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STUDY OF THE DETOXIFICATION METHOD OF MINERALISED WATER SEDIMENTS BY NATURAL SORBENTS

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Abstract. *Sediments after reagent treatment of mineralised water are a rather complex mixture of various substances of mineral and organic composition. It is necessary to recycle these sediments in order to reduce the negative impact on the environment. The article considers the possibility of sediments detoxification by natural sorbents to bind organic and inorganic toxicants into non-toxic complexes and reduce the negative effect on the environment.*

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Introduction

Nowadays, many environmental protection and restoration issues have no optimal solutions due to the lack of cheap, accessible, and environmentally friendly technologies in environmental protection. The most appropriate solution to reduce the negative impact of sewage treatment sludge is the use of humic substances. Humic compounds fulfil the functions of natural adaptogens, detoxicants and have a wide range of biological effects. They improve soil structure and are environmentally safe to use [1]. The advantage of this raw material is its availability worldwide. Humic substances (HS) largely determine soil fertility, but their origin, molecular structure, and stability are a matter of debate [2, 3]. Humic substances are organic compounds of very complex composition containing about 15 types of functional groups: carboxyl, phenol-hydroxyl, alcohol, amide, carbonyl, etc. (Fig. 1 [4]). The number of methoxyl groups, according to L.N. Aleksandrova, depends on the degree of humification and composition of the original plant residues. However, they are residual in the macromolecule of humic acids [5, 6]. Hydroxyl groups and phenolic hydroxyls, containing hydrogen capable for substitution, determine the acidic properties of humic acids.

