

## Article

# Adsorption of Fulvic Acid and Water Extractable Soil Organic Matter on Kaolinite and Muscovite

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**Abstract:** The interaction of organic matter with mineral components of the solid phase of soils is the most important process that regulates the cycle and balance of carbon in the biosphere. The adsorption of humic acids on minerals is accompanied by their fractionation in size, composition, and amphiphilicity, thus decreasing their heterogeneity. Despite a strong interest in studying the regularities and mechanisms of the interaction between natural organic matter and layered aluminosilicates, it is necessary to take into account the natural diversity of soil organic matter, adsorption conditions, and mineral composition. This study was designed to investigate the adsorption regularities of fulvic acid (FA) and water-extractable organic matter (WEOM) isolated from horizon H of peaty-podzolic-gleyic soil on kaolinite and muscovite. Sorbates and sorbents were examined by the following methods: high-pressure size exclusion chromatography (HPSEC), high-performance liquid chromatography (HPLC), and potentiometric titration. The specific surface areas of the sorbents were determined by the sorption of N<sub>2</sub> molecules. We found that hydrophobic components of FA and WEOM are mainly adsorbed on mineral surfaces. The adsorption of FA and WEOM on kaolinite and muscovite is followed by decreased hydrophobicity of organic matter and decreased heterogeneity of its amphiphilic properties in an equilibrium solution. At pH levels around 6, sorption of organic matter from FA solution containing 19% and 81% hydrophilic and hydrophobic components, respectively, onto kaolinite and muscovite occurs mainly due to hydrophobic components. Hydrophobic interactions on siloxane surfaces are the main mechanism to fix FA on both minerals. Kaolinite adsorbs slightly more organic carbon per unit area than muscovite. The adsorption of WEOM from a solution with 41% hydrophilic and 59% hydrophobic components results not only from hydrophobic and hydrophilic components but also from hydrophobic and electrostatic interactions and depends on pH. The most hydrophobic fractions of organic matter are adsorbed from the hydrophobic components on the surface of both minerals. Under conditions of the performed experiments at pH < 5, more WEOM is adsorbed on muscovite than on kaolinite.

**Keywords:** fulvic acids; clay minerals; adsorption; amphiphilicity



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## 1. Introduction

The interaction of organic matter with mineral components of the solid phase of soils is the most important process that regulates the cycle and balance of carbon in the biosphere. Organic matter adsorbed on minerals becomes more resistant to microbial decomposition [1]. Adsorption prevents the leaching of organic matter from the soil profile. Attachment to mineral surfaces and increasing resistance to biodegradation promote organic matter accumulation in soils and ensure carbon sequestration [2–6]. Humic acids attached to the surface considerably modify the surface of minerals [7] and change their adsorption properties [7–10].

The adsorption of humic acids on minerals is accompanied by their fractionation in size [11], composition [12], and amphiphilicity [13], thus decreasing their heterogeneity. The experiments on the adsorption of humic acids and water-soluble organic matter show that

larger molecules are adsorbed to a greater extent than smaller ones [11,14–16]. Humic acids with a large molecular size are adsorbed on the mineral surface, while fulvic acids with a smaller molecular size are adsorbed in the pores and reduce the mineral surface area [15]. Humic acids with a molecular weight of more than 100,000 Da are mainly represented by aliphatic compounds, while fractions of less than 30,000 Da mostly consist of aromatic components [11,17]. Aliphatic fractions of humic acid isolated from peat were revealed to have a higher affinity for the surface of kaolinite compared to aromatic fractions [13]. Wang and Xing established that aliphatic fractions of humic acid were predominantly adsorbed on both kaolinite and montmorillonite, while aromatic structures primarily remained in the solution. The humic acid adsorbed on both minerals was found to be more condensed than the original acid. The authors suggested that more condensed structures under low load could form on mineral surfaces as a result of strong surface interactions [12]. Experiments with water-soluble organic matter from lake water revealed that in a wide pH range, large hydrophobic molecules had a greater affinity for kaolinite, while small molecules high in carboxyl functional groups had little or no adsorption on the mineral [14]. Organic substances can be fixed on the mineral matrix of soil through various mechanisms, such as electrostatic interactions, hydrophobic interactions, ligand exchange, cation bridging, as well as hydrogen and van der Waals bonds [15,18–21].

High molecular weight compounds, hydrophobic fractions, and aromatic components can be selectively adsorbed on siloxane surfaces of kaolinite, while hydrophilic fractions with low molecular weight are adsorbed on the lateral surfaces of kaolinite crystallites [6,16].

