

## The sorption ability of humic acids of black alder fen peat on montmorillonite containing clays in the presence of heavy metal ions

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### Abstract

It is determinate that the adsorption of humic acids by the different forms of montmorillonite increases with a decrease in pH. Maximum adsorption of humic acids is observed in the presence of zinc ions, which is associated with the formation of chelate complexes of humic acids with zinc ions. Organic mineral systems based on humic acids of black alder fen peat and aluminum montmorillonite form observe maximum adsorption of lead and zinc ions, which is associated with an increase in their specific surface and adsorption capacity, due to the formation of a layered-columnar structure and slit-shaped micropores.

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## 1. Introduction

Humic acids (HAs) play a key role in the functioning of natural ecosystems and are participants in the small biological cycle of aquatic and terrestrial biogeocenoses [1]. One of the important processes in the environment is the sorption of HAs on the mineral component of the soil, which stabilizes soil organic carbon in the global carbon cycle [2], affects the mobility and availability of nutrients and pollutants in the soil [3], is a possible mechanism for the conservation of labile biopolymers [four]. As a result of various interactions (ion exchange, chemisorption and complexation), an organo-mineral complex is formed, consisting of humic acids and clay minerals [5]. An important ability of HAs is a binding to sedentary and hardly dissociating complexes of toxic elements, some of which are heavy metal ions — cadmium, copper, zinc, chromium, nickel, lead, etc. Soils with high adsorption capacity, characterized by a high content of clays and organic matter, can hold metal ions, especially in the upper horizons. In such soils, leaching into groundwater and the absorption of toxic compounds by plants is minimal, but the formation of technogenic anomalies of heavy metals [6,7,8]. However, each natural object is an individual chemical system in which a large number of factors can influence the forms of finding heavy metal ions: the pH of the medium, the amount of humic substances, the chemical composition of the soil itself. The presence of inorganic anions and cations in the systems affects the process of complexation with HAs, due to the occurrence of competing reactions [1]. Accounting for these factors is necessary to predict the forms of the presence of metals in soils. Therefore, modeling the sorption processes of humic acids on various forms of clay minerals in the presence of heavy metal cations is the relevant for understanding the relationship between the structure and the reactivity of the organo-mineral complex in the relation to heavy metals.

The aim of this work is to identify the absorption of humic acids of black alder fen peat from natural and aluminum forms of montmorillonite containing clays, as the main component of the soil, in the presence of heavy metal ions (lead and zinc).

## 2. Materials and methods

The objects of this research were humic acids of black alder fen peat (BFP) [9–10, 22, 25–26] and commercial sample of montmorillonite (MMT) containing clay, manufactured according to TU 14-9-364-89 (Moscow) [11] and the aluminum form of montmorillonite containing clay Bento Group Minerals [12]. The concentration of humic acids in the solution was determined photometrically using an SF-104 device at a wavelength of 350 nm, using a pre-constructed calibration curve  $D = (C_{\text{HAs}})$  [12]. A series of runs were carried out to study the montmorillonite-containing clays in the model systems for the absorption of humic acids with montmorillonite, varying the following parameters: pH of the medium (3–10) and the concentration of metal ions in the solution (10–200 mg/l) at a concentration of HAs 250 mg/l. 0.5 g of clay mineral, 5 ml of solution of HAs with a concentration of 1 g/l, 5.0 ml of lead nitrate working solution and from 0 to 0.6 ml of 0.1 M solution of nitric acid to reveal the effect of pH on ion absorption were added to a series of vessels with tightly closing lids heavy metals in the organo-mineral system based on humic acids and clay minerals. The total volume was adjusted to 20 ml with a background electrolyte solution (0.1 M  $\text{NaNO}_3$ ). The solutions were shaken for 24 hours, after which they were centrifuged for 30 minutes at 3 thousand rpm [12, 13]. The pH was measured on the Anion 4154 pH meter, the concentration of humic acids remaining in the solution was determined spectrophotometrically on an SF-104 instrument using the calibration curve  $D = (C_{\text{gv}})$  [12], the concentration of heavy metal ions remaining in the solution was measured on an atomic absorption spectrometer MGA-915 MD. The sorption capacity of HAs was calculated by the formula (1):

$$G = \frac{(C_0 - C)V}{m} \quad (1)$$

G-adsorbability of HAs, mg/g; C-concentration of humic acids remaining in the solution, mg/l;  $C_0$ - the initial concentration of HAs, mg / l; V- the volume of the solution, l; m - the mass of montmorillonite, g;

The absorption of humic acids and metal ions (%) of the applied amount was calculated by the formula (2):

