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PHOTODEGRADATION OF PHENANTHRENE IN THE PRESENCE OF HUMIC SUBSTANCES AND HYDROGEN PEROXIDE

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Abstract

The photodegradation of phenanthrene in water was investigated for a variety of reaction conditions employing various fulvic acids (FAs) as photosensitizers and hydrogen peroxide as oxidant. All experiments were conducted by using artificial sunlight from Suntest apparatus (Hanau, Germany) as light source. The relative rates of phenanthrene photodegradation for the different experimental conditions were computed. Fulvic acids of different origins influenced the rate of sunlight-induced photodegradation of phenanthrene in different ways. Hydrogen peroxide vigorously enhanced the photodegradation rate of phenanthrene. The photoproducts identified were oxygenated products of aromatic ring, such as 9,10,-phenanthrenquinone, a group of hydroxyphenanthrene with hydroxyl at different position (1,3,4, and 9), 2,2'-biphenyldicarbonic acid, 2,2'biphenyldialdehyde and 2-phenylbenzaldehyde. It can be consumed that the phenanthrene photodegraded via free radical mechanism.

Key Words: Phenanthrene; Photodegradation; Fulvic Acids; Hydrogen Peroxide; Interaction

Introduction

Phenanthrene (Fig. 1) is a compound of polycyclic aromatic hydrocarbons (PAHs) consisting of two or more fused benzene rings. PAHs are ubiquitous environmental contaminants (Cook and Pierce 1983; Evans 1993)

which derived from a variety of anthropogenic sources involving mainly incomplete combustion of organic matter and by industries (Wild1990). It has been reported that many PAHs show a high toxic, carcinogenic, and mutagenic potential (White 1986; Pahlman and Pelkonen 1987; Depierre and Ernster 1978; Newsted and Giesy 1987; Huang et al. 1993). They are hazardous to ecosystems and human health. Therefore, it is important to investigate the fate of PAHs in aquatic environments and find a way to eliminate them or reduce their toxicity.

Humic substances (HSs) are major organic matter in natural water bodies (Fischer and Kliger 1985). They play an important role in the fate and transfer of organic xenobiotics in the aquatic environment (Steinberg 1993). They can change the physico-chemical state or specification of the xenobiotics in aqueous systems by binding or associating with them. Several investigators have demonstrated that HSs can enhance water solubility of some hydrophobic compounds, such as DDT, PAHs, and polychlorinated biphenyls. HSs also can modify the hydrolysis kinetics of hydrophobic compounds and decrease or increase their bioavailability and toxicity. It has been recognized that these interactions between organic chemicals and HSs may vary depending on the sources of HSs.

Since solar radiation is the largest energy source in the environment (Zika and Cooper 1987), photocatalytic degradation represents one of the most important abiotic degradation processes. Abiotic degradation of environmental chemicals is mediated both by direct and sensitized photochemical processes. Sensitized reactions occur either by energy transfer from HSs to substrate molecules (Zepp Schlotzhauer and Sink 1985) or via formation of other reactive intermediates, such as siglet oxygen, organic peroxy radicals and hydroxyl radicals (·OH) (Hoigne et al. 1989, Faust and Hoigne, 1987). Since HSs are the major organic light absorbers in natural waters (Bruccoleri et al. 1993), most studies have focused mainly on effects of HSs on photoreactions of pollutants, such as pesticides (Shahamat and Gamble 1983) and nitroaromatic compounds (Simmons and Zepp 1986).

Hydrogen peroxide (H_2O_2) appears to be ubiquitous in the hydrosphere and has been found in rainwater, seawater and freshwater (Daum 1985; Mill, Hendry and Richardson 1980). In the presence of light, H_2O_2 can produce \cdot OH radicals (Beltran, Ovejero and Acedo 1993) which can attack the environmental chemicals.

The objective of this study was to investigate the photodegradation of phenanthrene in water system in the presence of photosensitizer fulvic acids and an oxidant H_2O_2 . Five fulvic acids belonging to different sources were used in order to compare the effects on the photodegradation of phenanthrene. The mechanism of phenanthrene photodegradation was studied through the identification of the photoproducts.

Materials and Methods

Two of five samples of fulvic acids (FAs) were obtained from the drinking water of Kaschin Beck disease (KBD) prone areas of China, while the other three were collected from either water, soil or peat of KBD-free locations in China. The characterization of these samples has been reported elsewhere (elemental composition, FT-IR, E_4/E_6 ratio, ¹H- and ¹³C-NMR) (Wang et al, in press).