The fulvic acid (FA) adsorption on T-basal surfaces occurs due to hydrogen bonds and hydrophobic interactions. Adsorption on the lateral surfaces of layered aluminosilicates and on the O-basal surfaces of kaolinite occurs mostly through ligand exchange and electrostatic interactions [21]. Ligand exchange was found to make a higher contribution to the adsorption of humic acids on kaolinite than on montmorillonite [18]. Using molecular-scale technologies of two-dimensional FTIR correlation spectroscopy and X-ray photoelectron spectroscopy, Chen et al. [22] showed that carboxyl and phenolic hydroxyls were adsorbed on the surface of kaolinite, forming C-O-Al/Si bonds. The interaction of carboxyl groups with  $\equiv\text{AlOH}^{2+}$  kaolinite resulted from ligand exchange and/or electrostatic attraction, depending on pH, and accounted for 13.9%, 7.76%, and 0% of the total adsorption at pH 4.0, 6.0, and 8.0, respectively [22].

The lower the pH, the more humic acids can be adsorbed on pH-dependent surfaces. The pH effect is more pronounced for kaolinite than for montmorillonite [21].

There are different points of view about the existence of a pH-dependent charge on planar surfaces of kaolinite. Brady et al. studied kaolinite with a surface area of 10–11 m<sup>2</sup>/g using force electron microscopy. The authors found that the lateral surface area of kaolinite could be from 10 to 50% of the total surface area, depending on the size and shape of the crystallites. Based on the obtained data, the authors concluded that not the basal but mainly the lateral surfaces produced the electron density calculated from the proton adsorption isotherm [23]. When comparing the area of the lateral surfaces, cation exchange capacity (CEC) values, and the data of titrimetric analysis, Zhou and Gunter [24] concluded that the pH-dependent charge of kaolinite could be found, not only on the lateral surfaces.

Gupta and Miller [25] studied the charge distribution on the surface of kaolinite using atomic force microscopy. The authors showed that at pH > 4, the siloxane surface was negatively charged, and the surface of the octahedral network was charged positively at pH < 6 and negatively at pH > 8. The results obtained suggest that the isoelectric point of the silicon-oxygen tetrahedral surface is at pH < 4, and the aluminum hydroxyl octahedral surface is in the pH range from 6 to 8. Additionally, a pH-dependent charge is present both on the siloxane surface and on the surface of the aluminum hydroxyl octahedral network [25].

Despite a strong interest in studying the regularities and mechanisms of the interaction between natural organic matter and layered aluminosilicates, it is necessary to take into

account the natural diversity of soil organic matter, adsorption conditions, mineral composition, and properties of sorbents. Thus, further research is required to build predictive models for the fixation and mobilization of organic carbon in soils. There are many research papers devoted to the interaction of humic acids with the surface of kaolinite. However, the information on adsorption regularities of water-soluble organic matter and humic acids on illite and muscovite, the main mineral components of most soil types, is extremely limited.

The aim of this research was to study adsorption regularities of fulvic acid (FA) and water-extractable organic matter (WEOM) isolated from soil on kaolinite and muscovite.

## 2. Materials and Methods

### 2.1. Sorbents

For adsorption experiments, we used kaolinite from the Glukhovetskoe deposit (Ukraine) and muscovite (fractionated micromica (particle size 5  $\mu\text{m}$ ) of ZAO 'GEOKOM'). The mineral composition of clays was determined by X-ray diffractometry on a MiniFlex-600 device (Rigaku, Tokyo, Japan) with a  $\text{CuK}\alpha$  and  $\text{K}\beta$  filter, a voltage of 30 kV, and a current of 15 mA and D/teX Ultra silicon strip detector.

Evaluation of the specific surface area was carried out using a Quadrasorb SI/Kr analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). Adsorption was performed at the temperature of liquid nitrogen (77.35 K). Nitrogen with a purity of 99.999% served as an adsorbate. Helium grade 6.0 (99.9999%) was used for the volume calibration of the measuring cells. The calculation was carried out by the BET multiple-point isotherm in the range of  $P/P_0$  from 0.05 to 0.30.

The pH of the point of zero charge ( $\text{pH}_{\text{PZC}}$ ) was determined by potentiometric titration. Thirty milliliters of NaCl solution with concentrations of 0.001, 0.01, and 0.1 mol/L were poured onto 0.025 g of the mineral, and then stirred for 30 min and titrated with 0.1 M HCl and 0.1 M NaOH in  $\text{N}_2$  atmosphere with an electrode DG111 on a Mettler Toledo DL 58 autotitrator (Mettler-Toledo AG, Schwerzenbach, Switzerland).