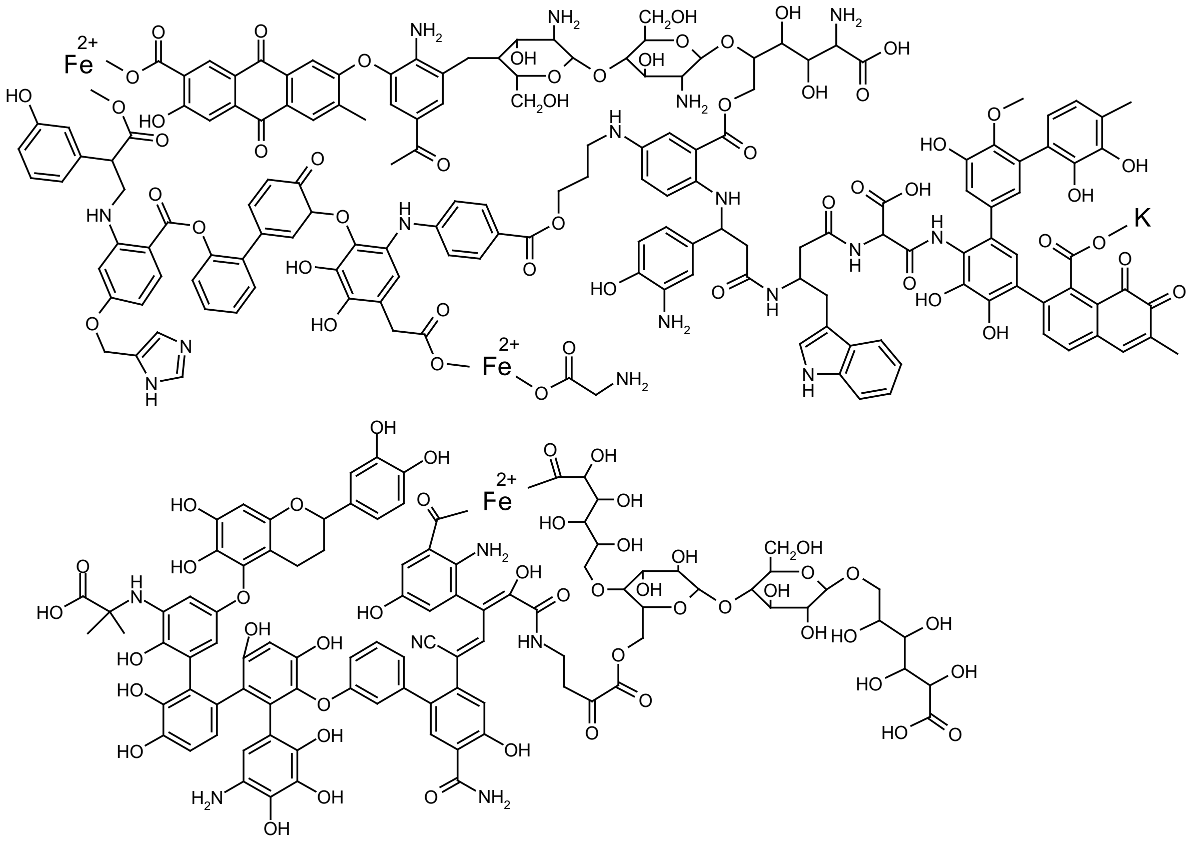

Fig. 1. Hypothetical formula of humic acids [4]

The qualitative composition of functional groups in fulvic acids and humic acids is similar. However, in fulvic acids, hydroxyl and methoxyl groups predominate in the quantitative composition. Free amino groups are not detected. Moreover, the presence of many functional groups such as -NH_2, -OH, -COOH, -$CONH_2$, and -SH allows us to consider HFs as highly reactive substances capable of reacting with a wide class of chemical compounds [7]. Therefore, humic acid molecules are randomised polymers of aromatic and aliphatic structural fragments containing a variety of functional groups capable to react with many chemical substances in the soil.

Main body

Most humic substances occur in a bonded state in the soil and are insoluble in water. The activator of peat organic matter in laboratory conditions was aqueous solutions of alkalis. The activator of peat organic matter in laboratory conditions was aqueous solutions of alkalis, which were used to produce humic compounds in the form of humates and humic acids by extraction followed by their precipitation in acidic medium. We analyzed the obtained humic acids by infrared spectroscopy. We recorded infrared absorption spectra on a FT-IR spectrometer RX (Perkin Elmer) with an NPVO Spectrum Two attachment in the frequency range of 500–4000 cm^{-1}, with a resolution of 4 cm^{-1}. We quantified the content of functional groups of humic acids based on the ratios of the optical densities of the absorption bands of oxygen-containing groups to the optical densities corresponding to aromatic polyconjugated systems at 1600 cm^{-1} and aliphatic substituents at 2920 cm^{-1} (Table 1).

Table 1. Ratio of optical densities of absorption bands of humic acids of upland peat

Peat type	$\frac{A_{OH\ 3300}}{A_{C=C\ 1600}}$	$\frac{A_{C=O\ 1700}}{A_{C=C\ 1600}}$	$\frac{A_{\text{алк}\ 2920}}{A_{C=C\ 1600}}$	$\frac{A_{1039}}{A_{1600}}$	$\frac{A_{C-O-C\ 1210}}{A_{\text{алк}\ 2920}}$	$\frac{A_{C=O\ 1700}}{A_{\text{алк}\ 2920}}$	$\frac{A_{OH\ 3300}}{A_{\text{алк}\ 2920}}$
Upland	1.5	1.0	1.3	1.5	0.97	0.67	1.0

Table 1 shows the ratio of $A_{alk\ 2920}/A_{C=C\ 1600}$ is greater than one, indicating the predominance of alkyl structures over aromatic structures. A high content of hydroxyl and carbonyl groups ($A_{3300}/A_{1600} > 1$ and $A_{1700}/A_{1600} = 1$) as well as substituted hydrogen atoms can be observed in the aromatic ring. Humic acids of upland peat are characterised by aromatic and carbonyl-containing structures ($A_{C=O\ 1725}/A_C = C_{1600} < 1$). The high content of hydroxyl groups may indicate the presence in the structure of HAs of flavonoid structures involved in natural immunity, resistance to pathogenic factors of bacterial, viral, and fungal origin [3, 5].

