The interaction between humic acid and naphthalene after exposure to visible and UV light

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ABSTRACT

Dissolved organic matter plays an important role in pollution migration from human waste to aquatic environments. In this study, the effect of humic acid (HA) on the photo-chemical transformation of naphthalene by irradiation model solar and UV light was reported using fluorescence quenching titrations. It was calculated the interactions between naphthalene and humic acids. It is found that the molecular complex of humic acid and naphthalene is more stable to UV irradiation, compared with the model solar radiation. The application of molecular fluorescence spectrometry is a useful sensitive tool evaluate intermolecular HA and naphthalene interactions.

Keywords: naphthalene, humic acid, binding constant, irradiation, photolysis

1. INTRODUCTION

Naphthalene - a typical representative of the class of polycyclic aromatic hydrocarbons (PAHs). Polycyclic aromatic hydrocarbons - toxic organic substances released into the environment by burning coal and oil products, industrial waste and household garbage. [1] PAH are formed in large quantities during forest fires, are present in tobacco smoke [2]. PAH molecules are absorbed by micro-particles suspended in the air and deposited on the surface of the soil and water bodies. [3]. Due to the low water solubility and stability PAH accumulate in the environment, in the body of plants, animals and humans.

Humic acid (HA) - natural organic matter is a complex mixture of polymers of the irregular structure [4]. They are formed as a result of microbial decomposition of plant residues. GC are the main components of soil organic matter, peat and sapropel. They may bind the toxic organic compounds into stable complexes hindering the migration of hazardous substances in the natural environment [5]. On the other hand, the soluble fraction of humic acids by reaction with toxic organic compounds transferred them in a solution, increasing thereby the concentration of these substances in the aqueous phase. In the upper layers of the soil and in the aqueous solution formed complexes are exposed to solar radiation. Visible radiation and, in particular, UV rays contribute to photochemical transformations resulting complexes PAH and humic acids, releasing toxic substances, either by destroying them. Thus, the solar radiation is one of the key factors determining the fate of PAH molecules in the natural environment [6].

In accordance with the above, the aim of this work is to study the photochemical transformation of naphthalene - the most important compound of a class of PAHs - in the presence of humic acids under the influence of visible and UV light. Our work is devoted to the study of the photolysis of naphthalene in solutions of HA. This distinguishes it from photolysis studies of PAHs adsorbed to soil particles [7], as well as airborne ash particles [8]. The practical problems posed in the course of our research is to find the optimal conditions for the photochemical oxidation of naphthalene in the presence of humic acids with a maximum quantum yield predominantly in the visible radiation. The results obtained in the course of the study may be useful in the design of photochemical reactors for the remediation of soil and water sediments.

2. EXPERIMENTAL SECTION

As the object of study were selected humic acid and naphthalene of Aldrich Company. Source of model solar radiation - helium lamp «Solar» with filter BGG-24 (λ_{rad} ÷ 300-800 nm, W_{peak} до 160 $mW \cdot cm^{-2}$). The source of UV radiation - impulse KrCl-excilamp ($\lambda_{rad} \sim 222$ nm). Both lamps designed by a team of employees IHCE SB RAS (Tomsk). Irradiation was carried out for 2, 8, 16 and 32 minutes. There were obtained absorption and fluorescence spectra of control and irradiated solutions, complex formation constants were calculated.

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Stock solution HA with a concentration of 1 g/L was prepared in 0,1 n. NaOH solution by incubation for 30 minutes in an ultrasonic bath heated to 45 ° C, and then for one day in the dark at room temperature. A stock solution by diluting with distilled water was prepared a series of solutions of HA in a concentration range $2 \cdot 10^{-6} – 2 \cdot 10^{-2}$ g/L. To each of the resulting solutions was added an equal volume of a solution of naphthalene in water to a concentration of $2 \cdot 10^{-4}$ mol/L. Total concentration of naphthalene was 10^{-4} mol/L, the concentration of HA varied from 10^{-6} to 10^{-2} g/L. The calculated values of pH of the solutions ranged from 7 to 9. It was recorded absorption and fluorescence spectra of solutions in accordance with the standard procedure on spectrofluorometer SM2203 (Belarus), $\lambda = 270$ nm. Complexation constants were calculated from the Stern-Volmer equation:

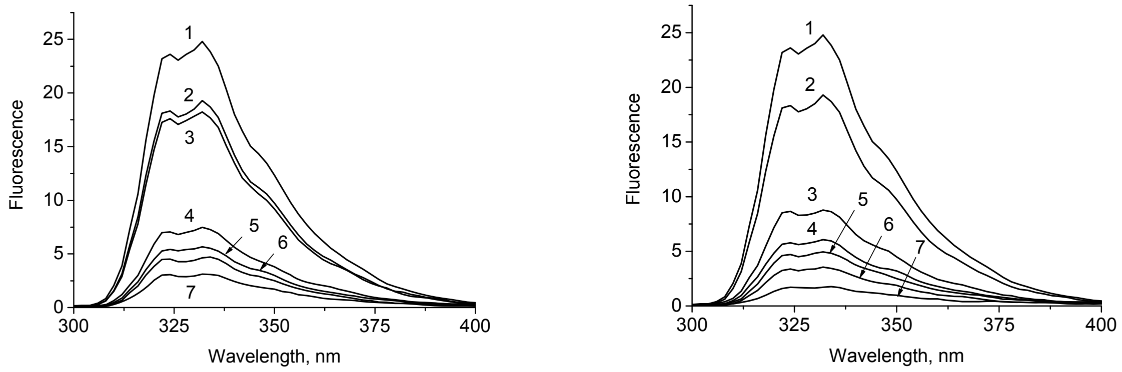
$$F_0/F = 1 + K_b[\text{HA}],$$

where F_0 - the intensity of the fluorescence emission of PAHs at the maximum, F - naphthalene fluorescence intensity at the maximum of the radiation after addition of HA, [HA] - HA concentration, kgC/L. The method is based on the determination of the constants of quenching of fluorescence in the presence of PAHs [9]. According to this method was built graph showing the relationship F_0/F from the HA concentration, expressed in kgC/L (kg carbon per liter solution). Then schedule approximated to the line and determined the slope of this line to the x-axis. The obtained value is numerically equal to the complexation constant HA and naphthalene.

The maximum fluorescence quenching of naphthalene is characteristic of a solution containing 10^{-2} g/L of the HA. Therefore, to further investigate the effect of HA on the photochemical transformation of naphthalene was chosen this solution. Two series of solutions were prepared containing naphthalene were prepared at a naphthalene concentration of 10^{-4} mol/L and HA concentration 10^{-2} g/L, as well as two series of solutions containing the individual substances: naphthalene at $2 \cdot 10^{-4}$ mol/L and HA at $2 \cdot 10^{-2}$ g/L. Also were prepared two series of solutions with a concentration of naphthalene 10^{-4} mol/L. A series of solutions containing a mixture of materials, a series of solutions with a concentration of naphthalene $2 \cdot 10^{-4}$ mol/L, a series of solutions with a concentration of HA $2 \cdot 10^{-2}$ g/L and a series of solutions with a concentration of naphthalene 10^{-4} mol/L were irradiated for 2, 4, 8, 16 and 32 minutes by «Solar» lamp at 10 cm from the radiation source with constant stirring using a magnetic stirrer. Solutions of naphthalene with a concentration of naphthalene $2 \cdot 10^{-4}$ mol/L and solutions of HA with a concentration of HA $2 \cdot 10^{-2}$ g / l were mixed after irradiation. The same procedure was done for KrCl-excilamp. It was recorded absorption and fluorescence spectra of the initial and irradiated solutions in accordance with the standard procedure on spectrofluorometer SM2203 (Belarus), $\lambda = 270$ nm. It was conducted a comparative analysis of the data and conclusions.

3. RESULTS AND DISCUSSION

The absorption spectra of HA and naphthalene solutions have a characteristic long-wavelength shift (especially for high concentrations of HA), indicating the formation of a complex HA with the data obtained in our previous study [10]. Figure 1 shows the fluorescence spectra of naphthalene and HA irradiated «Solar» lamp. Fig. 1a shows the spectra of solutions of naphthalene and HA mixed after irradiation, and Fig. 1b – before irradiation. It draws attention to the difference in the spectra 3 of Figure 1a and Figure 1b. The fluorescence intensity of naphthalene in the solution obtained by mixing the irradiated for 2 minutes naphthalene and HA 1.5 times higher than the fluorescence intensity of naphthalene in the solution in which it was mixing prior to irradiation. Thus, we can assume that in the case of solutions obtained by mixing irradiated naphthalene and HA, we are dealing with fluorescence quenching. At the same time for solutions of naphthalene and HA mixed prior to irradiation, typical of photochemical decomposition of naphthalene. Further confirmation of this hypothesis is the fact that a number of fluorescence intensity maximum naphthalene Fig. 1b is characterized by the lowest values, not only in comparison with Fig. 1a, but also in comparison with Fig. 2a and 2b. Irradiation of a solution of naphthalene in the presence of HA for 32 minutes gives a minimum value of the fluorescence intensity equal to 1.86 r. u. This minimum is not typical even for solutions of naphthalene, irradiated for 32 minutes with UV light. To test the hypothesis of photochemical transformation of naphthalene by irradiation lamp «Solar» more research is required.

