clay with Na ions. The obtained suspension was then centrifuged, the supernatant removed, and the clay-precipitate was treated three times with new salt solution. Then the clay was washed, dried, and stored for further use.

Table 1. Properties of the kaolin clay.

BET surface (N ₂), m ² g ⁻¹	15.0
pH _{zpc} [†]	2.2
C-content, wt%	0.106
identified minerals [‡]	kaolin clay, quartz
identified [§] , wt%	Na ₂ O: 0.08, MgO: 0.18, Al ₂ O ₃ : 35.79, SiO ₂ : 45.24, K ₂ O: 1.93, CaO: 0.12, TiO ₂ : 0.54, Fe ₂ O ₃ : 1.57, loss at red heat: 13.41, sample dried before analysis at 105°C
mineral surface composition , atomic %	C: 2.6, O: 68.2, Al: 12.1, Si: 16.0, Na: 0.9, K: 0.2
bulk density, kg L ⁻¹	2.72
particle size	<20 μm with a mass frequency maximum at 5 μm

[†] PCD02, Muetek, Titrator Mettler DL25, polyelectrolyte/polydiallyldimethylammoniumchloride.

[‡] Determined by x-ray diffraction, Siemens D5000, powder technique.

[§] By x-ray fluorescence detection, Siemens SRS3000, Li₂B₄O₇ 1:7 parts at 1200°C in Pt-crucible.

^{||} By x-ray photoelectron spectroscopy, SAGE 100, SPECS, Berlin, Germany.

Humic Materials

Eleven HS samples used in this study were isolated from different sources: soil, peat, lignite, and a brown water lake.

Soil HA were isolated from four soils. They included two sod-podzolic soils (HBW and HBW1; Moscow region, Russia), and two chernozemic soils (HST and HSM; Voronezh region, Russia). The HA were isolated using 0.1 M NaOH extraction according to (Orlov and Grishina, 1981). The chernozemic soils were treated with 0.1 M H₂SO₄ prior to extraction to destroy soil carbonates. The HA precipitated after acidification of the alkaline extract were desalted by dialysis.

Soil FAs were extracted from two samples of sod-podzolic soils (FBW1 and FBG1; Moscow region, Russia). To isolate FA, after precipitation of HA, the supernatant was passed through an Amberlite XAD-2 resin as described elsewhere for aquatic HS (Mantoura and Riley, 1975).

Peat HA originated from a bog peat near Kranichfeldt (H8, Western Erzgebirge, Germany), and commercial preparations (HTO) purchased from Biolar (Latvia).

Coal HA (AGK and Roth HA) were commercial preparations of lignite supplied by Biotechnology Ltd. (Russia) and Carl Roth GmbH (Karlsruhe, Germany), respectively.

Aquatic HA (HO13 HA) is a standard of the Deutsche Forschungsgemeinschaft research program "ROSIG". It was extracted from the brown water lake Hohlohsee (Schwarzwald, Germany) using Amberlite XAD-8 as described elsewhere (Abbt-Braun et al., 1991).

Stock Solutions

Stock solutions of humic materials for adsorption experiments were prepared as follows: 200 mg of dry HS sample were dissolved in 1 mL of 0.1 M NaOH under continuous stirring. Then the pH value of the solution was adjusted immediately to 5.6 using 0.1 M HCl. The obtained HS solution was diluted with 0.1 M NaCl (pH 5.6) to a volume of 50 mL. The stock solution was used immediately after preparation. The organic C (OC) content of the stock solutions was measured using a Shimadzu TOC-5050 analyzer (Shimadzu-Europe, Duisburg, Germany).

Structural Characterization of Humic Substances

Elemental Analyses

Elemental analyses (C, H, N) were conducted on a Carlo Erba Strumentazione analyzer (Carlo Erba, Milan, Italy). The ash content was determined by combustion of the HS sample in a quartz tube at 750°C. Because the S content of all humic substances under investigation is <1% (wt/wt), oxygen was approximated as the difference between total dry weight of organic matter and the portions of C, H, and N. The contents of all elements were calculated on ash-free basis. The H/C and O/C atomic ratios were calculated as indicators of saturation degree and polarity of HS, respectively.

