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SOIL CHEMISTRY

The Effect of Humic Acid Adsorption on the Coagulation Stability of Soil Suspensions

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Abstract—Humic acid adsorption and its effect on the coagulation stability of soil suspensions were studied. The humic acid (Aldrich Chemie) adsorption from its dilute aqueous solutions was examined for gray forest soil (Greyzemic Phaeozem (Loamic)), its components (clay fraction and parent rock), and chernozem (Chernozem (Pachic)). Physicochemical methods proved that the sorption of humic acid in these objects is determined by the time of interaction, concentration of the acid, and the properties and concentration of the solid phase; it may be accompanied by ion exchange. The effect of humic acid adsorption on the coagulation stability of soil suspensions was judged from changes in the volume of gel-like precipitate released from the suspensions and the time required for the suspension brightening. It was shown that the stability of suspensions increases with an increase in the concentration of humic acid and depends on the type of soil.

Keywords: clay mineral, gray forest soil (Greyzemic Phaeozem (Loamic)), chernozem (Chernozem (Pachic)), humic acid, adsorption, coagulation, stabilization

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INTRODUCTION

As is known, the most important factors that determine the soil structure and consistency are the composition of soil particles and the properties of their surface. Correspondingly, any change in the state of the surface necessarily alters the physical state of soils, their structure, and their consistency. In particular, the sorption of organic substances by clay minerals and soils significantly changes their surface characteristics and the stability of their aggregates.

According to the general principles of physicochemical mechanics, the interaction of structure-forming particles, which is determined by the nature of their surface in the disperse phase [23], is one of the most important stages in forming of the structured body. Modification of these particles, be it adsorption or chemical process, affects the structuring of natural minerals and soils. The dependence of the properties of structured body on the nature of the surface of mineral particles modified by adsorption has been studied by many researchers [1, 3, 9–13, 24, 27–29]. For example, the montmorillonites modified by saturating their interlayer space with the alkylamine cations with long chains of organoclay structures are used for sorption of nonionic toxic organic compounds [1, 26]. The interaction of organic substances of specific nature with clay minerals and soils is one of the most relevant issues in soil science. The interest in organomineral interaction in the world literature is associated not only with the insight into the formation of humus and soil adsorption complex but also with the ecological problems related to the anthropogenic soil pollution with organic and mineral toxicants. In particular, a descriptive ability of two integral biotic indices derived from laboratory experimental data on the effect of humic preparations on the microbiota in a copper-polluted model substrate (sand, kaolin, and peat) was estimated [30]. A statistical model utilizing Harrington's desirability function and an integral parameter of the well-being of a microbial system (test culture) was used to generalize the ecotoxicological data on polluted specimens (660 mg Cu/kg) and integrally estimate the effect of humic preparations on the biotic component. It was found that humic preparations stimulate multispecies bacterial complexes, while the test cultures of higher plants and algae are less sensitive to the introduced humates. The authors infer that the integral approach based on the generalized desirability function provides a more complete and reliable system of biotic characteristics.

The kinetic and thermodynamic parameters of the Cu^{2+} and Zn^{2+} sorption by humic acids (HAs) were computed for peat gley tundra soil [17]. The sorption of the studied heavy metal ions by HA preparations was reliably approximated by a pseudo-first order kinetic equation. Negative changes in the Gibbs energy at 298.0

and 314.3 K for Cu^{2+} (–26.2 and –24.5 kJ/mol, respectively) and Zn^{2+} (–22.2 and –22.0 kJ/mol, respectively) ions suggest a possible spontaneous sorption of these ions in the studied temperature range. The recorded changes in the enthalpy of sorption (–33.1 and –4.5 kJ/mol for Cu^{2+} and Zn^{2+} ions, respectively) suggest that both reactions are exothermal. The sorption equilibrium constant for Cu^{2+} ions considerably decreases with an increase in temperature and does not change significantly for Zn^{2+} ions. The decrease in the sorption equilibrium constants with an increase in temperature demonstrates the shift of equilibrium towards desorption, which is a characteristic features of the physical sorption and suggests that two mechanisms—physical sorption and chemisorption—can be involved in the ion binding on the surface of HA preparations.

Correspondingly, both the interest and difficulty in solving ecological problems associated with pollution with different toxicants result from their complexity and insufficient insight into the structure of HA (fulvic acid included) molecules, as well as from an intricate and heterogeneous soil composition. In particular, the nature and character of the surface of minerals, pH values, water content, and other factors considerably influence the interaction between organic molecules and soil mineral components. It is well known that the organic and mineral substances actively interact in soils and represent one of the mechanisms contributing to structure formation and controlling the size and physicochemical properties of the formed aggregates [3, 27–29, 32]. In particular, evaluation of the aggregate stability of clay particles in the chronosequence of texturally differentiated soils in the Czech Republic demonstrates that intensive tillage moves the colloidal system to coagulation, while the colloidal system tends to restore its initial state after withdrawal of plowed soil from agricultural production and subsequent afforestation [32]. In other words, the equilibrium is shifted towards peptization, as is suggested by the trends of an increase in the ξ potential. In addition, Artem'eva and Kirillova [3] considered the role of organic–mineral interactions in the structure formation and humification of the main soil types in the center of the Russian Plain. A modified variant of the particle size fractionation was described; thus, functionally important components of the soil organic matter in different parts of the soil matrix could be separated. This approach allows for the most adequate evaluation of the soil microstructure. Another study [35] revisits the concept organomineral clay complexes in the chronological order [35].

The organomineral compounds formed on the surface of soil aggregates and mineral components via adsorption of organic molecules modify this surface making it specific and selective in sorption. This significantly changes the mobility of components of the soil organic matter as well as the chemical and energy inhomogeneity of the surface of clay minerals and amorphous silicon, aluminum, and iron compounds with corresponding changes in the sorption and migration capacities of metals in soil. Organomineral pedofeatures or surface compounds, even in a small quantity, exert a significant influence on the aggregate stability of suspensions, their structural sorption properties, and exchange and hydrophysical properties of minerals and soils [10–13, 24, 31, 33, 34, 36–41]. New concepts of soil organization have recently appeared, including the matrix, fractal [5, 27–29, 42–44], and cluster hypotheses [10–13, 22].

