Spectral-luminescent properties of humic acids

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The spectral properties of humic acids in water have been studied by electron absorption and fluorescence methods. Spectra of humic acids with different degree of humification have been compared. It has been shown that in the process of humification the intensity of absorption first decreased in all spectra and then increased in the region of 220–360 nm. The fluorescence intensity fell down in the process of humification, while the fluorescence region did not change strongly. It has been shown that more efficient photodegradation of humic acids occurred under short-wave irradiation with an excilamp (at 222 nm wavelength).

Introduction

The study of chemical and photochemical processes occurring in the environment is taking the growing significance. The impact of the optical radiation (first of all, in the UV and visible) on the biosphere is extremely important. Natural photochemical processes affected the evolution and continue to affect the current life on the Earth. The optical radiation is finding the increasing application for solution of the problems associated with protection of the environment aimed at both detection and decomposition of environmental toxicants.[1,2]

Properties of humic substances

When considering the processes occurring in the environment, especially, in water media, one should necessarily take into account the presence of humic substances (HSs), because they are almost always present in natural waters. The lifetime of these substances amounts to hundreds and even thousands years. These substances are those, which embrown soils, as well as river and boggy waters. They are produced due to decomposition of organic residues, during which numerous products of random reactions are synthesized. Natural selection of the most stable products determines their extremely complicated structure.

Humic substances, representing a very important class of natural high-molecular compounds absent in the living organisms but forming, finally, the basis for their vital activity, are intensely studied by both chemical and physical-chemical methods for more than 200 years.[3,4] The HSs have irregular structure, which is still not fully known. However, the HS structures are characterized by some internal regularities. All these macromolecules have an aromatic carbon skeleton enriched with functional groups and alkyl radicals, as well as the periphery part of carbon-peptide fragments and mineral components. Their composition includes the residues of various monosaccharides (up to 25% w/w) and amino acids (up to 10%). HSs contain many various functional groups, such as phenol, amino, carboxy, metoxy, ketyl, and quinoid, which assume the possibility of various photochemical processes, though HSs are, in general, relatively resistant to irradiation.

The considerable attention is paid to the study of the HS composition and structure parameters by different methods (ESR, NMR, and others), and certain progress has been achieved in this field.[5–7] The HS functional properties are more poorly studied, though it is known that these organic substances compensate, to a significant degree, for the negative anthropogenic impact.[8] As examples of their effect, we can mention the reduction of the content of mobile forms of some heavy metals[9] and the regulation of the effect of acid precipitations.[10] It is also believed that the Great Vasyugan Bog, the largest marsh in the world, which is located in Siberia, is the huge natural filter absorbing atmospheric and hydrospheric pollutants largely due to the abundant humic substances.[11] In addition, some amount of the humic and fulvic acids is present even in the purified tap water, as was demonstrated by the data obtained using laser-induced fluorescence.[12]

Humic substances execute a number of important functions in the biosphere, namely, accumulative, transportation, regulation, protection, physiological, and some other functions.[3–5] The HSs represent the group of natural compounds which are most difficult for study, and their numerous functions are to be studied yet. The HSs act in many ways: as sorbents and as catalysts in the hydrolysis processes, as solubilizers; they affect microbiological processes and serve photosensitizers and quenchers.[13] Their photochemical properties are still unclear, though it is known that humic substances can absorb the light and transfer the light energy to other components of aqueous solutions, strongly affecting, in some cases, the photolysis of xenobiotics.[14] It was found that HSs can act as photosensitizers under irradiation at the wavelengths higher than 290 nm (Ref. 15). The

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capability of HSs to produce active forms of oxygen after irradiation was reported,[16] as well as their capability to photoinduce the transformations of herbicides.[17]

The fact is known that the photodecomposition of environmental toxicants under the exposure to sunlight completes for 85 hours in the pure water and for 60 hours in the natural water.[18] There are some contradictory data about the mutual effect of humic substances and organic environmental toxicants in the process of photolysis. The study of basic regularities in photolysis of humic substances (in particular, in the presence of environmental toxicants of different kind) is extremely urgent, since it reveals the effect of the natural and artificial optical radiation on biosystems. As was noted by the prominent photochemist J.H. Porter, the optical radiation is of a governing factor for functioning of the biosphere.

HSs include in three fractions: fulvic acids (FAs) water-soluble at all pH values, acid-deposited humic acids (HAs), humines soluble in water at pH > 2 and insoluble. According to the modern ideas, the humic acids form the most representative group of humic substances,[4] therefore, the results concerning these acids are of a great interest for investigators.

We have studied the spectral-luminescent properties of humic acids before and after UV irradiation using the spectroscopic methods.