Size-Exclusion Chromatography Analysis

Size-exclusion chromatography (SEC) analysis was performed at the Engler-Bunte Institute, Technical University of Karlsruhe (Germany). The procedure according to Perminova was applied using a Toyopearl HW-50S gel (TosoHaas, Stuttgart, Germany) (Perminova et al., 1998). Polydextranes were used for calibration. HS solutions were set at a concentration of 1–2 mg L⁻¹ of OC by equilibrating with the SEC mobile phase (0.028 M phosphate buffer, pH = 6.8) prior to analysis. Ultraviolet (UV) and dissolved OC (DOC) detection were

employed to analyze HS concentrations (Huber and Frimmel, 1996). SEC with DOC detection provides the weight number averaged molecular weight (MW) of a HS under study (Perminova et al., 1998).

Potentiometric Titration

Titrations were conducted under N₂ atmosphere using an automatic titrator (TitroLine Alpha, Schott, Mainz, Germany). About 10 mg of dry HS sample were dissolved in 4 mL of carbonate-free 0.1 M NaOH and 2 mL of deionized water. Then 5 mL of 0.1 M HCl were added to adjust the pH-value at the starting point of the titration (pH = 2.6). The HS solutions were titrated slowly with 0.1 M NaOH until pH = 11.0 was reached. The same titration was carried out with a blank sample without HS. The quantification of the carboxyl and the phenolic acidity of HS was performed according to Frimmel et al. (1985), and Frimmel and Abbt-Braun (1999), respectively. The molar amount of NaOH consumed for the rise in the pH value from 2.6 to 7.5 (corrected by the blank value) was normalized to the amount of HS and treated as its carboxyl acidity (COOH, mmol g⁻¹). Analogously, the NaOH consumption from pH = 7.5 to the end point of titration was considered as the phenolic acidity of HS (ArOH, mmol g⁻¹). Furthermore, the molar amount of NaOH consumed from pH = 2.6 until 5.6 (the operating pH value in the sorption experiments), was regarded as a measure of dissociated carboxyl groups or as the partial negative charge of HS at pH 5.6 (Z, mmol g⁻¹).

The data on elemental analysis, molecular weight, and concentration of functional groups are given in Table 2.

Quantitative Carbon-13 Solution-State Nuclear Magnetic Resonance Spectra

Quantitative ¹³C solution-state NMR spectra were recorded on a Varian VXR-400 spectrometer operating at 100 MHz. Each HS sample of 100 mg was dissolved in 3 mL of 0.1 M NaOD/D₂O and transferred into a 10-mm NMR-tube. Sodium trimethylsilylpropylsulfonate was used as an internal standard. About 12 000 to 14 000 scans were collected for each spectrum using 45° pulse and inverse gate decoupling. A spectrum width of about 26 000 Hz, and an acquisition time of 0.5 s and a 4-s pulse delay were applied (Kovalevskii et al., 2000). To quantify

the spectra obtained, the assignments were made as described in Kovalevskii et al. (2000): 5 to 50 ppm—aliphatic H- and C-substituted C atoms (C_{Alk}), 50 to 108 ppm—aliphatic O-substituted C atoms (C_{Alk-O}), 108 to 145 ppm—aromatic H- and C-substituted C atoms (C_{Ar}), 145 to 165 ppm—aromatic O-substituted C atoms (C_{Ar-O}), 165 to 187 ppm—C atoms of carboxyl and ester groups (C_{COO-H,R}), 187 to 220 ppm—C atoms of quinone and ketone groups (C_{C=O}). In addition to the normalized signal intensities of these given ranges, combinatory NMR descriptors were calculated: the sum of all aromatic carbon (C_{Ar} + C_{Ar-O}) and the ratio C_{Ar}/(C_{Ar} + C_{Ar-O}) as an indicator of the contribution of polar aromatic structures. The corresponding data are summarized in Table 2.

Adsorption-Desorption Experiments

Adsorption

Each sample was prepared in a 24-mL glass vial with PTFE lid. One gram of Na-kaolin clay was dispersed in 20 mL of 0.1 M NaCl solution containing a particular aliquot of HS stock solution. Adsorption isotherms were recorded for initial HS concentrations ranging from 0 to 250 mg L⁻¹ HS. The pH value remained at 5.6 throughout all the experiments. The samples were equilibrated for 12 h by means of a rotary shaker. Afterwards the probes were centrifuged for 10 min at 1800 × g (4000 rpm). The equilibrium concentration of HS was determined by UV spectroscopy (240 nm, ACI-photometer, Unicam, quartz cuvette 1.0 cm).