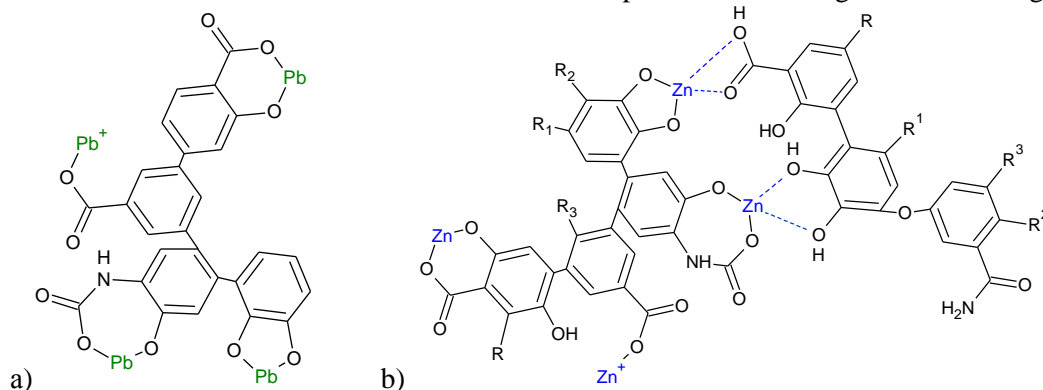
$$Q = \frac{(C_0 - C)}{C_0} \times 100\% \quad (2)$$

C-concentration of humic acids remaining in the solution, mg/l;  $C_0$  - the initial concentration of HAs, mg/l

It was established [12] that the highest sorption capacity of humic acids on the aluminum form of montmorillonite at pH 6.5, therefore, the absorption of lead and zinc ions in the organomineral system was studied at a given pH value and the initial salt concentrations of heavy metals 0, 50, 100, 150, 200 mg/l. To do this, 0.2 g of initial montmorillonite or his aluminum form, 5 ml HAs with a concentration of 1 g/l and various volumes of metal nitrates (0; 0.5; 1.0 ; 2.0; 3.0; 4.0; 5.0 ml) were added to the flasks; the volume was adjusted to 20 ml of the solution of 0.1 M  $\text{NaN}_3$ . The desired pH was achieved by adding to the solution of 0.05 M  $\text{HNO}_3$  or 0.05 M NaOH. The solutions were shaken for 24 hours, and then centrifuged for 30 minutes at 3 thousand rpm [13]. The concentration of remaining humic acids in the solution was determined photometrically, the concentration of heavy metal ions remaining in the solution on an MGA-915 MD atomic absorption spectrometer. The sorbability of humic acids was calculated by the formula (1). All experiments were performed in the six replications.

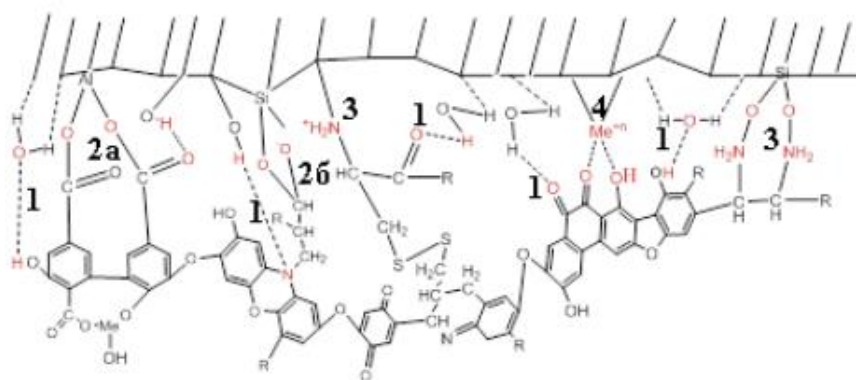
### 3. Results and discussion

The interaction of HAs and cations of zinc and lead proceeds according to the following schemes (Fig. 1):