The articles [7-10] deal with the presence of hydroxyl, carbonyl and carboxyl groups in combination with aromatic structure provides the ability of HAs to enter into ion-exchange and donor-acceptor interactions, form hydrogen bonds, participate in sorption processes, form complexes with metals, and adducts with various classes of organic compounds. Bound substances lose their toxicity. It explains the use of HAs as natural detoxicants.

Sediments formed during the reagent treatment of mineralised water under mining were studied as an object of humic substances interaction. Sludge after treatment of open pit water is a rather complex mixture of various substances of mineral and organic composition. The technology of reagent treatment sludge utilisation using natural components of organic nature is the most environmentally friendly.

We dried the samples at $T = 105$ °C after treating the sediments with a solution of humic acid with a concentration of 1 g/dm^3 and obtained IR spectra of the samples under study. We obtained the spectra of sediments treated with humic acid containing calcium, barium, and sulphate compounds on a Perkin Elmer RX FTIR spectrometer (RX Perkin Elmer) with an NPVO Spectrum Two attachment at the frequency range of 400-4000 cm^{-1}, with a resolution of 4 cm^{-1} (Fig. 2).

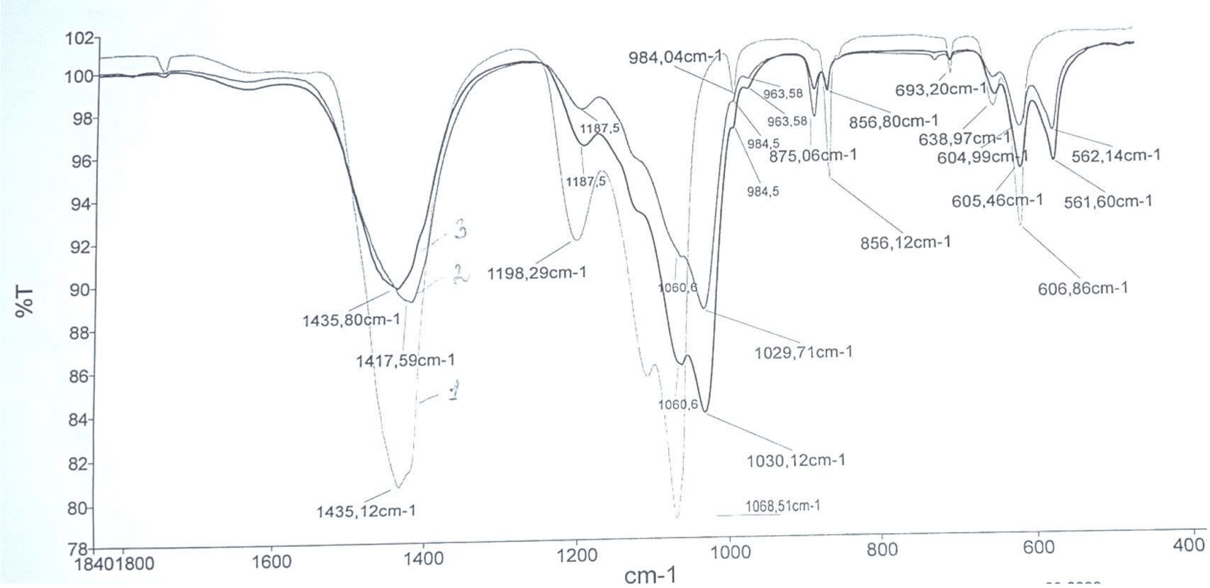

Fig. 2. IR spectra of sediments of reagent treatment with humic acid: 1 - with the content of barium compounds in sediment 0.047 mol/dm^3; 2 - with the content of calcium and barium compounds in sediment 0.12 mol/dm^3; 3 - with the content of calcium and barium compounds in sediment 0.095 mol/dm^3.