Desorption

Sodium-kaolin clay samples with adsorbed HS (from adsorption experiments with initial HS concentrations of 200 mg L⁻¹) were used for desorption experiments. For desorption, the ratio of solid/liquid phase was kept the same as in the adsorption experiments. Twenty milliliters of 0.1 M NaCl solution (pH = 5.6) were added to the moist remainder of centrifugation. The vials were then shaken end over end for 12 h and centrifuged again. The supernatant was removed, processed for HS analyses as described above, and replaced by fresh 0.1 M NaCl (pH = 5.6). This procedure was repeated eight times until the HS concentration in solution remained below about 1 mg L⁻¹. Each adsorption-desorption step was carried out in

Table 2. Properties of the HS used for a correlation between structural characteristics of HS and their sorption behavior onto kaolin clay.

HS sample unit	H/C	O/C	MW kDa	C _{Alk}	C _{Alk-O}	C _{Ar}	C _{Ar-O}	C _{COO-H,R}	C _{C=O}	C _{Ar} +C _{Ar-O}	$\frac{C_{Ar}}{C_{Ar}+C_{Ar-O}}$	COOH	ph-OH	Total acidity	Z
											%				
Aquatic HA															
HO13HA	0.90	0.44	11.9	17	29	27	12	13	4	39	0.69	2.9	1.4	4.3	1.7
Soil FA															
FBW1	1.09	0.71	6.9	25	12	22	12	20	4	34	0.65	3.4	1.2	4.6	2.3
FBG1	1.10	0.73	7.6	18	13	28	13	18	3	41	0.68	3.3	1.1	4.4	2.3
Soil HA															
Sod-podzolic soil HA															
HBW	0.99	0.58	13.3	19	19	32	12	17	1	45	0.72	3.4	0.2	3.6	1.3
HBW1	1.36	0.64	15.6	26	14	24	9	20	4	33	0.73	2.9	0.3	3.2	0.9
Chernozemic soil HA															
HSM	0.86	0.51	13.0	14	14	43	12	15	2	55	0.78	3.3	0.2	3.5	1.9
HST	0.77	0.52	12.8	13	13	41	14	16	2	55	0.75	3.8	0.4	4.2	2.2
Peat HA															
HTO	1.05	0.57	20.0	16	24	31	13	13	3	44	0.70	1.6	1.0	2.6	0.8
H8	1.19	0.58	12.2	17	13	37	18	16	2	55	0.67	2.4	0.3	2.7	0.8
Lignite HA															
AGK	0.96	0.49	13.4	21	8	41	12	17	1	53	0.77	3.4	0.2	3.6	1.5
Roth HA	0.97	0.69	11.0	11	13	48	18	17	2	66	0.73	2.9	1.2	4.0	1.8

Table 3. Parameters of adsorption onto and desorption of humic substance (HS) from Na-kaolin clay.†

HS sample	K_L , L g ⁻¹ OC	b , g OC kg ⁻¹ of kaolin clay	H	IHS, by carbon combustion g OC kg ⁻¹ of kaolin clay‡	IHS by UV-detection, g OC kg ⁻¹ of kaolin clay‡
<u>Aquatic HA</u>					
HO13HA	0.21	1.11	13.3	1.20	0.90
<u>Soil FA</u>					
FBW1	0.09	0.87	4.8	0.56	0.38
FBG1	0.09	0.86	5.0	0.57	0.39
<u>Soil HA</u>					
Sod-podzolic soil HA					
HBW	0.11	2.25	29.1	1.40	1.19
HBW1	0.19	2.42	18.1	1.55	1.47
Chernozemic soil HA					
HSM	0.30	1.51	16.7	1.36	1.21
HST	0.34	1.48	13.1	1.39	1.25
<u>Peat HA</u>					
HTO					
H8	0.10	2.31	31.6	1.65	1.39
	0.17	1.89	18.1	1.77	1.25
<u>Coal HA</u>					
AGK	0.34	1.54	2.8	1.28	0.88
Roth HA	0.19	1.76	4.5	1.31	1.10

† K_L , adsorption coefficient; b , maximum sorption capacity; H , desorption hysteresis coefficient.

‡ For comparison we give the C-normalized concentration of irreversibly sorbed HS (IHS) determined by C combustion and UV absorbance.

four replicates. The deviation between measured values of replicates was in average <2%.