Fedotov et al. [27–29] have found that soils contain an integrated network of organomineral gel. The insight into the colloid chemical properties of the gel structures on the surface of solid soil particles suggested that the gel structures in soil should form an integrated colloidal gel network, a single matrix, including the soil solution. Such a colloidal gel matrix should affect the soil properties. Thus, the soils can be considered as the systems, whose properties are largely determined by the type, state, and properties of the soil gels formed by humic substances and inorganic nanoparticles. In addition, the colloidal particles are orderly arranged in the humic gel and form fractal structures, which is characteristic of all examined soils and soil horizons. Fedotov with coauthors believe that the presence of an integrated organomineral gel network in soils requires the insight into additional characteristics, such as diffusion adsorption potentials, soil piezo effect, diffusion of substances in soil, and their electric and structural–mechanical properties.

The use of fractal dimension as a characteristic of colloidal structures and surface properties of soil minerals and soils, described earlier [11], is promising for description of the structural state and cluster properties of the soil surface with adsorbed polyelectrolytes. Correspondingly, the formation of soil structure, including coagulation stability of soil suspensions during HA adsorption, is a poorly studied and relevant problem in soil science.

The goal of this work was to study how the HA adsorbed by soil influences the coagulation stability of soil suspensions.

OBJECTS AND METHODS

We studied the gray forest soil (Eutric Retisol (Loamic, Cutanic, Ochric)) sampled at the experimental field station of the Institute of Physicochemical and Biological Problems of Soil Science (Pushchino, Moscow oblast, Russia), leached chernozem (Luvic Chernozem (Loamic, Pachic)) sampled in the Krapivna district (Tula oblast), and the clay fraction of gray forest soil. The clay fraction is very important in soil fertility. This fraction has a high sorption capacity and high concentrations of humus, ash elements, and nitrogen; it contributes to soil aggregation [31]. The

Table 1. Physical and chemical characteristics of gray forest soil and chernozem

Soil	C_{org}, %	Cation exchange capacity, cmol(+)/kg	pH H_2O	Clay, %	Specific surface area, m^2/g	ξ potential, mV
Gray forest soil	1.33	17.80	6.45	14.3	8.86*, 11.5**	–22.6
Leached chernozem	2.89	9.93	6.9	22.8	9.54*, 69.62**	–14.0

Specific surface area calculated according to * nitrogen and ** water.

clay fraction of gray forest soil in this work was separated by elutriation [26]. For this purpose, 3–5% water suspension of soil was thoroughly stirred with a mechanical agitator until the lumps disappeared and left for 50–60 min to decant the finest fraction with a trap. The clay fraction was obtained by triple elutriation and centrifugation (60000 rpm). The specimens of clay fraction were examined by X-ray analysis and IR spectroscopy.

The clay fraction of gray forest soil contained the following minerals: 32.6% hydromica, 1.2% smectite + chlorite, 20.7% kaolinite, 38.3% quartz, 7% microcline, and 1.81% organic matter (see [2, 31] for more detailed data on this fraction).

The parent rock of gray forest soil was also assayed. According to Alifanov [2], carbonate and carbonate-free loesslike loams with a thickness of 2–3 m are the most widespread parent rocks for gray forest soils. Their mantles overly glaciofluvial and moraine sediments. Loesslike mantles are represented by silty and silty clay loams and light clays with a prevalence of the silt fraction. The composition of the primary and secondary minerals in gray forest soil is determined by the parent rock and the environmental conditions during soil formation. The clay minerals in most cases are represented by montmorillonite, hydromicas, and their mixed-layer aggregates; kaolinites are scanty. The content of clay minerals increases in the illuvial horizons. Occasionally, loams are slightly sandy. In our study, we used the carbonate-free loam containing 32.6% hydromica, 1.2% smectite + chlorite, 20.7% kaolinite, and 38.7% quartz.

The organic substance—a high-purity preparation of HA isolated from peat—was purchased from Aldrich Chemie (D 7924, sodium salt). It had the following elemental composition: 11.96% water (of dry weight), 4.8% COOH, 41.9% C, 4.1% H, 50.4% O, 0.55% N, and 1.84% S; molecular weight, ~829–830. The HA was characterized according to its IR spectrum described earlier [7]. It is known [18, 19] that the HA IR spectra are specific and have a constant set of absorption bands, which distinguish them from the compounds belonging to other classes. For example, a wide compound band at 3600–2200 cm^{-1} comprises the valence vibration bands of a free hydroxyl group (3600 cm^{-1}), the hydroxyl groups linked by intermolecular hydrogen bonds (3448–3192 cm^{-1}), and minor valence vibration bands of the NH group. The weak absorption bands in high frequency region (2908, 2848, 2628, and 2328 cm^{-1}) are identified in the –C–H valence vibration region as the bands of methyl and methylene groups. In addition, these bands are observed in the region of deformation vibrations in the range of 1312–1372 cm^{-1} (several minor bands). The absorption bands in the range of 1200–1216 cm^{-1} are presumably determined by the hydroxyl and =C–O– groups. Distinct deformation vibration bands of alcohol hydroxyl groups and absorption bands of polysaccharides are observed at 1056 cm^{-1}. A carboxyl group appears as the band with a maximum of 1744 cm^{-1}. Part of the carboxyl groups is ionized, i.e., a free carboxyl group is converted into a carboxylate group forming HA–COONa salts; the latter group intensively absorbs vibrations at 1692, 1590, and 1400–1390 cm^{-1}. In addition, C=C bonds of aliphatic and aromatic systems as well as nitrogen-containing groups appear in the HA spectrum in the range of 1604–1508 cm^{-1}. The latter groups are associated with almost all major bands in the spectra of HA and fulvic acids, because nitric groups absorb in the same frequency ranges as the analogous carbon- and oxygen-containing groups. In particular, it is known that amide I variable groups appear at 1650 cm^{-1} and amide II groups, at 1540 cm^{-1} [16–18]. However, they coincide with aromatic groups (1604 and 1550 cm^{-1}) in the HA spectrum. Weak aromatic groups are visible at 748 and 848 cm^{-1}. The main physical and chemical properties of the examined soils are listed in Table 1.