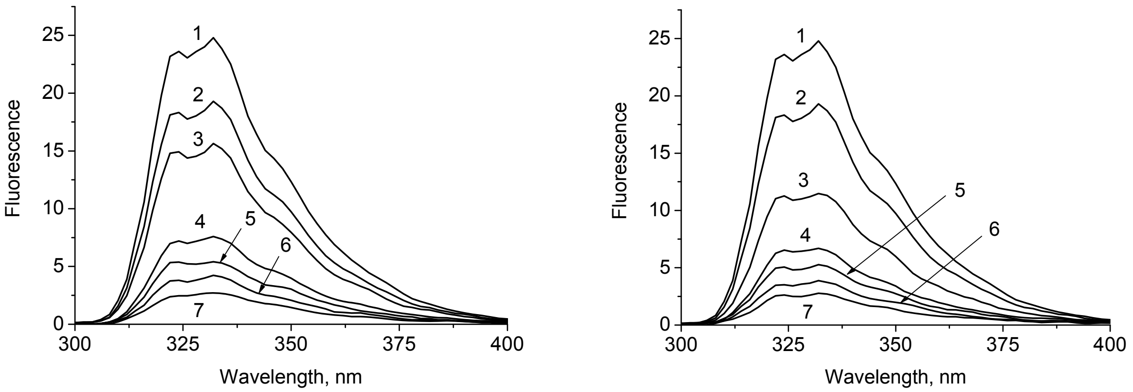


a

b

Figure 1 - The fluorescence spectra of naphthalene (10^{-4} mol/L) (1), naphthalene (10^{-4} mol/L) and HA (10^{-2} g/L) was irradiated with a lamp «Solar» within (min): 0 (2); 2 (3); 4 (4); 8 (5); 16 (6) 32 (7)

Figure 2 shows the fluorescence spectra of naphthalene and HA irradiated KrCl-Excilamps. Fig. 2a shows the spectra of solutions of naphthalene and HA mixed after irradiation, and Fig. 2b - before irradiation. Similarly to the previous example, irradiation of a mixture of naphthalene and HA within 2 minutes gives minimal fluorescence intensity naphthalene than mixing irradiated solutions. Though, it must be acknowledged that the difference in intensity is not as great as in the case of irradiation «Solar» lamp. Perhaps by mixing irradiated solutions photochemical degradation of naphthalene also plays a role, along with the process of quenching. For the interval of 4-32 minutes Fig. 2a and 2b do not differ from each other, photochemical transformation naphthalene undoubted in both cases.



a

b

Figure 2 - The fluorescence spectra of naphthalene (10^{-4} mol/L) (1), naphthalene (10^{-4} mol/L) and HA (10^{-2} g/L) was irradiated with a KrCl-excilamps (min): 0 (2); 2 (3); 4 (4); 8 (5); 16 (6) 32 (7)

The hypothesis of photochemical transformation of naphthalene by irradiation «Solar» lamp in the presence of HA can be supported by the following theoretical considerations. By interaction the molecules of naphthalene with HA macromolecule complex is formed, in which the connection due to the intermolecular π-π-electron interaction of aromatic naphthalene and the aromatic moiety of the macromolecule HA. The irradiation is the process of energy transfer from HA macromolecule – the donor – to an acceptor naphthalene. The energy transfer causes photochemical decomposition of the molecular complex and photo-oxidation of naphthalene.

4. CONCLUSIONS

1. The absorption spectra of HA solutions and naphthalene have a characteristic long-wavelength shift, indicating the formation of a complex HA-naphthalene.
2. Complexation constants of naphthalene and HA is $38{,}17 \cdot 10^4$ L/kgC.
3. Naphthalene fluorescence intensity upon irradiation for 2 minutes of the mixture naphthalene and HA is markedly different from the fluorescence intensity naphthalene irradiated for 2 minutes and mixed with irradiated for 2 minutes humic acids. This difference is characteristic for HA-naphthalene systems regardless of the source of radiation and may be indicative of photochemical transformation naphthalene model during irradiation with sunlight.

5. ACKNOWLEDGMENT

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