Technique

The samples of humic acids kindly presented at our disposal by L.I. Inisheva (Siberian Scientific and Research Institute of Peat, Russian Academy of Agricultural Sciences, Tomsk) were prepared by the team headed by N.V. Yudina at the Institute of Petroleum Chemistry SB RAS (Tomsk). The objects of investigation were extracted from low-moor peat (pH = 4.9) of the Tugan peat bog (Tomsk Region). The peat was characterized by the ash content of 37.6%, hydrolytic acidity of 9.8 mg-eqv/100 g, 42.8% of the humic acid, and by the 30% degree of decomposition. Sedge HA and cotton-grass HA are humic acids fractioned from the peat-forming grasses. Humified sedge HA and cotton-grass HA are extracts from the peat-forming grasses placed in a peat bed for two years. HA 2805, HA 2814, and HA 2820 are humic acids extracted from the lower-lying peat bed.

The series of solutions was prepared under laboratory conditions from dry weighted samples: sedge HA, cotton-grass HA, humified sedge HA, humified cotton-grass HA, HA 2805, HA 2814, and HA 2820. The HA concentration in matrix solutions of 0.1 H NaOH was 0.3 g/liter. These solutions were left for 24 hours in darkness at room temperature for swelling and more complete solution. The solutions of HA 2814 and HA 2820 had a suspended matter, and for more complete solution they were heated using water bath ~40°C. Then the matrix solution was diluted 250 times (the studied HA concentration amounted to $1.2 \cdot 10^{-3}$ g/liter).

The absorption and fluorescence spectra were recorded by the standard procedure with a Specord M40 spectrophotometer and a Hitachi M850 spectrofluorimeter. Medium pH was measured by a pH-meter of the pH-673 type. The sources of UV radiation for photochemical studies were:

1. An OKN-11M high-pressure mercury lamp.
2. A KrCl pulsed exciplex barrier-discharge lamp (of U-type with the following parameters $\lambda = 222$ nm, $\Delta\lambda = 5$–10 nm, $W = 18$ mW/cm^2, $f = 200$ kHz) developed by the team headed by Prof. V.F. Tarasenko at the Institute of High-Current Electronics SB RAS.[19]

The time of prior irradiation was varied from 1 to 80 min. To avoid heating of the solution during irradiation and for stable operation of the lamp, the setup was cooled by air with a fan. The time of irradiation by the Hg lamp was varied from 1 min to 10 hours, which corresponded to the energy deposited into the solution $E = 1$–36 J/cm^3. The time of irradiation by the KrCl excilamp was from 1 to 110 min, which corresponded to the deposited energy $E = 1$–10 J/cm^3.

The air-saturated aqueous HA solutions were placed in a rectangular quartz cell with the length $l = 1$ cm at the space of 4 cm from the excilamp and 25 cm from the mercury lamp.

Results and discussion

We have studied experimentally the series of solutions of various-nature HAs: sedge HA, cotton-grass HA, humified sedge HA, humified cotton-grass HA, HA 2805, HA 2814, and HA 2820, which were prepared from dry weighted samples extracted from the lower-lying peat bed.

Consider the absorption spectra of the studied solutions. The general shape of the electronic absorption spectra of HAs agrees with the data of other authors.[3,20] The electronic spectra (UV and visible regions: from 220 up to 750 nm) explain the dark color of the humic substances. HAs are characterized by an intense absorption in the UV spectral region, and the absorption decreases smoothly with the increase of wavelength. The HA spectra look like curves gently sloping toward long wavelengths, on which there are almost no peaks or dips (weak peaks are sometimes observed nearby 430, 448, 568, and 613 nm). Many authors explain this type of curves by the fact that the chain of double carbon-carbon is developed in such molecules. The break of this chain at photochemical degradation results in the gradual loss of color. As to our data, the absorption spectra of sedge HA and cotton-grass HA are almost identical, but in the region of 280–350 nm the molecules of sedge HA absorb more strongly (Fig. 1). In the spectra of humified sedge HA and humified cotton-grass HA, the absorption intensity decreases all over the spectrum. For the samples extracted from peat, the absorption intensity increases in the region of 220–360 nm.

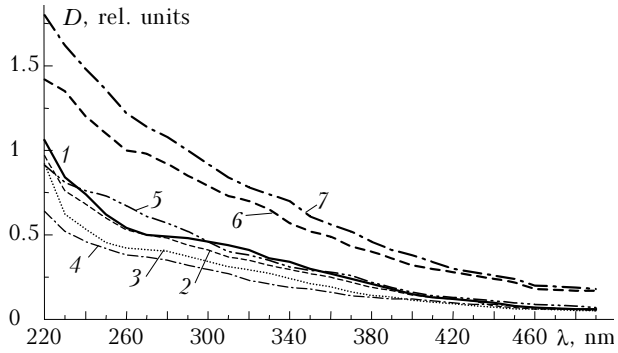

Fig. 1. Absorption spectra: sedge HA (*1*), cotton-grass HA (*2*), humified sedge HA (*3*), humified cotton-grass HA (*4*), HA 2805 (*5*), HA 2814 (*6*), and HA 2820 (*7*).