The pH of an aqueous mineral suspension was measured with a DG111 electrode on a Mettler Toledo DL58 device (Mettler-Toledo AG, Schwerzenbach, Switzerland) at a solid:liquid ratio of 1:50.

### 2.2. Sorbates

Fulvic acid (FA) was isolated from horizon H of peaty-podzolic-gleyic soil (Dystric Albic Gleyic Histic Retisol (Ruptic), WRB, 2014 [26]), sampled on the territory of the Central Forest State Nature Biosphere Reserve in the Tver region (the Russian Federation, 56° 28' 57.1" N; 32,059' 28.7" E) under the canopy of a blueberry-sphagnum spruce forest on a poorly drained watershed surface. The black smearing material of horizon H represents well-decomposed plant remains that lost their anatomical structure. Samples were taken from a depth of 15 cm at 10 locations over an area of about 20  $\text{m}^2$ , mixed, and dried at room temperature. The dried samples were crushed and sieved through a 1 mm sieve before extraction of FA and WEOM. To isolate FA, 500 g of the sample was poured with a 2.5 L 0.1 N NaOH solution, shaken for an hour on a rotator (230 rpm), and left for 23 h. Then, the supernatant was separated by centrifugation. Centrifugation was carried out in a centrifuge (Eppendorf Centrifuge 5804, Germany) for 10 min at 4000 rpm. The described procedure was performed 4 times in succession. Then, the obtained alkaline extract was acidified with HCl to pH 2 to precipitate humic acids and left for 24 h. After that, FA dissolved in the supernatant was isolated by centrifugation (4000 rpm, 10 min) and purified by the Forsyth method [27] with additional HF treatment using the IHSS method (International Humic Substances Society) [28].

The pKa of functional groups was determined from the titration data of an aliquot of an FA aqueous solution acidified to pH 2 by 0.1 N NaOH in an  $\text{N}_2$  atmosphere with a DG111 electrode on a Mettler Toledo DL 58 autotitrator (Mettler-Toledo AG, Schwerzenbach, Switzerland) and calculated using Gran functions [29].

Water-soluble organic matter (WEOM) was extracted from the same soil horizon as FA. The sample was poured with distilled water in a solid:liquid ratio of 1:5 (600 g of the sample and 3 L of distilled water) and left for 3 days at a temperature of 20 °C. After incubation, the liquid phase was separated from the solid by filtration through a filter paper. The obtained aqueous extracts were passed through a membrane filter with a pore diameter of 0.45 µm (OMNIPORE JHWP02500, Merck Millipore, Darmstadt, Germany) using a water jet pump.

In an aqueous solution of FA and WEOM, the pH was determined with an electrode (combined pH electrode LE438 IP 67) on an ion meter (F2-Standard (Mettler Toledo)). The total carbon content was measured using a liquid CN analyzer (High Temperature TOC/TN Analyzer liquidTOC, Elementar Analysensysteme, GmbH, Langenselbold, Germany). Molecular weight distribution was determined with a BioRad BioLogic LP System chromatograph (USA) on Sephadex G-50 Superfine gel (Sweden). Amphiphilic distribution was determined using OCTYL-SEPHAROSE CL-4B gel (Sigma-Aldrich, St. Louis, MO, USA).

### 2.3. Adsorption Experiment Technique

In the adsorption experiment with FA, 0.3 g of each mineral was placed into a 50 mL plastic centrifuge tube and poured with 50 mL of FA solution at a concentration of 61.01 mg/L for  $C_{org}$  (10.17 mg  $C_{org}$  per 1 g of mineral). The concentration of  $C_{org}$  in the FA solution was close to the concentration of  $C_{org}$  in soil solutions isolated from the H horizon of peaty-podzolic-gleyic soil (4.14–4.30 mmol/L) [30]. Then the suspension was shaken on a rotator for 24 h at 230 rpm and filtered through a membrane filter with a pore size of 0.45 µm. In the resulting solution, the pH values, carbon content, molecular weight, and amphiphilic distributions were determined by the same methods as in the initial solution. The amount of adsorbed carbon was determined from the difference in the carbon concentration between the initial solution and the solution after the interaction of FA with the mineral.

The experiments were performed in duplicate. The experiments on the FA adsorption on kaolinite are hereinafter referred to as FAK1 and FAK2, and on muscovite as FAM1 and FAM2.