Irreversibly Adsorbed Humic Substance

The amount of HS remained in the HS-clay complexes after eight desorption steps was regarded as an indicator of irreversibility of HS adsorption and designated as IHS (kg kg⁻¹). It is obvious from the experimental procedure that IHS may include a very slowly desorbing HS fraction. To determine this parameter, both total C (TC) analysis and mass balances were employed. For TC analysis, HS-clay complexes were freeze-dried and subjected to combustion at 900°C with subsequent near-infrared (NIR) CO₂ determination (C-Mat 1100, Ströhlein Inst., Korschbroich, Germany). According to the balance method the IHS fraction was quantified as the difference between HS input and the sum of all soluble HS fractions, measured by their UV absorbances. Results from combustion and the UV based calculations were compared and are discussed below. The IHS values are given in Table 3.

RESULTS AND DISCUSSION

Adsorption and Desorption Isotherms

Typical adsorption isotherms of HS of different origin onto Na-kaolin clay are shown in Fig. 1. At low concentrations, HA samples show a steep initial slope, whereas FA show low affinities to the clay surface. At high concentrations, a maximum adsorption capacity for all HS was observed.

Even though HS adsorption onto clay surfaces does not obey exactly Langmuir's law, for practical purposes data can be well fitted by this isotherm (Tipping, 1981; Vermeer et al. 1998a):

$$S = K_L \times c \times b / (1 + K_L \times c) \quad [1]$$

where S is the amount of sorbed HS (kg OC per kg clay), c is the equilibrium HS concentration (kg OC per L solution), b is the maximum adsorption capacity (kg OC per kg clay), and K_L is the adsorption coefficient of HS (L water per kg OC).

The calculated values for the HS samples and the Na-

kaolin clay under study are in the range of 70 to 360 L kg⁻¹ and $(0.89-2.40) \times 10^{-3}$ kg kg⁻¹ for K_L and b , respectively (Table 3). This is in good agreement with the data reported in the literature (Evans and Russell, 1959; Kretzschmar et al., 1997; Murphy et al., 1990). According to the obtained b values, the target HS can be put in the following ascending order: soil FA < chernozemic soil HA < peat and lignite HA < sod-podzolic soil HA. The K_L -values are arranged in a different order: soil FA < peat HA < sod-podzolic soil and coal HA < chernozemic soil HA.

Desorption of HS from Na-kaolin clay is characterized by a considerable hysteresis (Fig. 1). To quantify this effect, a hysteresis coefficient (H) was calculated according to Celis by the following equation (Celis et al., 1997):

$$H = n_a/n_d \quad [2]$$

where n_a and n_d are the Freundlich coefficients calculated from the adsorption and desorption isotherms. According to the H values summarized in Table 3, HS samples can be put into the following ascending order: soil FA ≈ lignite HA < chernozemic soil HA < peat HA ≈ sod-podzolic soil HA.

Irreversible Adsorption of Humic Substance

The amount of IHS serves as an integral indicator characterizing both HS adsorption onto and desorption from Na-kaolin clay. The obtained IHS values of the target HS increased in the following order: soil FA < brown coal HA < chernozemic soil HA < sod-podzolic soil HA < peat HA (Table 4). Hence, peat HA can be considered as the most beneficial material for preparing HS-kaolin clay complexes with maximum HS content.

The application of UV spectroscopy to quantify sorption processes of heterodisperse mixtures needs to be discussed here. It cannot be assumed that all humic molecules have equal extinction coefficients normalized to their C content. Preferential adsorption of some HS fragments can result in extensive fractionation of the

