Spectral, luminescent and photochemical properties of humic acids with different genesis of organic raw materials

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Abstract. Spectral-luminescent properties of different samples of humic acids (HAs) are investigated. The samples of HAs fractions were obtained from Fluka Chemical Co, prepared from peat of Western Siberia region, other HAs and lignins were isolated from Arkhangelsk Region. The comparative analysis of these HAs with the sample of humic acids allocated from brown coal is carried out. The presence in the solution of herbicide 2,4-dichlorophenoxyacetic acid the humic acids has a significant effect on the processes of photochemical degradation under the action of light from an excilamp.

1. Introduction
Humic substances are natural organic formations, widespread in soils and peats, coals and shales, marine and lake sediments, waters of rivers and lakes. These substances are decomposition products of organic residues, mainly of vegetable origin. Humic substances are a major component of soil organic matter. They improve soil structure, regulate the water-air and the thermal regimes, and accumulate the necessary elements for plants. In general, it may be said that the content of humic substances determines soil fertility and stability of soil ecosystems [1].

The ability of humic substances to bind metal cations and toxic organic compounds is important. An adverse effect of pesticides on living organisms decreases in soils with a high content of humic substances. Such soils could play the role of a geochemical barrier, warning the flow of toxic substances into the ground water. On the other hand, humic substances distributed in an aqueous phase are capable of binding hydrophobic organic compounds, increasing their concentration in water, and carrying out their transportation in the environment [2].

Humic substances include three fractions: fulvic acids soluble in water at all pH values; humic acids precipitated by acid, soluble in water at pH>2; and insoluble humins. According to modern views, the most representative group of humic substances are humic acids that can be attributed to a special class of organic compounds in view of specific characteristics of the elemental composition as well as specific electronic and IR spectra [3].

The solubility, reactivity, and biological activity of humic acids depend on conditions of their formation, methods of isolation from natural materials, dimensions and configuration of macromolecules [4].

In a series of papers [5-8] it has been shown that the isolation method affects the structure and properties of humic substances. Methods based on the ability of humic substances to dissolve in alkaline solutions and precipitate from solutions upon acidification are most frequently used. Methods
differing in the composition and the concentration of solvents used, and the sequence of isolation of separate groups of organic matter, are widespread as well [9-13]. To increase the yield of humic substances and to increase their bioavailability some authors propose to carry out isolation with the use of ultrasonic cavitation, temperature, and other types of impacts on the natural source of humic substances [14]. There are data on the chemical and the electrochemical oxidation of humic substances at the isolation stage for the purpose of increasing their bioavailability [8, 15].

The study of the impact of UV radiation on properties of humic substances is an urgent task, as it allows understanding processes occurring in the structure of molecules of humic compounds under the influence of radiation. However, this question has been underserved in the literature.

The aim of this work is the isolation of humic acids from peat samples of different fields, the study of their spectral-luminescent properties, as well as the identification of the impact of humic acids on the effectiveness of herbicide degradation.

2. Methods and materials

Objects of the study were humic acids (HA) isolated from peat collected from the key site “Khanimey” of the Yamalo-Nenets Autonomous District – flat-hummocky lakelet complexes covering virtually all plain interfluvial spaces. Peat samples used in the work were taken from different depths. Consequently, their botanical composition is different.

**Sample 1**: The depth 0-10 cm. Botanical composition: sphagnum mosses (Sphagnum magellanicum) – 83%; bushes (Ledum palustre, including leaves and living roots) – 10%; hare’s-tale (Eriophorum vaginatum) – 5%, as well as wood culls (conifer bark, pine needles), and green mosses (Warnstorfia fluitans, Drepanocladus aduncus, Calliergon richardsonii).

**Sample 2**: The depth 20-30 cm. Botanical composition: sphagnum mosses (Sphagnum magellanicum) – 20%; bushes (including roots and leaves of Ledum palustre) – 5%; cotton grass (Eriophorum sp) – 40%; sedge – 15% (Carex rotundata – 10, Carex limosa – 5); wood culls (bark of conifers), and green mosses (Warnstorfia fluitans – 10%, Calliergon sp).

**Sample Z-80**: bottom sediments.

A standard sample of humic acids isolated from brown coal was investigated for a comparison (a sample of the company “Fluka”; Code -130794430907051).

Other samples were HAs and lignins isolated from Arkhangelsk Region.

2,4-dichlorophenoxyacetic acid (2,4-D) was selected as a herbicide. Acidic herbicides are widely used for the control of broad-leaved weeds and other vegetation. They are relatively inexpensive and very potent even at low concentrations. The majority of herbicides is directly applied to soil or sprayed over crops fields and as consequence of large production and high stability, they are released directly on environment. The halogenated phenols are the parent chromophores of a number of widely used pesticides, among them phenoxyacetic acid, and of other biocides. The photolysis of these substances in the environment has become a subject of increasing interest [16]. The presence of the chlorine groups causes such compounds to be more resistant to biodegradation than the unsubstituted analogs.