The studied soils considerably differed in the content of organic carbon, physicochemical characteristics, and particle size distribution (Table 2). The particle size distribution is among the most important characteristics of soil fertility since it influences the hydrophysical, physicomechanical, aerial, and other soil properties. The Kachinskii classification of soil particle size distribution [6] is currently used in Russia. The particle-size distribution analysis of the gray forest soil was performed by the pipette method with pyrophosphate pretreatment; for the chernozem, particle-size distribution data were obtained according to Kachinskii. These analyses were performed for the Ap horizons of the gray forest soil and chernozem sampled from the upper layers (0–20 and 0–12 cm, respectively).

These data, obtained by different methods, are applicable to characterization of soil specimens. As seen from Table 2, gray forest soil and chernozem have the particle size distribution patterns characteristic of a sandy loams. The content of sand fractions (1–0.05 mm) reaches 21–33.3% of the absolutely dry soil. It is known [2] that the sand fraction consists of primary minerals and is characterized by the high water conductivity, the absence of swelling, and the absence of plasticity in the wet state. It possesses certain capillarity and water retention capacity. Gray forest soil contains a considerable amount of clay and differ from chernozem in a lower content of humus.

The specimens were prepared for physicochemical assays as described in [19]. Weighed portions (100 g) were placed on clean sheets of paper to remove the roots, inclusions, and various pedofeatures by hand. Large soil clods were manually broken or crushed in a porcelain mortar using a pestle with a rubber cap to small fragments (5–7 mm) in order to get more homogenous samples. Then, the samples were quartered and the selected part was comminuted again in a porcelain mortar with a rubber-capped pestle. The comminuted samples were sifted through the sieve with pore size of 0.25 mm.

The HA adsorption on the soil surface was studied using dilute aqueous solutions in the concentration range of 1×10^{-3} to 1×10^{-1}%. The HA concentration in the solution was determined colorimetrically; the solid and liquid parts of suspensions were separated by centrifugation. The suspension specimens for studying adsorption were prepared by mixing a weighed soil sample of 0.2 or 2.0 g and 100 mL water or HA solution of the above mentioned concentrations; thus, 0.2 and 2.0% soil suspensions were made. The supernatant after centrifugation was collected to determine the HA concentration with calibration curves. Adsorption was computed using the following equations:

$$\Gamma\ (\mathrm{mg/g}) = (c_0 - c_t)V\ 10/m$$

$$\text{or}\ \Gamma_1\left(\mathrm{mg/m^2}\right) = (c_0 - c_t)V\ 10/mS,$$

where Γ and Γ_1 are the HA adsorption by soil (mg/g and mg/m^2, respectively); c_0 is the initial HA concentration in solution; c_t is the HA concentration at time moment t (g/100 mL or %); m is the weighed sample of adsorbent (soil particles, g); V is the volume of solvent (mL); and, is the specific surface area of adsorbent (m^2/g).

The specific surface area of adsorbent was determined according to the sorption of water vapor in a McBen–Bakr vacuum sorption system equipped with a spring balance at 25 ± 0.1°C and according to physical sorption of nitrogen. The spring sensitivity was 4–6 μmol/g sorbent. The monolayer capacity and specific adsorbent surface were determined according to the sorption of water vapor using the BET polymolecular adsorption equation [4].

The ζ potential for the suspensions containing 50 mg soil sample in 50 mL water or HA solution was determined using a Zetasizer Nano ZS Malvern (United Kingdom) molecular size analyzer [46]. Two soil–HA suspension samples were assayed in parallel, and three measurements of electrophoretic mobility of particles in disperse medium (water) were performed with an accuracy of ±2 mV o determine the ζ potential. Statistica software package installed in the analyzer was used for automated statistical data processing. Table 1 lists the mean values of ζ potential computed according to Henry's equation:

Table 2. Particle size distribution in the of gray forest soil and chernozem, %

Particle size range, mm	Gray forest soil	Chernozem
1–0.25	21.4	30.30
0.25–0.05	15.1	21.50
0.05–0.01	33.0	23.92
0.01–0.005	8.3	9.64
0.005–0.001	8.8	–
<0.001	13.4	10.80
<0.01	30.5	24.38

$$\zeta = (3\eta u)/(2Df(\kappa a)),$$

where u is the electrophoretic mobility; D is the dielectric permittivity of liquid; η is the liquid viscosity; and $f(\kappa a)$ is Henry's function. For water, $D = 81$, $f(\kappa a) = 1.5$ (Smoluchowski approximation), and $\eta = 0.01005$ at 20°C and 0.00894 at 25°C. The pH was measured with a HANNA pH 211 (Germany) pH-meter. The chemical structure of the surface of both soils and components of the gray forest soil (clay fraction and clay loamy parent material) modified by HA adsorption was examined by IR spectroscopy. The IR spectra of the initial soil specimens and the samples with preadsorbed HA were recorded on a Specord M80 spectrometer using KBr (salt to sample, 1 : 200) in the wavenumber range of 4000–400 cm^{-1}.

The volume of the precipitate was determined in 10% soil suspensions (10 g dry soil was mixed with 100 mL water or 0.01–0.05% HA solutions) using graduated test tubes (25 cm^3) with ground-glass stoppers. Suspension was ten times stirred top to bottom and left at rest. The sedimentation kinetics was examined visually depending on the HA concentration in a wide range of interaction time.

