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Photochemical and Detoxifying Properties of Humic Substances in Water Solution

The degradation of herbicides 4-chloro-2-methylphenoxyacetic acid (MCPA) and 2,4-dichlorophenoxyacetic acid (2,4-D) in water by the combination of UV-irradiation and humic acids has been studied. The photoreaction rate of all irradiated samples was lowest for the sample irradiated at 308 nm in the absence and in the presence of humic acids (HAs), and highest for the sample irradiated at 222 nm. HAs apparently catalyzed the formation some different not toxic photoproducts of 2,4-D and MCPA after UV-irradiation treatment by excilamps. We have observed a dependence of the detoxification both on the structure of the studied compounds and on the characteristics of the source.

Изучена деградация гербицидов 4-хлор-2-метилфеноксиуксусной (MCPA) и 2,4-дихлорфеноксиуксусной (2,4-D) кислот в воде под действием УФ-излучения эксиламп и гуминовых кислот. Скорость фотореакции ниже в случае облучения длиной волны 308 нм как в присутствии, так и без гуминов и наивысшая при облучении длиной волны 222 нм. Гуминовые кислоты способствуют образованию нетоксичных фотопродуктов. Обнаружена зависимость эффективности детоксикации как от структуры исследованных соединений, так и от характеристик источника облучения.

Humic substances (HS) are the products of extremely complex chemical and microbial processes of the decomposition and secondary synthesis of plant and animal residues in soil and water. HS are the main global reservoir of carbon.

Humic substances representing the main fraction of organic matter receive increased attention because of their reactivity as light absorbers. Depending on their origin and structure, HS have a remarkable ability to absorb light and transfer this energy to other substrates and in some cases strongly affect photolysis of xenobiotics. In water and in soils humic substances have been found to act as photosensitisers and they have also been reported to produce oxygen species upon irradiation, and be able to photoinduce the transformation of ecotoxicants. The photoquenching effects of humic substances on some chemicals are also known. Also, the possibility of an UV screening by humic substances on chemicals cannot be excluded since the energy-transfer and charge-transfer between the chemical and humic substances can deactivate the excited molecules. Excited singlet and triplet states of dissolved humic acids (HAs), the major component of humic substances, are important players for the transformation of organic chemical contaminants in natural waters. Our knowledge about these processes is still very limited.

Photochemical processes also play an essential role in engineering water treatment systems which use UV light for water purification and disinfection [1]. Nowadays studies of the effectiveness of UV modern sources are still very important. The irradiation of these sources is absorbed by the high-lying electronically excited states of the organic molecules and may lead to the influence of radiation wavelength on optimal canals of the molecule phototransformation. Recently considerable attention focused on the development of excilamps and their applications [2]. The UV-radiation sources used for investigations were three barrier discharge excilamps (KrCl, XeBr and XeCl), emitting maximum UV-radiation at 222, 283 and 308 nm, respectively. The samples of HAs fractions were obtained from Aldrich Chemical Co and prepared from peat of Tomsk region.

The degradation of herbicides 4-chloro-2-methylphenoxyacetic acid (MCPA) and 2,4-dichlorophenoxyacetic acid (2,4-D) in water by the combination of UV-irradiation and humic acids has been studied. The 2,4-D phototransformation rate in water and in the presence of HAs was determined by evolution of the initial bands of 2,4-D absorbance at 230, 256 and 285 nm vs irradiation time. The photoreaction rate of all irradiated samples was lowest for the sample irradiated at 308 nm in the absence and in the presence of humic acids, and highest for the sample irradiated at 222 nm. Estimation of biodegradability of phototreated MCPA solution was carried out according to ratios of biological oxygen demand (BOD_5) to chemical oxygen demand (COD). The biodegradability of MCPA solutions increased after irradiation. HAs apparently catalyzed the formation some different not toxic photoproducts of 2,4-D and MCPA after UV-irradiation treatment by excilamps. The main photoproducts were identified by gas chromatograph/mass spectrometry (GC/MS).

It was also found that the fluorescence quenching ability of HAs in the presence of ecotoxicants (naphthalene and other polycyclic aromatic hydrocarbons) depends strongly of their origin.

The other aim of this work was to use a bioluminescence test system to study the effect of two factors on solutions of new substituted furocoumarins (sensitizers for phototherapy) and common phenoxyl herbicides: UV radiation from different sources, and humic substances. The toxicity of solutions was assessed using the bioluminescence assay, which is based on lyophilized luminous bacteria *Photobacterium phosphoreum*, produced at the Institute of Biophysics (Krasnoyarsk, Russia). The UV-radiation sources used for investigations were: a DRT-240 high-pressure mercury lamp (Hg) and three barrier discharge excilamps (purchased from the Institute of High Current Electronics of the Siberian Branch, Russian Academy of Sciences). The parameters and choice of the lamps are discussed elsewhere (1). As the sample of humic substances, we used a Gumat-80 preparation (Gumat OOO, Irkutsk, Russia). The preparation was obtained by mechanochemical reaction of oxidized brown coal (Cheremkhovskoe field, Russia) with alkali (KOH, NaOH). The concentration of humic substances was selected so that the intensity of bioluminescence differed from the control by no more than 20%. The other samples of humic acids (HA) fractions were obtained from Fluka Chemical Co and prepared from peat of Tomsk region. We have shown that efficient detoxification of an alcoholic solution of investigated furocoumarins (synthesized in Taras Shevchenko Kiev National University, Ukraine) occurs as a result of addition of humic substances. We have observed a dependence of the detoxification both on the structure of the studied compounds and on the characteristics of the source. After photoexcitation the bond lengths in the furocoumarins change and the humic substances detoxify the irradiated solution more efficiently.

Acknowledgements

This work is supported by the Russian Basic Research Foundation (Project № 12-02-31681_ mol_a) and Grant of President RF for the Support of Leading Scientific School № 512.2012.2.

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