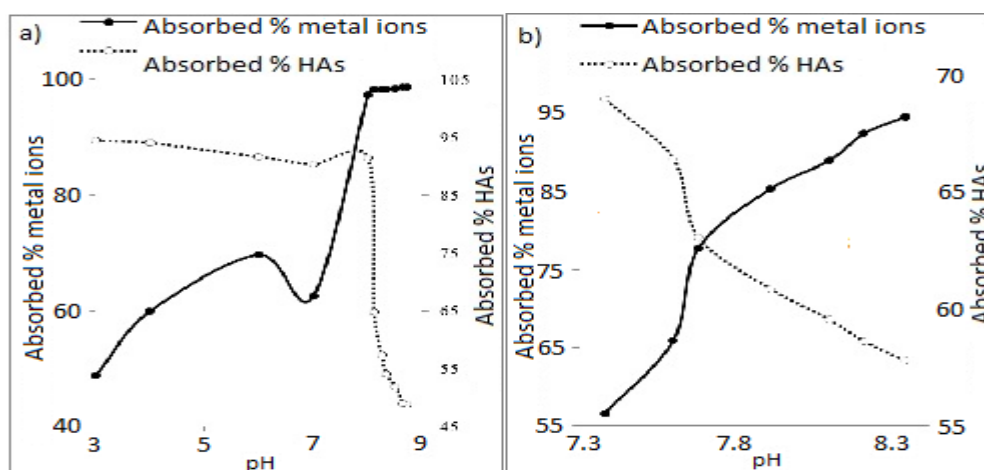
**Figure 1.** The binding of metal ions with humic acids: a)  $\text{Pb}^{2+}$ ; b)  $\text{Zn}^{2+}$

The binding of lead cations with humic acids takes place with the participation of predominantly carboxyl groups and belongs to the ion-exchange mechanism, and the steric factor has a significant effect: the closer the ion-exchange capable groups are located to each other, the more complete the binding of lead ions proceeds (Figure 1- a). The ion-exchange mechanism of binding to humic acids is also characteristic of zinc cations, capable of binding to both phenolic groups and carboxyl groups. In addition, zinc cations, in contrast to lead cations, are capable of forming chelate complex compounds with humic acids, in which the metal enters the anionic part of the molecule (inner sphere complexes). In this case, the binding mechanism refers to ion-covalent (Figure 1-b) [13-14]. The interaction of humic acids with soil minerals includes the following types of interactions [13–17]: cation exchange, protonation, ligand exchange, water binding, cationic bridges, hydrogen bonds, Van der Waals forces (Figure 2).

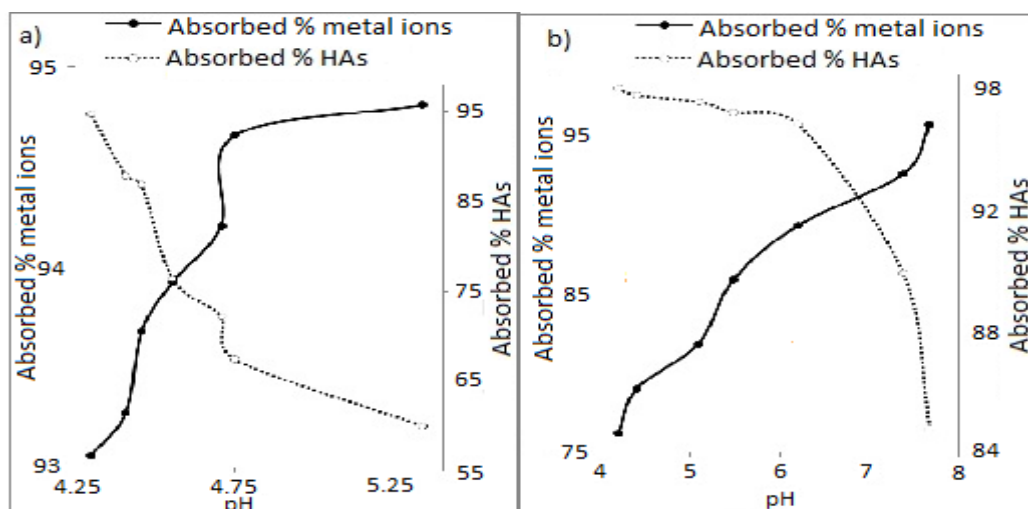


**Figure 2.** The interaction of humic acids with clay minerals

1. Hydrogen bonds; 2. Ligand exchange a) protonated hydroxyl group of the mineral; b) unprotonated hydroxyl group of the mineral; 3. Ion bond; 4. Cationic bridges. Humic acids associated with the mineral surface can both increase the adsorption of metal cations by solid particles due to an increase in the number of complexing centers on the surface, and decrease by blocking the active centers on the surface of the mineral [18]. The process of complexation can be represented as a competition between metal ions, electrolyte cations, and hydrogen ions for the free carboxyl groups of humic acids bound to the mineral surface [18–20]. The interaction of metal ions with clay minerals and HAs is possible through cation exchange reactions and with the formation of cation bridges between the surface of the MMT and the HAs molecule [13–16]. Ternary surface complexes can form between hydroxyl centers, electrolyte cations, and ionized groups of HAs [13, 14, 23] at high pH and in the presence of two and three valent cations. Metal-humate complexes are formed at pH values lower than metal hydroxides. In addition, the probability of the formation of metal hydroxides at high pH values in the presence of humic acids is low [13-14,21-23]. It has been found that desorption of metal ions due to dissociation of colloidal metal-humate complexes or from the surface of the mineral is practically not observed [13-14]. At the first stage of work, the absorption of HAs from the initial (Fig. 3) and aluminum form of montmorillonite (Fig. 4) in the presence of zinc and lead ions was compared at different pH values.