RESULTS AND DISCUSSION

Adsorption of Humic Acid

It is known that the structure formation in clay mineral and soil suspensions in the presence of organic additives is in many respects determined by the adsorption on the surface of solid phase [25, 26]. We have shown here that the HA adsorption in the gray forest soil and chernozem is determined by the time of adsorbent–adsorbate interaction, the concen-

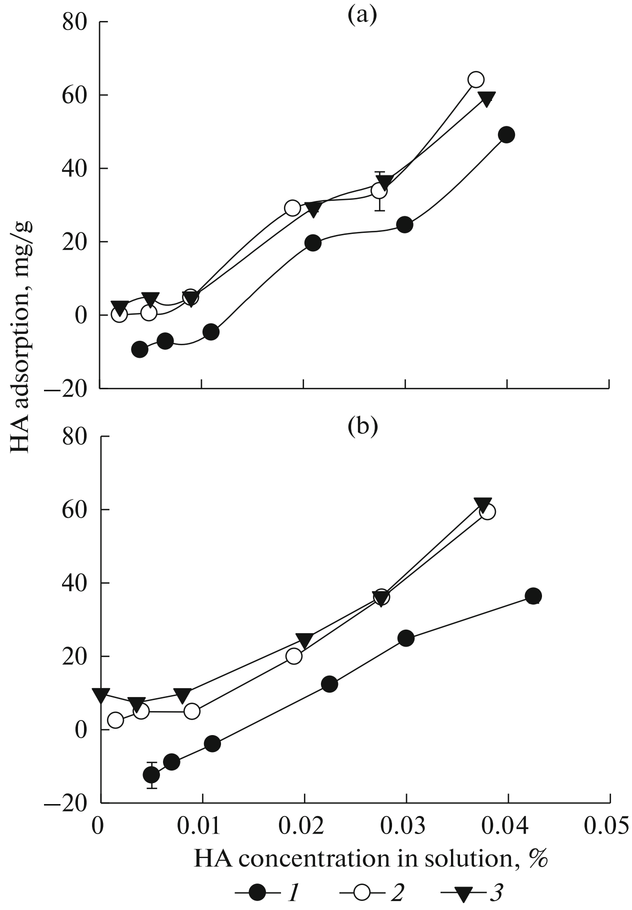

Fig. 1. Dependence of HA adsorption by (a) gray forest soil and (b) chernozem on HA concentration after (*1*) 48 h, (*2*) 120 h, and (*3*) 168 h.

tration of the modifying additive (HA), and the soil solid phase properties and concentration. In particular, a negative adsorption on both soil specimens (gray forest soil and chernozem) is observed upon the short-term interaction (up to 48 h) and small (0.01–0.025%) HA concentrations (Fig. 1). The adsorption changes to positive with an increase in HA concentration to 0.05% and the of the HA–soil interaction time to 120 and 168 h. The negative adsorption is explained in several ways. For example, the negative adsorption for the adsorbents modified with polymers making their surface hydrophilic in the case of polar solvents is explained [15] by the prevalent adsorption of the solvent on the surface of adsorbent disperse phase. A competitive effect of the solvent (water) versus HA macromolecules suggests the need in prehydration of hydrophilic sorbents. Our study into the sorption of water vapor for anhydrous sorbents, such as dehydrated potassium aluminum sulfate, calcium silicate, calcium aluminate, and dehydrated alum stone [8], gives an example of prehydration of the surface. Only physical sorption of water vapor was observed in the monolayer, while chemical hydration (avalanche-type water binding) commenced with formation of condensed water. The effect of preliminary moistening of the surface of clay minerals on the adsorption of organic substances was also demonstrated in other studies [1]. The most likely explanation of a negative HA adsorption on soil particles in terms of thermodynamics is the presence and effect of native organic carbon in the studied soils. Correspondingly, the addition of HA to soil suspension in small concentrations enhances leveling of the concentrations of organic matter, thereby shifting the adsorption equilibrium leftward according to Le Chatelier's principle. Le Chatelier's principle states that if a system at equilibrium is disturbed from the outside by a change in an equilibrium condition, for example, the concentration of an organic substance, the system amplifies the processes providing the counteraction, i.e., the desorption of the organic matter.

However, we also observed a negative adsorption when studying the adsorption of polyacrylic acid (**PAA**) on the synthetic negatively charged silica gel free of organic matter [21]. In this case, Pinsky suggested another explanation for negative adsorption in terms of negative–positive adsorption: a negative PAA adsorption on silica gel is observed at the initial time interval (10–12 h), because the silica gel surface prevalently repulses the like-charged molecules (a rapid barrierless process). A slower process of positive adsorption requiring the activation energy takes place concurrently. After a certain period, the positive PAA adsorption becomes prevalent. The mechanisms of this phenomenon have been discussed [21], and the method has been proposed to compute the kinetic parameters of the curves with a negative–positive PAA adsorption dynamics for the negatively charged silica and aluminosilicate gels.

The adsorption curves for gray forest soil and chernozem at different HA concentrations are concave or S-shaped and the corresponding curve regions drastically run upward with an increase in HA concentration (0.03–0.05%). This demonstrates that it is impossible to reach the saturation of the surface with an increase in the HA concentration, which points to a polylayer adsorption. Thus, gray forest soil and chernozem insignificantly differ in the amount of adsorbed HA in the regions of both small and large occupations of the surface. However, the kinetics of 0.05% HA adsorption displays considerable differences in the values of adsorption on the soil particles and on the particular fractions of gray forest soil (Fig. 2). Moreover, all adsorption kinetic curves in both the positive and negative adsorption variants are ascending and tend to saturation. In this case, the HA adsorption in the gray forest soil and chernozem differing in their humus contents depends not only on the time of interaction but also on the dose of adsorbent in the suspension. As is evident from Fig. 2, the values of HA adsorption by chernozem, gray forest soil, and its fractions are almost an order of magnitude higher for the dilute 0.2% suspension versus 2% suspension. This phenomenon is explainable [15]: with a decrease in the distance between the disperse particles of adsorbent in a concentrated suspension and the onset of certain conditions making part of earlier adsorbed HA macromolecules able to additionally interact with the surface of other absorbent particles in the suspension via forming particle–macromolecule–particle bridges. The soil specimens can be ranked as follows according to their capacity (absolute adsorption values, mg/m^2) to adsorb HA: clay fraction of gray forest soil > chernozem > gray forest soil > parent rock of gray forest soil.