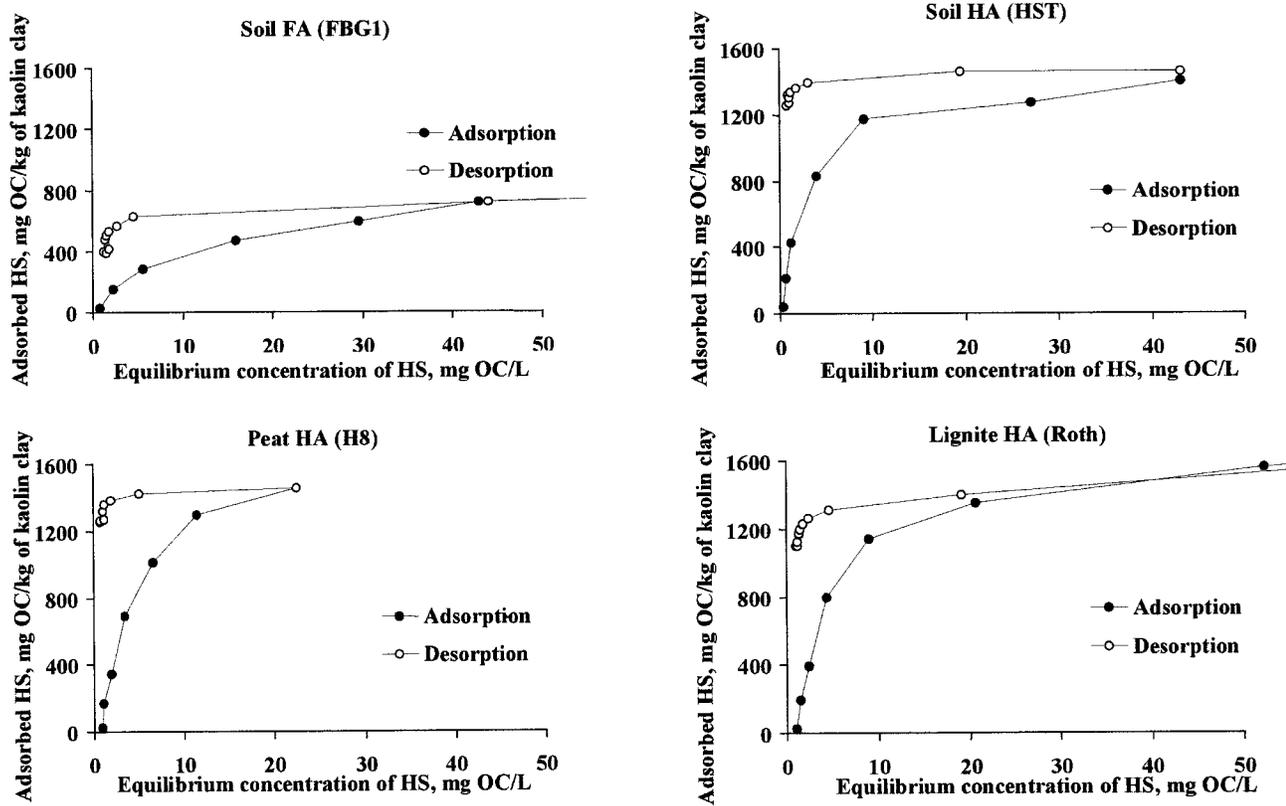


Fig. 1. Adsorption-desorption isotherms of humic substance (HS) of different origin onto Na-kaolin clay.

sorbate. Therefore, we compared IHS values calculated from UV data with those directly measured as TC of HS-loaded clay samples (for details see Table 3). The calculated *t*-test parameter of 0.39 (*f* = 10, *P* < 0.05) was less than the tabulated critical value, *t*_{0.05}, indicating statistical insignificance of the differences between the two data sets. These results give evidence of the feasibility of using UV absorbances for determination of HS

concentration in solution. In other words, in our studies there was no significant difference observed between C normalized absorbances at 240 nm of HS molecules sorbed onto Na-kaolin clay and those remaining in solution.

The results obtained in our study are in good agreement with data of Vermeer and Koopal (1998b) who showed that UV absorbance of HS is only poorly sensi-

Table 4. Correlation coefficients of a linear regression analysis between sorption characteristics and structural features of 11 (HS) humic substances.