As to the fluorescence spectra, the fluorescence methods find the increasing utility in biochemical, medical, and ecological studies,[21–23] because they are characterized by high sensitivity and convenient time range: the fluorescence radiation is emitted roughly in 10^{-8} s (10 ns) after absorption. Many different molecular processes can occur for this time, and these processes can change the spectral characteristics of the fluorescing compound. This combination of the high sensitivity with the convenient time range has led to the wide use of the fluorescent methods in various fields of research, in particular, to study the humic substances.[7,24] The HA samples studied in this work have the fluorescence spectra in the long-wave region with a peak nearby 490 nm (Fig. 2). The data obtained suggest that the fluorescence intensity decreases in the process of humification, and the fluorescence range change not appreciably. The change of the fluorescence intensity is likely connected with some restructuring of the molecule and variation of the percentage of the components.

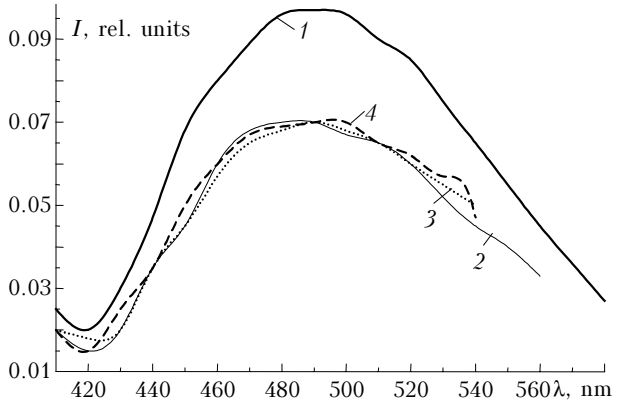

Fig. 2. Fluorescence spectra: sedge HA (*1*), humified sedge HA (*2*), HA 2805 (*3*), HA 2814 (*4*).

Discuss now the properties of the irradiated samples. At irradiation of the aqueous HA solutions by the mercury lamp, no significant spectral changes were observed even after 4 hours of irradiation. Consequently, the considered HAs are rather stable to irradiation at $\lambda = 365$ nm. The absorption spectrum of sedge HA has a bend nearby 250–350 nm, and during irradiation the absorption intensity in this region increases (Fig. 3). The changes in the fluorescence spectra upon irradiation are more significant than those in the absorption spectra (Fig. 4). The fluorescence spectrum changes by jump. The fluorescence intensity decreases during the first 10 min of irradiation, and during the further irradiation (> 10 min) the intensity increases markedly and the fluorescence band shifts to the shortwave region (Fig. 4).

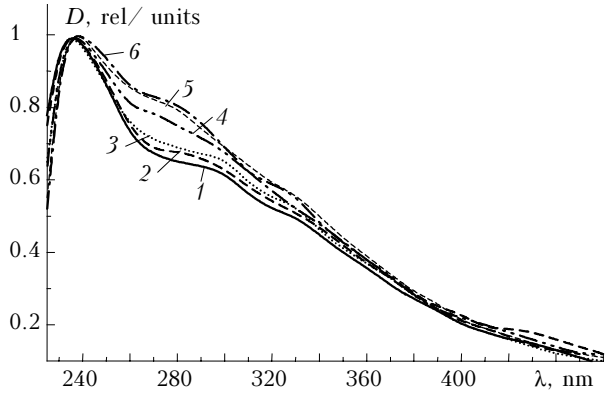

Fig. 3. Normalized absorption spectra of sedge HA irradiated by KrCl excilamp ($\lambda = 222$ nm) for 0 (*1*), 1 (*2*), 5 (*3*), 10 (*4*), 20 (*5*), 40 min (*6*).

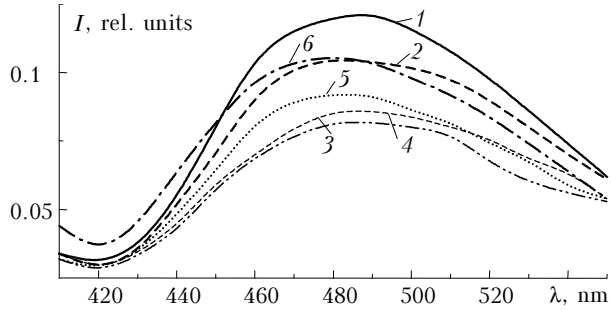

Fig. 4. Fluorescence spectra of sedge HA irradiated by KrCl excilamp for 0 (*1*), 1 (*2*), 5 (*3*), 10 (*4*), 20 (*5*), 40 min (*6*).

Conclusion

So, the comparison of the absorption and fluorescence spectra of the humic acid samples with different degree of humification has revealed that in the process of humification the absorption intensity first decrease all over the spectrum and then increased in the region of 220–360 nm. The fluorescence intensity decreased in the process of humification, and its region changed not appreciably. Under the exposure to the shortwave (222 nm) excilamp radiation, a significant photodestruction of the humic acids occurred.

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