Thus, the character of HA adsorption by the chernozem, gray forest soil, its clay fraction, and its parent material is determined by the time of adsorbent–adsorbate interaction, concentration of HA solutions, and concentration of the solid phase in suspensions.

Studying the pH in Solution after HA Adsorption in the Supernatant

The specificity and distinctions in the HA adsorption patterns for gray forest soil and chernozem are confirmed by the exchange processes observed when measuring pH in the supernatant after HA adsorption by the soil. It has been shown that the pH of HA solution increases from 6.7 to 7.07 with an increase in the solution concentration. In the gray forest soil, pH of the soil–HA system changes insignificantly (6.4–6.5) for the interaction time of 48 and 120 h. Upon a longer interaction (168 h), pH grows to 7.5, i.e., the solution is alkalinized at the expense of the soil itself. HA at different concentrations causes an increase in pH increase from 6.5 to 7.7 upon 48- to 120-h interaction and from 7.7 to 7.8 upon further interaction by 168 h. It would seem that the presence of HA must decrease the pH of the solution, yet it increases.

The change in pH for chernozem is less dependent on the time of HA–soil interaction and stronger depends on the HA concentration. In particular, the pH of chernozem in the presence of HA increases from 6.7–7.2 (control) to 7.75 independently from the interaction time. Similar to gray forest soil, the presence of HA in this case does not decrease pH but increases it. These data suggest the possibility of an exchange adsorption with the release of alkaline components, which leads to the rise in its pH. Thus, the adsorption of sodium humate may be accompanied by ion exchange because of a concurrent increase in pH of the solution and its pH dependence.

The case study of the HA and polyacrylamide adsorption on clay minerals [11, 33, 36, 38] demonstrates an increase in the adsorption in the acid range, i.e., with an increase in the ionic strength of the solution. Presumably, this is explained by the fact that a high concentration of protons at low pH values neutralizes a negative charge of the surface of these minerals, thereby bringing the polyelectrolyte macromolecules and mineral particles nearer and, consequently, increasing the attraction between them. According to another opinion [34, 42, 45], HA is bound by kaolinite via nonspecific and specific adsorptions between the positively charged kaolinite centers and HA carboxyl groups, as well as at the expense of hydrophobic binding.

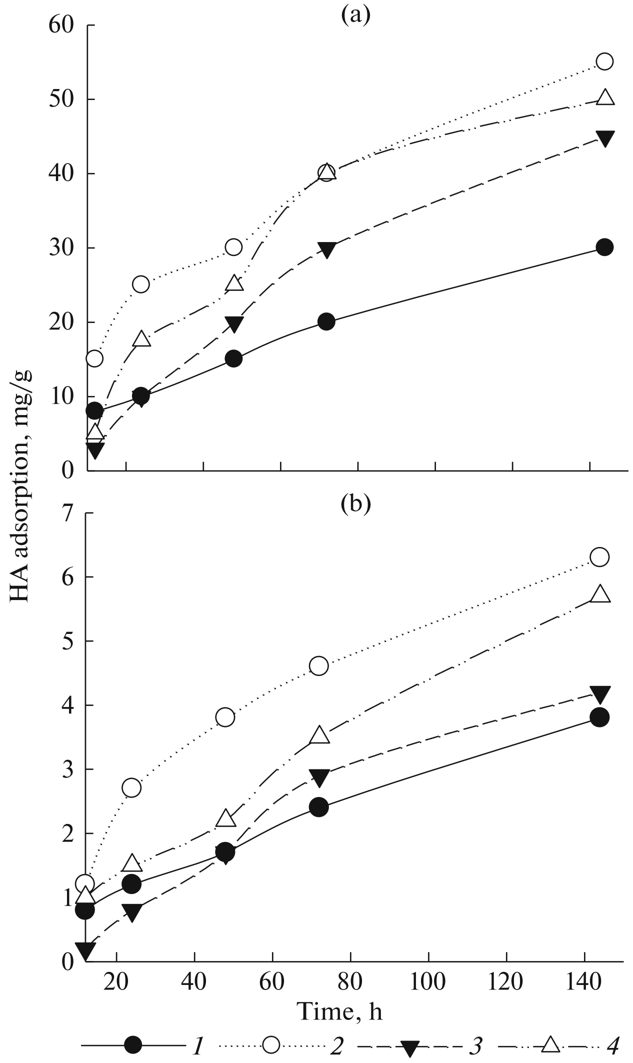

Fig. 2. Adsorption kinetics of 0.05% HA solution on (*1*) gray forest soil; (*2*) and (*3*) clay fraction and parent rock of gray forest soil, respectively; and (*4*) chernozem in (a) 0.2% and (b) 2.0% suspensions.