3. Experimental part

The isolation of humic acids was carried out using the method of aqueous-alkaline extraction followed by precipitation in acid environment. The prepared peat samples with a weight of 2 g were preliminary screened through a sieve with a hole diameter of 1 mm, poured with 0.1 N. NaOH solution, and heated for 2 hours on a water bath with occasional stirring. A day later, the supernatant clear brown-colored alkaline solution of humic substances was centrifuged and separated by decantation. In order to precipitate humic acids, 0.1 N of the solution HCl was added to the solution. The resulting suspension was filtered; the precipitate was washed prior to peptization. For an additional precipitation of humic acids, 5 ml of 0.1 N HCl was added to the colloidal solution, the precipitate was filtered and dried up to a fixed mass.

Matrix solutions of humic acids with a concentration of 0.5 g/l were prepared by mixing of a sample of a dry substance with the calculated volume of 0.1 N of the solution NaOH. The resulting
mixture was incubated for 30 minutes in an ultrasonic bath heated up to 45 °C. For further studies the matrix solution was diluted 10 times. The concentration of the studied solution was 0.05 g/l.

The irradiation of a series of solutions was carried out in a stationary mode at a distance of 10 cm from the irradiation source for 40 minutes with constant stirring using a mechanical stirrer. For photochemical studies, an excilamp on working molecules KrCl with \( \lambda_{\text{rad}} \sim 222 \) nm, developed at the Institute of High Current Electronics of the SB RAS, was used as a source of UV radiation [17].

To study the impact of humic acids on processes of herbicide photodegradation to aqueous solutions 2,4-D (50 mg/l), the studied humic acids were added at various proportions of concentrations (from 25 to 100 mg/l), and the irradiation of solutions was carried out in a flow photoreactor [18], registering the absorption and the fluorescence spectra. The irradiation time of aqueous solutions containing 2,4-D and humic acids was 1 – 150 minutes.

4. Results and discussion
Figure 1 shows absorption spectra of tested samples. These objects are characterized by an intense absorption in the UV-region of the spectrum, and with an increase in the wavelength the absorption smoothly decreases.

![Figure 1. Absorption spectra of the studied humic acids](image)

Humic acid of the company “Fluka” has the greatest intensity among tested samples: as compared to other samples, its spectrum is shifted to the long-wave side. This fact can be explained by significant differences in the structure of the studied humic acids, in particular, by a predominance of aromatic structures in their composition. Each sample corresponds to its own absorption maximum. The broadened shape of bands gives evidence of a complex structure of tested compounds, and of the presence of stabilizing intermolecular interactions.

When we consider the spectra of the Arkhangelsk samples, intense absorption in the UV region of the spectrum is seen, then, with increasing wavelength, the absorption decreases. The most intensive absorption has sample - sulfate lignin, and the least intensive has sample - humic-like chaglic acid in comparison with the standard we have chosen. Dependence on the degree of dilution of the sample is observed. The dependence of the fluorescence spectra of the investigated samples on the fluorescence...
excitation wavelength was found. Each sample of HAs and lignin has its own characteristic features, due to the complexity of the structure.

Fluorescence spectra of the studied Khanimey samples (Fig. 2) show a faint glow in the range from 400 to 600 nm. The sample of humic acids “Fluka” has the highest intensity, as in absorption spectra. Perhaps such difference in the intensity and the shape of spectra is caused by different ratio of aromatic structures, as well as by the difference in functional groups of HA samples.

The irradiation of the studied objects did not reveal significant changes in absorption spectra. Therefore, it is assumed that these substances are sufficiently photostable. However, examination of fluorescence spectra reveals the tendency of an increase in the intensity of the spectrum during the irradiation process. Perhaps this change is caused by a certain rearrangement of the molecule and the change in the percentage composition of components.

Addition of humic acids to the herbicide solution leads to a deeper level of herbicide conversion and to a less intense accumulation of photolysis products. Thus, in the case of a direct photolysis of 2,4-D, the disappearance of characteristic toxicant peaks takes place at the last-minute of irradiation but a significant broadening of the spectrum does not occur, which indicates the accumulation of aromatic intermediates in the system [19]. In the case of the presence of humic acids, a similar tendency is not so much expressed.

As for fluorescence spectra of the system herbicide-humic acids, the glow of humic acid molecules is observed. The spectra show that in the first few minutes of the process a slight increase in the intensity, and then a smooth decrease, is noted. This change may be caused by a variety of photophysical processes such as energy transfer and photosensitivity, by formation of charge-transfer complexes, as well as by changes in the structure of the humic acid molecule in the process of solution detoxification.

5. Conclusion
Each sample of humic acids or lignins has its characteristic features of absorption and fluorescence spectra, conditioned to their structure. Samples isolated from peat differ significantly from the standard
sample of humic acids obtained from brown coal. Irradiation of humic acids by KrCl-excilamp did not reveal significant spectral changes in all investigated objects, which indicates a sufficient photostability of tested compounds. Addition of humic acids to the herbicide solution and the subsequent UV irradiation leads to a more profound transformation of the toxicant, unlike the direct photolysis of a pure solution 2,4-D. The impact of the selected samples turned out to be different as well: samples Z-80 and “Fluka” are most effective. The presence in the solution of herbicide humic acids has a significant effect on the processes of photochemical degradation under the action of light from an excilamp.

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