The adsorption experiment with WEOM was carried out in two variations as follows. One g of mineral placed in a 50 mL centrifuge tube was added to 50 mL of an aqueous WEOM extract with  $C_{org}$  concentration of 337.06 mg/L (16.85 mg  $C_{org}$  per 1 g of mineral). In the first variation of the experiment, as well as in the experiment with fulvic acid, the suspension was shaken on a rotator for 24 h at 230 rpm and then filtered through a membrane filter with a pore diameter of 0.45 µm. In the resulting solution, the pH values, carbon content, molecular weight, and amphiphilic distributions were determined by the same methods as in the initial solution. The amount of adsorbed carbon was determined from the difference in carbon concentration before and after the interaction of WEOM with the mineral. In the second variation of the experiment with WEOM, the pH of the suspension was maintained at 4–4.5 for 24 h. These pH values are common to soil solutions from H horizons of peaty-podzolic-gleyic soil (4.14–4.30 mmol/L) [30].

The experiments were performed in duplicate. The experiments on the interaction of WEOM with kaolinite and muscovite without acidification of the suspension are hereinafter designated as WK1, WK2, WM1, and WM2, respectively. In the variation with acidified suspension, the experiments with kaolinite are designated as WK1a and WK2a, and with muscovite as WM1a and WM2a.

## 3. Results

*Textural and surface properties of kaolinite and muscovite.* Kaolinite was composed of 71% particles with an average diameter of <5 microns. Muscovite was represented by larger fractions: 81% particles with an average diameter of 5–50 microns. The outer surface area

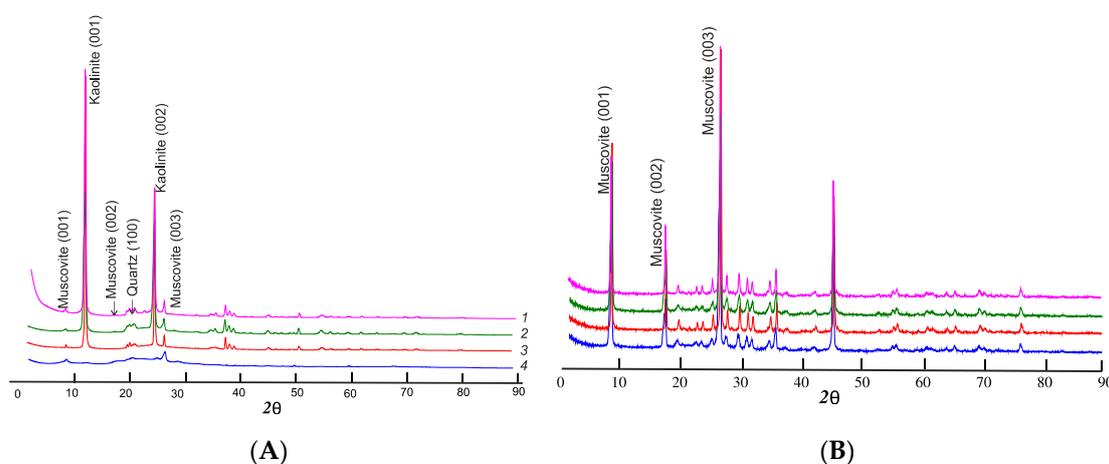
of kaolinite was twice the surface area of muscovite. The volume and average pore size of kaolinite were larger than that of muscovite. Both minerals lacked micropores (Table 1).

**Table 1.** Textural and surface properties of kaolinite and muscovite.

Mineral	Particle Size Distribution		Surface Area $S$ , m <sup>2</sup> /g (BET)	Pore Volume/Average Pore Size, nm (DET)	Micropore Volume, cm <sup>3</sup> /g (t-Plot Method, Halsey)	pH	pH <sub>PZC</sub>
	d, μm	%					
Kaolinite	<1	22.3	12.2	0.066/29.4	0	8.4	7.2
	1–5	48.7					
	5–10	14.3					
	10–50	14.7					
	50–250	0					
Muscovite	<1	2.1	6.4	0.027/7.0	0	7.7	8.1
	1–5	12.8					
	5–10	29.9					
	10–50	51.2					
	50–250	4.0					

The pH<sub>PZC</sub> of kaolinite was 7.2 units, and that of muscovite was 8.1.

X-ray diffraction (XRD) analysis revealed that kaolinite contains minor admixtures of muscovite and quartz, yet quartz was not detected in the muscovite sample (Figure 1).