	IHS	b	K	H	H/C	O/C	MW	C=O	COOH	Ar-O	Ar	Al-O	Al	Ar+Ar-O	Ar/(Ar+Ar-O)	COOH Ph-OH (titr.)	Ph-OH (titr.)	Z	total acid.
IHS†	1.00																		
b‡	0.83	1.00																	
K§	0.32	-0.04	1.00																
H	0.64	0.73	-0.27	1.00															
H/C	0.05	0.30	-0.54	0.10	1.00														
O/C	-0.62	-0.34	-0.74	-0.34	0.49	1.00													
MW#	0.81	0.82	0.17	0.74	0.05	-0.58	1.00												
C=O	-0.29	-0.23	-0.45	-0.06	0.61	0.68	-0.15	1.00											
COOH	-0.44	-0.09	-0.23	-0.42	0.50	0.59	-0.49	0.14	1.00										
Ar-O	0.22	-0.02	-0.01	-0.15	-0.22	0.09	-0.17	-0.27	-0.24	1.00									
Ar	0.39	0.13	0.63	-0.16	-0.67	-0.49	0.12	-0.70	-0.31	0.62	1.00								
Al-O	0.20	0.13	-0.28	0.56	0.04	-0.04	0.38	0.39	-0.68	-0.17	-0.35	1.00							
Al	-0.27	0.01	-0.28	-0.08	0.67	0.23	-0.11	0.34	0.65	-0.66	-0.76	-0.19	1.00						
Ar+Ar-O	0.38	0.10	0.51	-0.17	-0.61	-0.38	0.06	-0.65	-0.32	0.76	0.98	-0.33	-0.79	1.00					
Ar/(Ar+Ar-O)	0.40	0.30	0.79	0.04	-0.54	-0.72	0.41	-0.64	-0.19	-0.16	0.66	-0.23	-0.33	0.51	1.00				
Ar/Al	0.29	0.07	0.44	-0.14	-0.64	-0.21	0.05	-0.43	-0.34	0.68	0.92	-0.17	-0.88	0.93	0.49	1.00			
COOH (titr.)	-0.50	-0.49	0.40	-0.52	-0.43	-0.05	-0.61	-0.29	0.47	-0.23	0.12	-0.48	0.11	0.04	0.30	0.04	1.00		
Ph-OH (titr.)	-0.54	-0.51	-0.49	-0.30	0.09	0.77	-0.35	0.65	-0.14	0.13	-0.34	0.44	-0.11	-0.25	-0.61	-0.04	-0.26	1.00	
Z††	-0.83	-0.85	0.09	-0.67	-0.51	0.34	-0.78	0.08	0.23	-0.02	0.05	-0.25	-0.16	0.03	-0.06	0.17	0.70	0.40	1.00
total acid.	-0.84	-0.81	0.01	-0.69	-0.34	0.46	-0.80	0.21	0.32	-0.12	-0.13	-0.12	0.02	-0.14	-0.17	0.01	0.72	0.48	0.92

† Irreversibly adsorbed HS.
 ‡ Maximum sorption capacity.
 § Adsorption coefficient.
 || Desorption hysteresis coefficient.
 # Weight averaged molecular weight.
 †† Charge.

tive to preferential adsorption of humic molecules onto minerals. In addition, they corroborate the findings of Georgi (1998) on a narrow range of variation of absorbances (measured at 280 nm) of different humic materials—not exceeding a factor of two.

Relationships Between Structure and Sorptive Properties of Humic Substance

The ideal approach to predict sorption properties from structural information of a compound is the QSAR approach. Because of variable composition and irregular structure characteristic for HS, and deficient methods to describe the humic structure exactly, constitutive molecular descriptors were used to characterize their structural features (Perminova et al., 1999). A regression approach was applied to establish relationships between structure and sorptive properties of HS of different origin.

By name, the atomic ratios (O/C, H/C), the MW, and the functional group content were used as structural features (Table 2). The adsorption properties of HS were characterized by the adsorption coefficient K_L and the maximum adsorption capacity b . The desorption properties were described by H and the amount of IHS concentration (Table 3).

Linear regression served in all cases as the model with the least error probability. At high correlation coefficients r (Table 4) data sets were subjected to an analysis of variance. If not stated otherwise, the r values given below passed the Student test valid for a confidence interval of 95% and a probability of being wrong in concluding that there is a true association between the variables of <0.05 (Doerffel, 1984).

The adsorption coefficient K_L , which is a measure of sorption affinity, revealed a strong inverse correlation with the polarity index (O/C ratio) and a positive correlation with two descriptors of aromaticity of HS (C_{Ar} and $C_{Ar}/[C_{Ar} + C_{Ar-O}]$). The corresponding correlation coefficients r accounted for -0.74 , 0.63 , and 0.79 , respectively. The obtained relationships suggest that the less polar the HS is, the higher is its adsorption affinity towards the clay surface.

The maximum adsorption capacity b revealed two strong correlations, a positive correlation with the molecular weight of the HS ($r = 0.82$) and an inverse correlation with the partial charge Z of HS ($r = -0.85$). Significant relationships were found as well for the desorption parameters H and IHS. For H versus MW and H versus Z relationships the r values accounted for 0.74 and -0.67 , respectively, for IHS versus MW and IHS versus Z , they were 0.81 and -0.83 , respectively.

It is noteworthy that no correlation could be observed between the sorption affinity K_L and the maximum sorption capacity b for the humic materials under study. Above we found that MW is strongly correlated with the maximum sorption capacity b . High molecular weight fractions of HS are usually considered to be more hydrophobic. In our study we could not find a significant interrelation between polarity markers and average molecular weight (see Table 4). We may conclude that structural properties of HS controlling their binding strength towards the surface are not necessarily identical with those controlling the amount of adsorbed C.

Table 5. Weight averaged molecular weights (MWs) of humic substance (HS) before and after adsorption onto Na-kaolin clay.