Presumably, a specific adsorption of sodium humate on soil particles accompanied by ion exchange contributes to the formation and localization of new organomineral compounds in certain sites of the surface, which is confirmed by pH measurements

IR Spectroscopy of HA Adsorption–Modified Soils and Fractions of Gray Forest Soil

The IR spectra of the initial soil samples and the specimens modified by HA adsorption (Figs. 4a and 4b) were studied to confirm the nature of HA–soil interaction. According to the IR spectra, gray forest soil

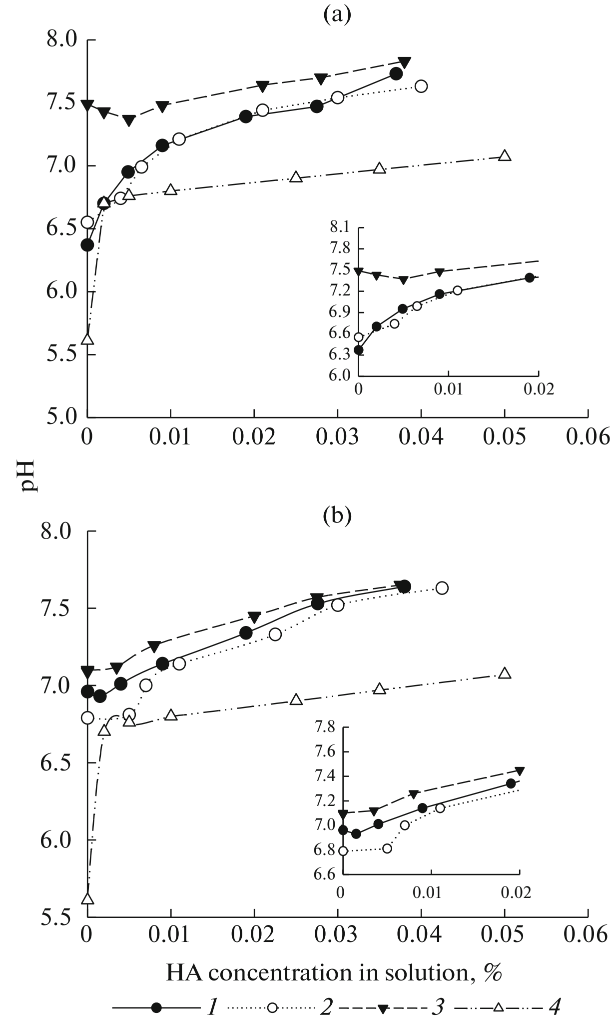

Fig. 3. Dependence of pH on the HA concentration in adsorption solution for (a) gray forest soil and (b) chernozem after (*1*) 48 h, (*2*) 120 h, and (*3*) 168 h of interaction and (*4*) in the initial HA solution; insets show the range of small concentrations.

and chernozem differ in the intermolecular interaction involving hydrogen and amide bonds, the degree of ionization or substitution of hydrogen in carboxyl groups for salt, as well as in the composition of aliphatic and aromatic groups. The effect of adsorbed HA in all specimens, first and foremost, appears in the intensity of absorption spectrum in both the high and low frequency regions. For example, the intensity of the absorption spectrum of the initial gray forest soil specimen in the high frequency region is 54%; of the specimen with HA, 61%; of the initial chernozem, 40%; and of the chernozem with HA, 60%. A wide compound band at 3600–2200 cm^{-1} comprising the valence vibration bands of a free hydroxyl group (3600 cm^{-1}) decreases. but the band for the hydroxyl groups linked by intermolecular hydrogen bonds increases (3448–3192 cm^{-1}). This suggests the formation of hydrogen bonds between HA and soil particles. In addition, the modified soil specimens acquire new absorption bands at 1752 and 1616 cm^{-1}, which belong to carboxylate group. This indicates different degrees of hydrogen substitution in the HA carboxyl groups. As for the mid- and low frequency regions, a small shift of the distinct absorption bands at 1528 cm^{-1} (1540 cm^{-1}) belonging to amide II group and at 1230–1250 cm^{-1} belonging to hydroxyl =C–O– group is observed. The bands reflecting OH deformation vibrations of the primary and secondary alcohols (1150–1050 cm^{-1}) are more distinct in the soil specimens modified by HA adsorption. The IR spectra of the gray forest soil mineral components—the clay fraction and parent material modified by HA adsorption (Figs. 4c and 4d)—also differ from the initial specimens. In particular, the absorption bands reflecting hydrogen bonds are more intensive in the presence of adsorbed HA in the clay fraction of gray forest soil. On the other hand, all bands of the parent rock of gray forest soil have low intensity in both high and mid-frequency regions of the spectra. However, note a new absorption band at 1705 cm^{-1}, which denotes the presence of a carboxyl group. Consequently, the changes observed in different intervals of the IR spectra of the adsorption-modified soil specimens and fractions of gray forest soil confirm that HA is adsorbed by different mechanisms ranging from physical adsorption to chemisorption accompanied by the formation of surface organomineral compounds at the expense of the polar groups of HA and soil aggregates.

The Effect of HA Adsorption on the Stability of Soil Suspensions

It is known that the structure formation of the natural minerals modified by organic molecules, in particular, polyelectrolytes, is controlled by the formation of hydrate and polymeric layers on the surface of particles and enveloping these particles by long chain macromolecules, which leads to coagulation or peptization of the adsorption-modified particles [9–13].

The effect of the HA present in suspension on the kinetics of changes in the volumes of precipitate was studied for the gray forest soil and chernozem; a change in their coagulation stability was observed (Fig. 5). In particular, the volume of precipitate of gray forest soil at the initial moment (5–10 min) increases with an increase in the HA concentration in the solution (water < 0.01% < 0.02% < 0.03% < 0.05%), which corresponds to the increase in the degree of soil surface coverage (Fig. 5a). Presumably, the HA adsorption interferes with the aggregation stability of suspension, so that it coagulates faster; the aggregates of particles become loose; and gel-like flakes are formed. The precipitate decreases over 12 h to approximately the same volume at all HA concentrations. Then the volume of precipitate increases with the rise in the HA concentration to reach its maximum values by 40–50 h; the curves pass through the maximum, except for the