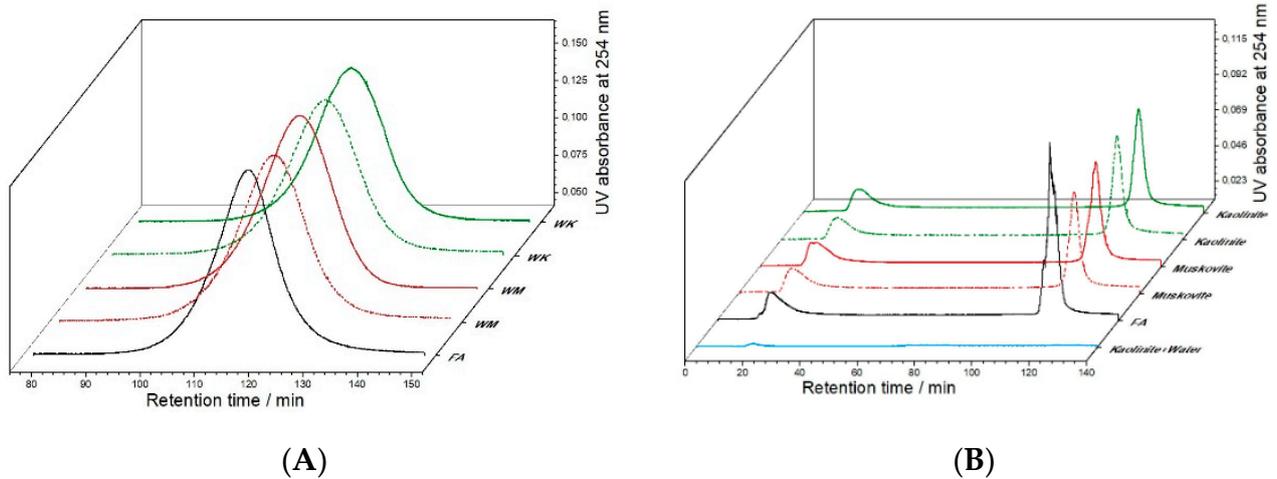


**Figure 1.** X-ray diffraction (XRD) patterns for kaolinite (A) and muscovite (B). The air-dried samples 1–4 were saturated with ethylene glycol and calcined at 350 °C and 550 °C, respectively.

**Fulvic acid and WEOM properties.** The aqueous solution of FA used for adsorption experiments contained a 61.01 mg/L concentration of C<sub>Org</sub> at pH 4.64. FA contained functional groups with pKa1 4.1 and pKa2 5.7—the latter significantly prevailed over the former. Titration data allowed us to distinguish another type of functional group with pKa3 ≈ 9; however, we failed to determine their exact number.

The molecular weight distribution (MWD) curve displays a single peak corresponding to a molecular weight of 22,000 Da (Figure 2A).

**FA has amphiphilic properties.** The amphiphilic distribution curve shows that the hydrophilic fraction is represented by a broad peak of relatively low intensity, while the more hydrophobic components are represented by a group of partially overlapping peaks (Figure 2B). The hydrophilic peak accounts for 19%, while the more hydrophobic components account for 81% of the total area of the peaks under the curve. The hydrophobicity coefficient of FA (hph), calculated as the ratio of the number of hydrophobic to hydrophilic components, is 4.26 units (Table 2).

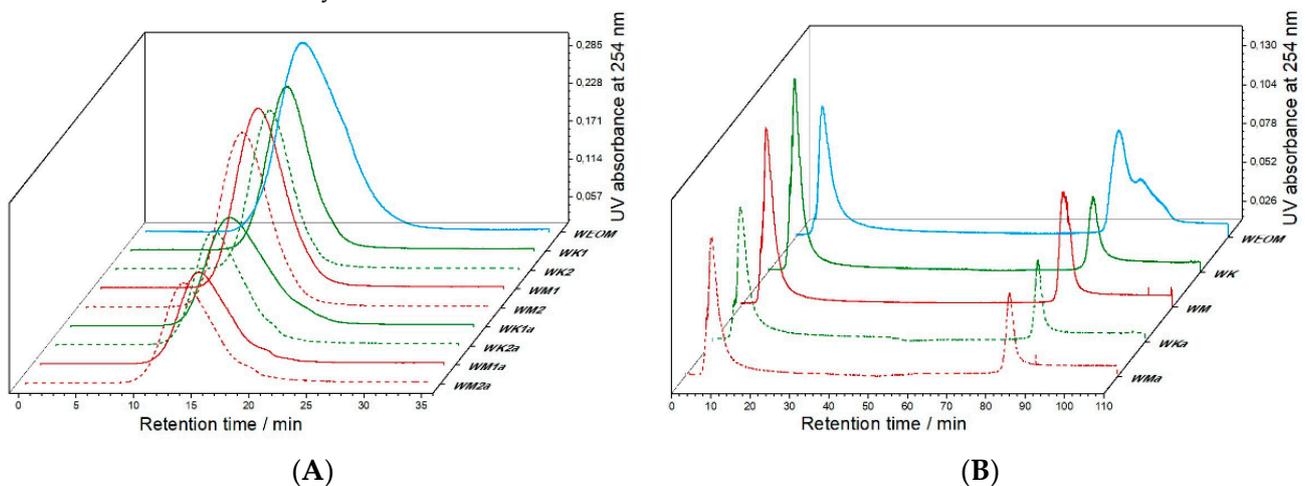


**Figure 2.** HPSEC chromatograms of FA (A) and amphiphilicity (B) before and after adsorption on kaolinite and muscovite.