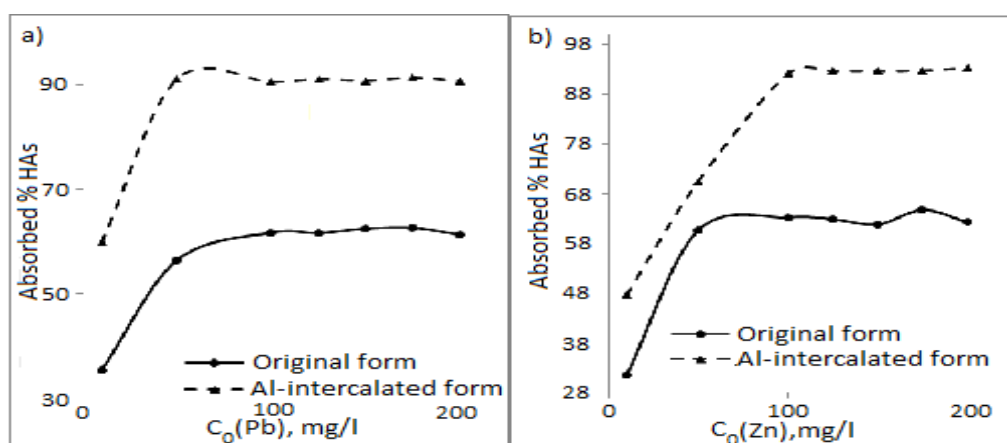


**Figure 3.** Sorption of humic acids on the initial form of montmorillonite and ions a)  $\text{Pb}^{2+}$ ; b)  $\text{Zn}^{2+}$



**Figure 4.** Sorption of humic acids on Al-intercalated form of montmorillonite and ions a) Pb<sup>2+</sup>; b) Zn<sup>2+</sup>

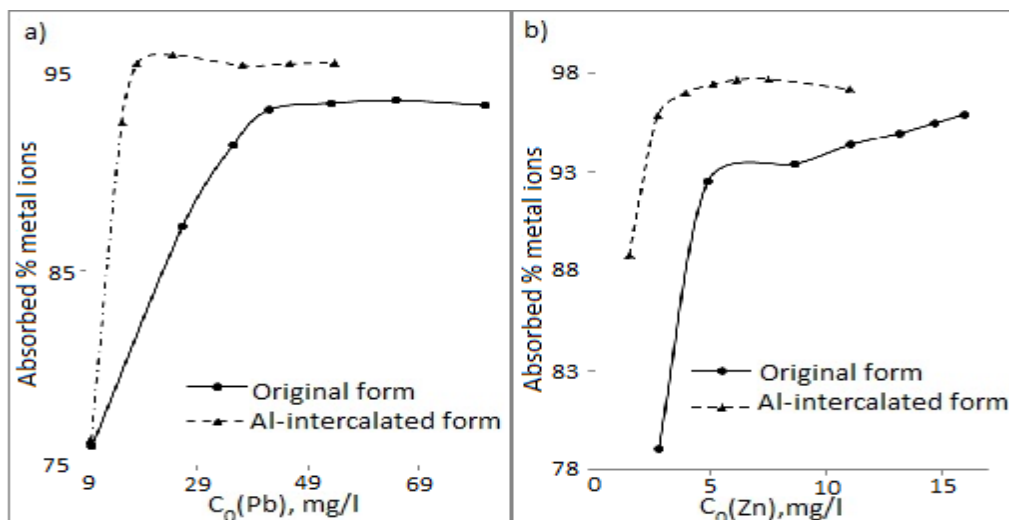
It was established that the proportion of bound metal ions increases while reducing the proportion of bound humic acids, on the initial and on the aluminum form of MMT with an increase in pH, which confirms the initial sorption of humic acids on clay minerals [13-14]. The sorption of metal cations increases with the increasing pH [22], and HAs are sorbed by the type of anions, i.e. their sorption increases with the decreasing pH [13-14,23]. The binding of metal ions with humic acids is evidenced by a sharp increase in the absorption of Pb<sup>2+</sup> and Zn<sup>2+</sup> ions, which is characterized by the onset of sorption of metal cations on the montmorillonite itself and on the resulting HAs-MMT complex (Figure 3-4) [13-14]. The binding of humic acids on the Al-intercalated form of montmorillonite is 26–29% more than on the initial form of MMT, and in the presence of Zn<sup>2+</sup> and Pb<sup>2+</sup> ions, the sorption of GW (NBT) increases by 27–33%, which is associated with an increase in interpacket space when modifying montmorillonite [11, 15-16, 18-19, 24]. The absorption of humic acids of the initial and Al intercalated forms of MMT in the presence of metal ions at pH = 6.5 was studied, and the initial concentrations of Zn<sup>2+</sup> and Pb<sup>2+</sup> ions (10–200 mg / l) were varied (Fig. 5).