According to results of the research, the interaction of barium with sulfates causes their complete sedimentation, characterised by an increase in the absorption bands in the 1198 cm^{-1} and 983 cm^{-1} regions compared to samples pretreated with calcium compounds followed by barium sedimentation. The most intense vibrations observed in the IR spectrum are obtained at the valence vibrational range ν_3 950–1200 cm^{-1}, characteristic of sulphates. We observed characteristic bands of valence and strain vibrations of the sulfate group in the region of 605, 1070 cm^{-1} in the spectra of all samples and is associated with the formation of insoluble barium sulfate. Additionally, we observed a shift of the absorption bands for the SO_4^{-2} bond in the region of 1080–1130 at 10 cm^{-1} in samples pretreated with calcium compounds and then with barium compounds. It is associated with an increase in the proportion of free sulfate in the sediment.

The presence of insoluble calcium and barium carbonates is characterised by a strong absorption band in the region of 1410–1450 cm^{-1}, which was found in all samples; the highest intensity of the band was observed in the sediment treated with barium compounds only.

The interaction of humic acid with the sediment is predominantly adsorptive [4, 10]. The proposed mechanism is confirmed by the high content of sulfates, metal cations in the adsorption complex of HA with sediment. The content of iron, calcium, barium, phosphates, sulfates increases in the precipitate compared to the content of compounds in humic acid. It correlates with the results obtained on X-ray fluorescence spectrophotometer EDX6000B with SDD silicon detector EDX Pocket Series. Table 2 presents the results of the analyses.

Table 2. Content of elements in samples of reagent treatment sediments with humic acid, % wt.

Element	Ca	Mg	Zn	Fe	Mn	Mo	Al	P	S	Ba	K
Concentration of calcium and barium compounds in the sediment 0.095 mol/dm^3	9.746	0.435	0.046	0.212	0.046	0.455	0.145	1.363	6.237	17.701	0
Concentration of calcium and barium compounds in the sediment 0.12 mol/dm^3	14.11	0.427	0	0.2	0.086	0.415	0.821	1.314	3.694	31.098	0
Concentration of barium compounds in the sediment 0.047 mol/dm^3	0	0.215	0.156	0	0.175	0.37	0.088	0.128	3.487	35.323	0
Humic acid concentration, g/dm^3	1.082	1.099	0.041	0	0	1.351	0.424	0.104	0	0	6.912

According to the papers [11, 12], humic substances have a significant ability to form complex and intra-complex compounds (chelates) with iron, aluminium, copper, and other polyvalent cations. The possibility of formation of complex alumina-iron humic compounds is described in [4, p. 127; 13, 14].

The papers [15, 16] suggested that "the process of salt formation, apparently, is accompanied by adsorption and complexation". Adsorption complexes are considered as products of interaction of humic substances with crystalline and amorphous minerals of soils or organomineral products of humic substances absorption by minerals. The formation of adsorption complexes is possible due to the intermolecular bonds (adsorption proper) and due to ionic and coordination bonds (chemisorption) [16, 17]. The high content of carboxyl groups and phenolic structures allows humic acids (HAs) to bind heavy metals into stable complexes, while the polyaromatic basis of the structure ensures the binding of organic pollutants.

The interaction of magnesium ions with HAs has a donor-acceptor and ion-ionic mechanism [18]. The mass fraction of magnesium ions in the complex with humic acids decreases more than twice as compared to the initial content.

Conclusions and recommendations

Thus, humic acids (HAs) are considered as perspective natural detoxicants with high reactivity towards heavy metal ions due to a wide range of functional groups (carboxyl, hydroxyl, carbonyl, nitrogen-, and sulfur-containing). In combination with aromatic fragments humic acids are able to bind organic toxicants into non-toxic complexes. It allows us to reduce the harmful impact on the environment. Moreover, it provides the new opportunities for resource-saving technologies and methods of decontamination of pollutants based on natural processes of self-purification.

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