**Table 2.** The FA solution properties before and after adsorption on minerals and the amount of C<sub>org</sub> adsorbed.

Sample	pH	C <sub>org</sub> , mg/L	Hydrophilic Fraction, %	Hydrophobic Fraction, %	hph	C <sub>org</sub> Adsorbed
						mg/g
FA	4.64	61.01	24	76	4.20	-
FAK1	6.14	54.20	31	69	2.21	1.14
FAK2	5.99	52.71	31	69	2.22	1.38
FAM1	6.21	58.52	36	64	1.80	0.42
FAM2	6.25	58.69	35	65	1.83	0.39

The water extract from the H horizon had an acidic reaction of the medium (pH 4.58), where the concentration of C<sub>org</sub> was 337.06 mg/L. The molecular weight distribution is represented by one well-pronounced peak corresponding to a molecular weight of 21,000 Da (Figure 3A). According to the amphiphilic distribution curve, hydrophilic components are represented by a narrow peak and hydrophobic ones by three partially overlapping peaks (Figure 3B). Hydrophobic components prevailed over hydrophilic ones both in the water extract from the H horizon and in the FA solution; however, the WEOM hydrophobicity coefficient is less than that of FA and is equal to 1.43 units (Table 3). The close similarity of WEOM and FA molecular sizes indicates that WEOM components are mainly represented by FA.



**Figure 3.** HPSEC chromatograms of WEOM (A) and amphiphilicity (B) before and after adsorption on kaolinite and muscovite.

**Table 3.** WEOM properties before and after adsorption on minerals and the amount of  $C_{org}$  adsorbed.

Sample	pH	$C_{org}$ , mg/L	Hydrophilic Fraction, %	Hydrophobic Fraction, %	hph	$C_{org}$ Adsorbed
						mg/g
WEOM	4.58	337.06	41	59	1.43	-
WK1	4.69	306.36	70	30	0.43	1.38
WK2	4.74	304.86	69	31	0.44	1.45
WK1a	4.07	281.86	68	32	0.47	4.46
WK2a	4.04	279.16	68	32	0.47	5.44
WM1	4.90	307.61	67	33	0.49	1.33
WM2	4.97	310.36	66	34	0.51	1.20
WM1a	4.38	268.36	68	32	0.47	3.19
WM2a	4.34	269.73	68	32	0.47	3.12

#### *WEOM and FA Adsorption*

As a result of the interaction between minerals and the FA solution, the pH of the equilibrium solution increased by two units compared to the initial value (Table 2).

The interaction with minerals resulted in the decrease of  $C_{org}$  concentration in the FA solution. A greater reduction of  $C_{org}$  concentration in the solution occurred after the adsorption on kaolinite in contrast with muscovite.

After the adsorption on minerals, HPSEC chromatograms of FA remained almost unchanged, while significant changes occurred on the amphiphilic distribution curve. The area of the peak corresponding to hydrophilic components after the adsorption of FA did not change, while the area under the curve corresponding to the site of hydrophobic compounds decreased, primarily due to the predominant adsorption of less hydrophobic components (Figure 2B). The adsorption led to the decreased proportion of hydrophobic components of FA and to the increased proportion of hydrophilic ones. The hydrophobic components were adsorbed mostly on the surface of kaolinite in comparison with muscovite. The hph coefficient of FA after the adsorption on kaolinite and muscovite decreased by 2.1 and 2.3, respectively (Table 2).

After adsorption on kaolinite and muscovite, the pH of WEOM increased on average by 0.1 and 0.2 units, respectively, in the variation of the experiment without acidification (Table 3), which is significantly less than the change in pH observed after FA adsorption on minerals.

Like FA, WEOM was adsorbed on both minerals. More organic matter was adsorbed in the experiment with acidification than in the one without acidification.

In both variations of the experiment, the concentration of  $C_{org}$  in equilibrium solutions after interaction with minerals proved to be quite similar in the experiments with both kaolinite and muscovite (Table 3).

As a result of the interaction of WEOM with kaolinite and muscovite, we did not observe noticeable changes in the size of the particles remaining in the solution after adsorption (Figure 3A).