HS sample	MW, kDa	
	before adsorption	after adsorption
FBW1	6.9	6.0
HST	12.8	11.2
AGK	13.4	13.0
Roth HA	11.0	5.6

The obtained relationships are in good agreement with findings reported in the literature (Davis, 1982; Wang et al., 1997; Murphy et al., 1990, 1994; Vermeer and Koopal, 1998b; Gu et al., 1995). They suggest that the larger the HS molecules are, the higher is the amount of irreversibly adsorbed OC at the clay surface. This conclusion was experimentally confirmed by direct SEC measurements conducted on four HS samples before and after adsorption onto Na-kaolin clay (Table 5). Throughout all humic materials examined, the MW value determined after elimination of the sorbed fraction was substantially lower than that before adsorption. The most significant decrease in the MW value (by a factor of two) was observed for the lignite-derived HA (Roth HA). For the other three materials, the effect was not so strong, but still accounted for about 10%. This shows that in all cases the adsorption onto Na-kaolin clay was accompanied by withdrawal of the higher molecular weight fraction of HS from the solution.

The high negative contribution of the partial charge Z to the adsorption behavior of HS onto clay corroborates well the findings of Evanko and Dzombak (1998), who reported on the key role of the quality and quantity of acidic units in HS for its sorption behavior onto metal oxides surfaces. They have shown that OH substituents on aromatic rings in ortho position to carboxyl groups (salicylic units) enhance HS adsorption much stronger than those in meta or para positions. We interpret our findings by a superposition of MW and Z descriptors ($r = -0.78$). Note that the descriptors COOH, ArOH, and Z are only achievable on a millimole of charge per kilogram basis ($\text{mmol}_c \text{ kg}^{-1}$) and not on a millimole of charge per mole ($\text{mmol}_c \text{ mol}^{-1}$) basis. Any conversion into a millimole of charge per mole ($\text{mmol}_c \text{ mol}^{-1}$) basis might reverse the sign of the correlation coefficient, for example b versus Z . Yet, we cannot resolve the parameter Z from its dependency from MW of the HS, we may only speculate about a contribution of Z to the maximum sorption capacity and sorption irreversibility.

Our regression analysis allows suppositions on hydrophobic interactions as the driving force of adsorption of dissolved HS onto metal oxide and clay surfaces. Given that the adsorption of the dissolved compound (HS molecules) is governed not only by its affinity to the sorbent (Na-kaolin clay), but is strongly dependent on its interaction with the solvent as well, the following speculation on the mechanism can be proposed. The more aromatic, more polymerized, less oxidized molecules of HS carrying lower negative charge are not as extensively hydrated as the more hydrophilic, enriched in carbohydrate fragments, strongly charged humic macromolecules. Introducing a solid sorbent into such a

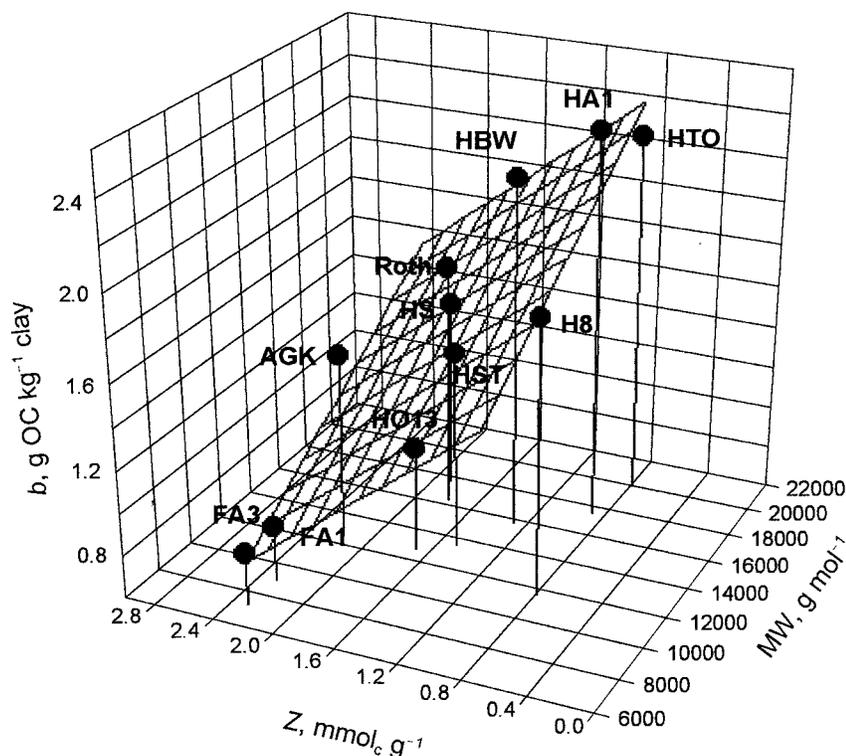


Fig. 2. Three-dimensional visualization of maximum organic C sorption (b) of 11 humic substances on kaolin clay—comparison between measured (black dots) and predicted values (plane) from humic surface charge (Z) and average molecular weight (MW) according to Eq. [3].