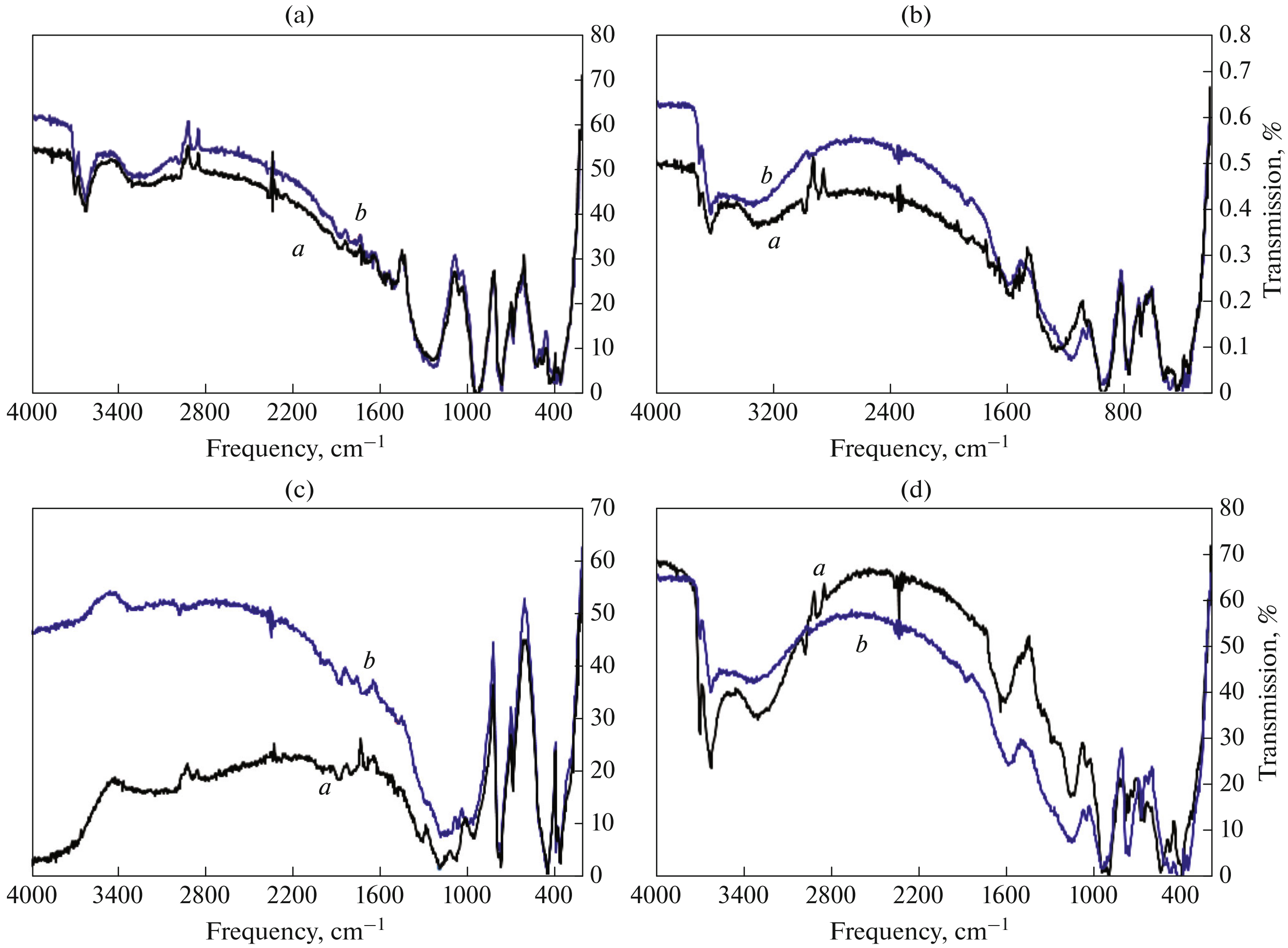

Fig. 4. IR spectra of (a) gray forest soil, (b) chernozem, (c) parent rock of gray forest soil, and (d) its clay fraction for (*a*) initial specimens and (*b*) specimens modified with 0.05% HA.

water–soil system, where the precipitate volume continuously decreases with time. The volumes of precipitate decrease with further increase in the interaction time and HA concentration to the same value of 14 mL. Most likely, this effect is determined by stabilization of suspension owing to formation of adsorption layer with its polar groups oriented into aqueous medium, i.e., the system is hydrophilized. The effects of a decrease in the volume of precipitate over 12 h are less pronounced in chernozem specimens (Fig. 5b). They insignificantly differ from one another in the *decrease* in the volume of precipitate over 12–24 h depending on the HA concentration. Later (24–60 h), the volume of the chernozem precipitate gradually decreases from 22 to 17.

Changes in the Structure of Soil Suspension Precipitates in the Presence of Different HA Concentrations during Long-Term Interaction

As is shown above, the change in the volume of gray forest soil and chernozem precipitates depends on the amount of adsorbed HA and interaction time. The patterns of particle segregation and precipitate separation into zones considerably differ during long-term interaction of soil suspensions with different HA doses. The coarse particles are the first to precipitate to the bottom with further flake formation, which precipitated as a stable gel at different rates; finally, the suspension is brightened depending on the interaction time, HA concentration, and soil type (Fig. 6). The suspension of gray forest soil in water gave dense precipitate with a volume of 2.5 mL during the first 12 h; the gel was formed in the remaining volume. Presumably, gel as a colloidal fraction is formed because of the presence of sodium humate, which leads to peptization of suspension particles. Later (25–50 h), the lower part of the precipitate becomes more compact, while a transparent solution appears in the upper part. The suspension continued its separation into zones and the gel precipitate disappeared by 150–200 h, while the supernatant solution brightened.