There was a marked decrease in the WEOM hydrophobicity due to a reduced  $C_{org}$  after the interaction with minerals. In both variations of the experiment, the proportion of hydrophobic components in the solution before adsorption decreased from 59% to 30–32% after adsorption on kaolinite and to 32–34% after adsorption on muscovite, respectively (Table 3). The decrease in hydrophobicity resulted from the adsorption of the most hydrophobic components (Figure 3B).

#### **4. Discussion**

*Acidity neutralization of FA and WEOM solutions.* The increased equilibrium pH in the experiments with FA and WEOM without acidification compared to the pH of the initial solutions can be explained by the buffer properties of clay minerals. The suspension pH for kaolinite and muscovite in distilled water was 8.4 and 7.7, respectively (Table 1). Despite the narrower mineral:solution ratio in the experiments with WEOM, we observed

a lower increase in the pH of the initial solution than in the experiments with FA. This can be explained by two factors: slightly higher  $C_{org}$  load in the WEOM experiments and higher acidity of WEOM organic matter than FA. The FA solution was dominated by pKa 5.7 functional groups. According to the data of Karavanova et al. [31], the pKa of acid components in soil solutions isolated from the H horizon of peaty-podzolic-gleyic soil vary from 5.15 to 5.36 units.

*Regularities of FA adsorption.* For these experiments, we used kaolinite and muscovite of different dispersion degrees. Moreover, both of these minerals had a rigid crystal lattice and showed little or no adsorption of organic matter under the performed experiments. Thus, it is reasonable to compare the adsorption capacity of minerals in terms of the amount of adsorbed  $C_{org}$  per unit surface area.

As a result of adsorption on both kaolinite and muscovite, size fractionation of FA components did not occur (Figure 2A). The particle size was similar to the pore size of both minerals [32,33].

Hydrophobic components were predominantly adsorbed on both kaolinite and muscovite. Therefore, it can be assumed that the main mechanism of FA fixation on both minerals is hydrophobic interactions. Hydrophobic interactions on kaolinite and muscovite occur on siloxane surfaces and do not depend on pH. In terms of per unit area, kaolinite adsorbs slightly more  $C_{org}$  than muscovite at similar pH values (Table 2, Figure 4a). This tendency can be explained by the higher constant charge of muscovite, compared to kaolinite, which spreads onto siloxane surfaces [34]. Increasing charge causes decreased surface hydrophobicity, leading to inhibition of hydrophobic interactions.



**Figure 4.** The dependence of adsorbed  $C_{org}$  (a) and  $K_d$  (b) on equilibrium pH.

The distribution coefficients of  $K_d$  were a little higher upon adsorption on kaolinite than on muscovite (Figure 4b), which may indicate stronger hydrophobic interactions of FA with the kaolinite surface as compared to the muscovite surface.

According to the data of potentiometric kaolinite titration,  $pH_{PZC}$  is approximately 7 (Table 1), which greatly exceeds the range of  $pH_{PZC}$  of kaolinite from 2.7 to  $\approx 5.7$  [14,24,35]. Kriaa et al. [36] report higher  $pH_{PZC}$  from 6.5 to 7.8 units for kaolinite from the deposits of Tunisia. As will be shown below, the kaolinite used in this study contains a minute amount of muscovite, which is likely to increase the  $pH_{PZC}$ .

The obtained value lies within the range of  $pH_{PZC}$  from 7.5–8.5 for muscovite and illite, according to the literature [37,38].

As shown by Huertas et al. [39], neutral aluminol and silanol groups prevail on the surface of kaolinite with  $pH_{PZC} \approx 5.5$  within pH from 4.5 to 8. The authors calculated that weakly acidic side aluminol groups were completely protonated at  $pH \leq 3$ , and hydroxyls on the basal surface were positively charged only at  $pH < 3$  [39]. Liu et al. [40] showed that silanol  $\equiv Si-OH$  and aluminol  $\equiv Al-OH_2OH$  groups had pKa 6.9 and pKa 5.7, respectively.

In this experiment, we used kaolinite with a higher  $pH_{PZC}$  than most kaolinite considered in the literature. Therefore, aluminol groups could be partially protonated at  $pH \approx 6$ . Gupta and Miller [25] demonstrate that the isoelectric point of the alumina hydroxyl octa-

hedra surface is within the pH range from 6 to 8. The FA solution is dominated by pK<sub>2</sub> 5.7 acid groups close to the pH of equilibrium solutions. Consequently, approximately 50% of the pK<sub>2</sub> functional groups were dissociated in the solution. Therefore, at least electrostatic interactions between the hydrophilic components of FA and the lateral surfaces of kaolinite or even protonated OH-groups on the aluminum hydroxyl octahedra surface can be possible in this experiment. However, the amphiphilic distribution curves do not display adsorption of the hydrophilic fraction. This might be due to the fact that hydrophobic components significantly prevail over hydrophilic ones in the FA solution used for the experiment (Table 2).