system can be accompanied by the preferential adsorption of the more hydrophobic, less charged fractions onto its surface. This is particularly the case when working close to the pH_{zpc} of the mineral or when a positive surface charge is neutralized by humic carboxyl groups. Albeit the net surface charge at the operating pH is negative because of the high quartz fraction in the kaolin clay (see Table 1), we assume the kaolinite surface charges to be neutralized in this pH range (Kretzschmar et al., 1997). This mechanism can also explain why the total amount of carboxyl groups (denoted by COOH) or the partial charge Z of the HS do not give evidence to high sorption affinity. Apparently, all HS possess sufficient groups to balance the positive charge at the Na-kaolin surface. Abundant carboxyl groups are expected to have no promoting effect on the sorption. Conversely, they may create a surface excess of negative charges, because they are deprotonated at the working pH of about 5.6. This situation is perfectly reflected by the strong negative correlation between Z and b ($r = -0.85$), whereas Z does not effect the sorption affinity K_L ($r = 0.09$), that is the adsorption of 'single' HS molecules.

The given considerations suggest that to meet the practical needs in generating HS-clay complexes, the high molecular weight humic materials enriched with aromatics, such as lignite and peat HA, should be selected among other humic materials.

The most significant correlations were obtained between the pairs b and MW as well as b and Z . Therefore, these two parameters were used for deriving the predictive relationship for the maximum adsorption capacity of HS as given in Eq. [3].

$$b = 1715 - 0.06 \times MW - 529 \times Z \quad [3]$$

The two-parametric regression is characterized by a rather high r value (0.92). This shows that the maximum adsorption of HS onto the Na-kaolin clay surfaces can be predicted from such structural features of HS as molecular weight and the amount of strong acidic units (see also Fig. 2). However, the closer relationship is only achievable in expense of statistical confidence ($P_{MW} = 0.171$, $P_Z = 0.069$ at a confidence interval of 95%). To increase the statistical significance of the equation, larger sets of humic materials are to be used.

Very recent studies (Simpson et al., 2002 and references cited there) give new evidence of the hypothesis that HS are aggregates of relatively low molecular weight components rather than a crosslinked, macromolecular network. These components are interconnected by metal cations rather than covalent bonds. If this hypothesis holds, sorption of such aggregates onto surfaces may be expected to cause an extensive reorganization and fractionation of the aggregates. This, however, was not observed in the present study.

CONCLUSIONS

The approach described in the paper allowed to reveal the following structural features responsible for the sorption of HS onto Na-kaolin clay: O/C ratio, aromaticity, molecular weight, and partial charge of humic materials. It was shown that higher aromaticity and less polarity of humic materials support higher adsorption affinity to the clay surface. The affinity determining structural properties do not simultaneously promote high sorbate

loadings. Higher molecular weight and less partial charge of humic material (on a mole per mass basis) govern the maximum sorption capacity. The same structural features favor an irreversible sorption of HS. Hydrophobic interactions are suggested to be the dominant mechanism of the adsorption of HS onto kaolin clay surfaces. Quantitative relationships between structure and maximum adsorption of HS can be beneficial for a well directed choice of humic materials yielding the highest content of absorbed HS upon their interaction with clay materials. This may lead consequently to a promising application of humic-clay complexes for purposes of remediation of polluted areas.

ACKNOWLEDGMENTS

We thank the Saxonian educational program "Leonardo" allocated the grant for N.A. Kulikova during her Ph.D. studies for a research stay in the group of Prof. Dr. F.-D. Kopinke at the Department of Remediation Research at the Centre for Environm. Res. (UFZ, Leipzig, Germany) in 1998. We express our deepest appreciation to Drs. N. Hertkorn (GSF, Munich, Germany) and D.V. Kovalevskii (MSU, Moscow, Russia) for valuable assistance with ¹³C-NMR measurements.

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