**Figure 5.** Absorption of humic acids by montmorillonite forms in the presence of ions a) Pb<sup>2+</sup>; b) Zn<sup>2+</sup>

The highest value of adsorbability of HAs in the presence of lead and zinc ions on the Al-intercalated form of montmorillonite, which is associated with an increase in the interpacket distance within the modified form of montmorillonite. In the Al-intercalated sample, the number of meso- and macropores increases, which become available for sorption of HAs molecules [13-14, 18-19]. The sorption capacity of humic acids increases in the presence of metal ions for all forms of montmorillonite. The introduction of the third component - metal ions into the

system "humic acids-montmorillonite" leads to an increase in sorption of humic acids on the forms of montmorillonite due to their interaction with metal cations. The sorption of HAs in the system containing zinc ions is slightly higher than in the system containing lead ions, which may be due to the formation of chelate complexes of HAs with  $\text{Zn}^{2+}$  ions. At the same time, the absorption of lead and zinc ions by organo-mineral systems formed from humic acids adsorbed on montmorillonite forms at pH 6.5 (Fig. 6) was analyzed.



**Figure 6.** Ion absorption a)  $\text{Pb}^{2+}$ ; b)  $\text{Zn}^{2+}$  in a system containing humic acids and forms of montmorillonite

If we assume that the primary sorption centers of humic acids are of the same nature, then the process of binding metal cations by an organo-mineral system consisting of the HAs molecules and a clay mineral is described by the Langmuir equation. In this case, only one metal ion is sorbed on one sorption center, and sorbed molecules interact only with sorption centers, but not among themselves, that is, there are no lateral interactions [14–15]. The dependences of the absorption of metal ions (Fig. 6) by an organo-mineral system consisting of the HAs molecules and a clay mineral have the form of sorption isotherms that are approximated by the Langmuir equation. Langmuir adsorption parameters of  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions in a system containing humic acids and the forms of montmorillonite

The forms of montmorillonite	Langmuir isotherm					
	$\text{Pb}^{2+}$			$\text{Zn}^{2+}$		
	$G_{\infty}$ , mg/g	K	R	$G_{\infty}$ , mg/g	K	R
The initial form	99,0	0,3	0,99	89,0	2,1	0,99
The Al-intercalated form	123,4	0,2	0,98	138,0	11,2	0,99

The maximum absorption of lead and zinc ions occurs by organo-mineral systems based on Al-intercalated form of montmorillonite and HAs. The limiting sorption for  $\text{Pb}^{2+}$  ions in the system, consisting of humic acids and Al-intercalated form of clay mineral is 1.3 times more than on the initial form of montmorillonite, and for  $\text{Zn}^{2+}$  ions - 1.6 times more, due to the increase in specific surface and sorption capacity of clay minerals in the process of their modification.



#### 4. Conclusion

It was revealed that an increase in pH on MMT forms leads to an increase in the proportion of bound metal ions, while simultaneously reducing the proportion of bounding HAs. The absorption of metal cations increases with increasing pH, while the absorption of HAs by MMT forms increases with decreasing pH. The binding of metal ions with humic substances is indicated by a sharp increase in the absorption of  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions by the “humic acids-montmorillonite” system. It was found that in the presence of  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions, the sorption of HAs on montmorillonite forms increases by 6–9% on the initial form of montmorillonite and by 27–33% on Al-intercalated form of montmorillonite. The sorption of HAs in a system containing  $\text{Zn}^{2+}$  ions is higher than in a system containing  $\text{Pb}^{2+}$  ions, which is associated with the formation of HAs chelate complexes with zinc ions. In the presence of HAs lead and zinc ions are better sorbed on the Al-intercalated form of montmorillonite due to the increase in the number of meso- and macropores in this form, which become available for the absorption of metal ions.

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