The pH<sub>PZC</sub> of muscovite is higher than that of kaolinite. Aluminol groups in muscovite are characterized by slightly lower pKa1 values than in kaolinite and vary from 3.9 to 5.52 units [37,41]. The pHPZC of the lateral surfaces of muscovite is  $7.5 \pm 0.5$  [38]. Therefore, the adsorption of the hydrophilic fraction on the muscovite surface is possible but was not revealed in this experiment.

The pore size in both kaolinite and muscovite is larger than the average size of molecules in the FA solution (Table 1). Thus, the pore size does not affect the regularities of FA adsorption under the conditions of the given experiments.

Figure 2B shows that less hydrophobic components of the hydrophobic fraction are adsorbed on both minerals. To explain this fact, further research is required, including the determination of hydrophobic fraction composition.

*Regularities of WEOM adsorption.* Hydrophobic components prevail in WEOM, but their share is slightly higher than that of hydrophilic components (Table 3). In the experiment without acidification, the most hydrophobic WEOMs are adsorbed on both kaolinite and muscovite (Figure 3B).

The chromatograms of amphiphilic distribution in the variation of the experiment without acidification show that the intensity of the peak from the hydrophilic components increases after adsorption on minerals (Figure 3B), while the concentration of C<sub>org</sub> decreases in equilibrium solution (Table 3). Thus, it can be concluded that WEOM is either transformed during adsorption, or that desorption of hydrophilic components occurs in the system within 24 h. The experiments on the FA adsorption on muscovite at pH 3.7 have revealed that the electron density of FA adsorbed on the mineral surface increases after three hours of interaction but decreases after 12 h. The authors suggest that the change in the electron density may be caused by a low rate of FA adsorption or fractionation during adsorption, i.e., replacement of small FA molecules by larger ones [42]. However, in the variation of the experiment with acidification at pH of the equilibrium solution  $\approx 4$ , an increasing proportion of hydrophilic components was not observed. Further research is required to explain the results obtained.

The adsorption of WEOM increases with a decreased pH (Figure 4a). The abovementioned pH-dependent surfaces of kaolinite and muscovite, and the fact that the pKa of functional groups of organic matter in solutions isolated from the H horizon of peaty-podzolic-gleyic soil varies from 5.15 to 5.36 [31], allow us to conclude that at pH < 5, the adsorption of WEOM components, along with hydrophobic interactions, occurs due to electrostatic interactions on pH-dependent surfaces. Such interactions can be carried out both due to deprotonated functional groups of organic matter and a positively charged pH-dependent surface of minerals, as well as due to protonated functional groups of organic matter and a constant charge of the mineral surface. The latter mechanism explains the greater adsorption of WEOM on muscovite compared to kaolinite (Figure 4a). The K<sub>d</sub> value also proved to be higher on muscovite than on kaolinite (Figure 4b).

In addition, under this study, we show that FA and WEOM can be fixed on the surface of kaolinite and muscovite via hydrogen bonding.

## 5. Conclusions

Our research showed that adsorption of FA and WEOM on kaolinite and muscovite is accompanied by decreasing hydrophobicity of organic matter and decreasing heterogeneity

of its amphiphilic properties in an equilibrium solution. Under the experimental conditions at a pH of about 6, the adsorption of organic matter from the FA solution containing 19% and 81% hydrophilic and hydrophobic components, respectively, on kaolinite and muscovite is performed predominantly due to hydrophobic components. Moreover, hydrophobic interactions occurring on siloxane surfaces are the main mechanism for the fixation of FA on both minerals. Kaolinite adsorbs slightly more  $C_{org}$  per unit area than muscovite since a highly negative charge of muscovite prevents hydrophobic interactions on siloxane surfaces.  $K_d$  appeared to be slightly higher during adsorption on kaolinite than on muscovite. The adsorption of WEOM from the solution containing 41% hydrophilic and 59% hydrophobic components is performed by hydrophobic and hydrophilic compounds, as well as by hydrophobic and electrostatic interactions and depends on pH. The most hydrophobic components are adsorbed on the surface of both minerals. Under the performed experiment at  $pH < 5$ , more WEOM is adsorbed on muscovite than on kaolinite. The  $K_d$  value is higher on muscovite than on kaolinite.

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