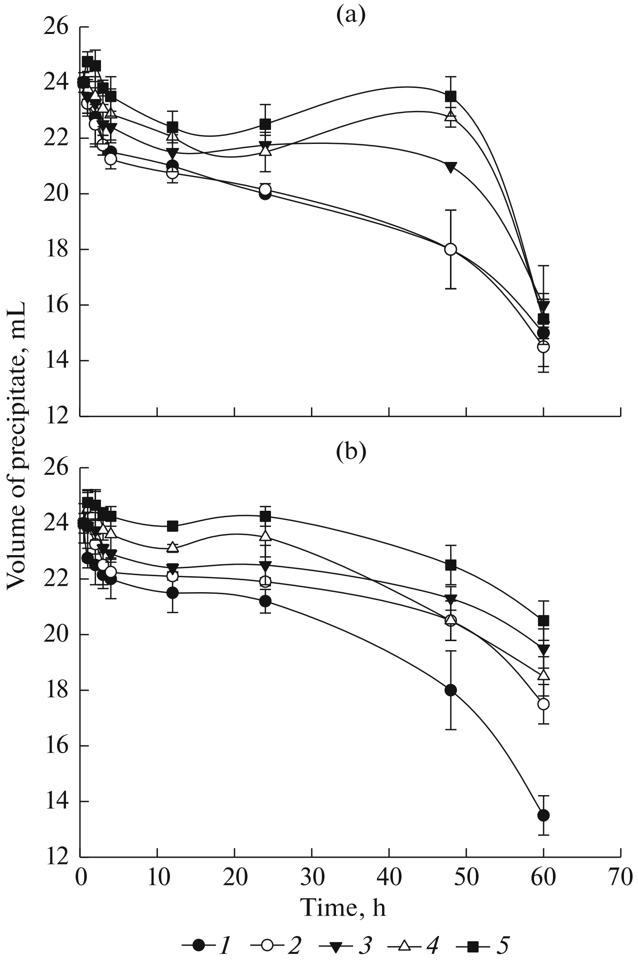

Fig. 5. Volumes of the precipitate of (a) gray forest soil and (b) chernozem at different HA concentrations: (*1*) water; (*2*) 0.01%; (*3*) 0.02%; (*4*) 0.03%; and (*5*) 0.05%.

The corresponding precipitation pattern for the chernozem containing approximately two time more humus that the gray forest soil is different with both water alone and HA solution. For example, the dense part of the precipitate had a larger volume (to 4 mL) in the water–chernozem system and a looser structure, presumably, because of a higher content of the native organic matter in this soil type. In this case, the forming gel precipitate gradually disappeared and the brightened solution appeared earlier. However, the gel-like precipitate in the presence of HA adsorbed on chernozem was formed in a larger amount, and its stability increased with the rise in the HA concentration in the suspension over 150–200 h. These data suggest that the humus–matrix composition of chernozem enhances stabilization of the gel-like precipitate even in a long-term interaction. Consequently, the patterns of precipitate formation in gray forest soil and chernozem specimens drastically differ and depend on both the duration of the process and the amount of organic matter.

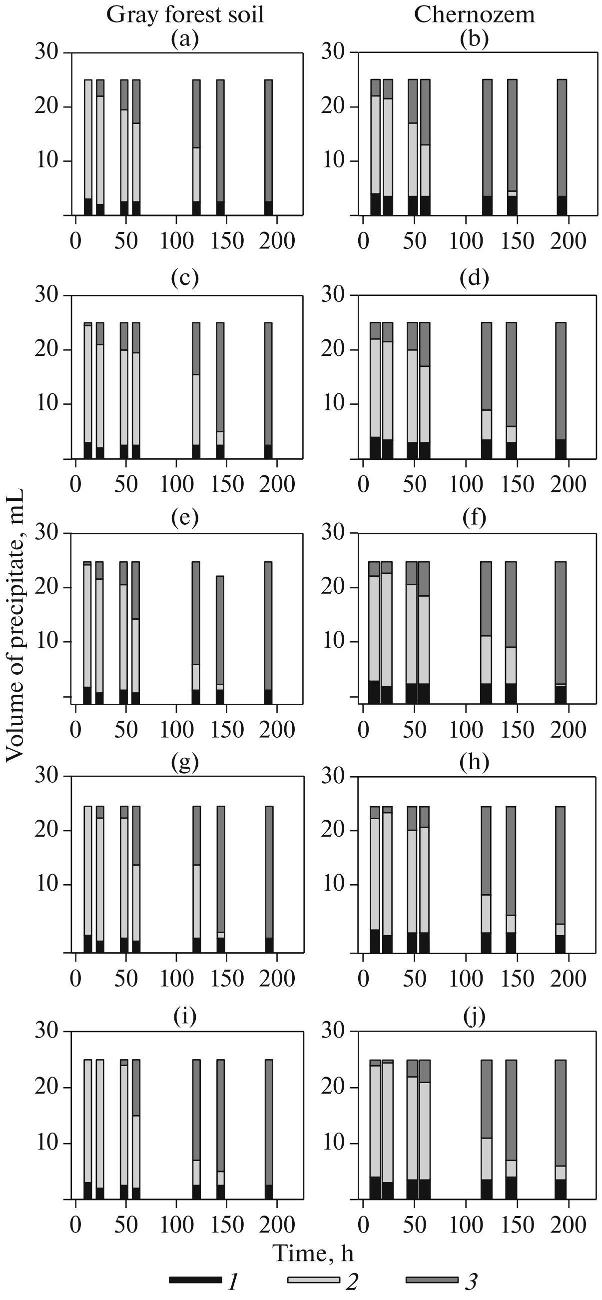

Fig. 6. Volumes of the precipitate of gray forest soil and chernozem after a long-term interaction (a and b) with water and at different HA concentrations: (c and d) 0.01%; (e and f) 0.02%; (g and h) 0.03%; and (i and j) 0.05%. (*1*) Dense precipitate, (*2*) gel-like precipitate, and (*3*) clear solution.

CONCLUSIONS

The HA adsorption from dilute aqueous solutions onto soil aggregates has been examined in the case study of gray forest soil, its components (clay fraction and parent rock), and leached chernozem. Physicochemical assays have shown that the HA adsorption on all these objects is determined by the time of interaction, HA concentration, and the properties and concentration of the solid phase and can be accompanied by ion exchange. The effect of HA adsorption on the coagulation stability of soil suspensions, accompanied by the formation of a gel-like precipitate and an increase in the time required for the suspension to brighten was assessed from data on changes in the volume of the precipitate. The stability of suspensions increased with an increase in the HA concentration and depended on the soil type.

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CONFLICT OF INTEREST

The authors state no conflict of interest.

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