Phenanthrene was purchased from Aldrich Chemical Company (99.5%+). Its stock solution was prepared as follows: First 4 mg phenanthrene was dissolved in 2 mL CH_2CI_2 . Then it was applied on a column packed with glass beads which offers a large absorption surface. The solvent was removed by nitrogen gas flow. A part of phenanthrene was subsequently eluted with 2 L sterilized distilled water. The concentration of phenanthrene in water was determined to be 0.5 mg L⁻¹ by a high performance liquid chromatography method (Hewlett Packard 1050 HPLC Series equipped with a 25.0 cm long, RP-18 column and a Hewlett Packard 3396 integrator),20µl samples were injected into the system directly. The mobile phase was comprised of methanol : water (70:30) which provided good resolution at a flow rate of 1 mL/min, the detection wavelength for phenanthrene set at 254 nm,

Photodegradation: The following three sets of solutions were prepared: a) phenanthrene solution, b) solutions of phenanthrene each with 5 mg L⁻¹ of a different FAs, c) phenanthrene with H_2O_2 (1*10⁻²M and 5*10⁻³M respectively). The solutions were transferred to 500 mL quartz flasks, stirred magnetically and irradiated using Suntest apparatus (Hanau, Germany) at >290 nm. Another set of identical solutions were also prepared but the quartz flasks were covered by aluminum foil to serve as dark control. At regular intervals, samples were collected from each reaction solution and the phenanthrene concentration was monitored by HPLC.

Identification of photoproducts: The reaction mixtures were extracted with cyclohexane. The organic phase was evaporated to dryness under reduced pressure at room temperature. The residues were dissolved in a small volume of methanol and subjected to HPLC analyses (Hewlett Packard 1090 Liquid Chromatography). The photoproducts were identified by comparison of their relative retention times, the UV spectra with those of standards and the "bank" of PAHs and their photoproducts established by other coworkers in the institute through HPLC-UV, HPLC-MS and GC-MS.

Results and Discussion

The present experiments show that the rate of phenanthrene photodegradation was greatly accelerated by the presence of H_2O_2 as shown in Figure 2. With regards to the influence of FAs as shown in Figure 3, mixed results were obtained. Two FA samples catalyzed photodegradation of phenanthrene with an efficiency comparable to that of H_2O_2 (Figures 2 and 3). The other three FA samples retarded the photodegradation of phenanthrene. In order to compare the photochemical behaviour differences among these five fulvic acid samples, we used the same fulvic acid concentration (5mg/L). Apparently, the combination of sunlight and H_2O_2 is an effective way to remove PAH contaminants, such as phenanthrene from water.

The major photoproducts have been identified were 9,10,-phenanthrenequinone, a group of hydroxyphenanthrene with hydroxyl at different position (1,3,4, and 9), 2,2'-biphenyldialdehyde, 2,2'-biphenyldicarbonic acid and 2-phenylbenzaldehyd (Fig. 1). Although, all of these major photoproducts were identified in every set of experiment, their rate of formation was influenced by the presence of FAs and H₂O₂. Therefore, it can be said that the same mechanism must be involved in the degradation of phenanthrene. It is well known that light-induced generation of free radicals such as \cdot OH can bring about the nuclear oxidation of aromatic rings when dissolved O₂ is present. The photochemical reaction of phenanthrene is primarily controlled by \cdot OH radical which react with the aromatic rings. In this case, the reaction rate is directly

dependent on the oxygen partical pressure. In the present study the O_2 pressure in the solution was equal to the conditions of the room temperature and pressure. Our purpose was to find out the differences between the various fulvic acid samples used, therefore the O_2 pressure remained the same.

Kinetics of phenanthrene photodegradation: According to the photochemical theory (Zepp et al. 1981: Kawaguchi 1993), in a well-mixed aqueous system containing a very low concentration of a chemical, both direct and photosensitized reactions can be described by first-order rate equation:

$$\ln (Co/Ct) = kt + A$$

where Co is the concentration of phenanthrene at irradiation time t=0; Ct is the concentration of phenanthrene



2,2'-biphenyldialdehyde

2,2'-biphenyldicarbonic acid

2-phenylbenzaldehyde

Fig.1 Chemical structures of phenanthrene and its photoproducts



Fig.2 Photodegradation of phenanthrene in the presence of hydrogen peroxide



- ----- : Jiangjiashan drinking water FA, Shanxi province, KBD free area but neighboured with KBD area
- ---------: Phenanthrene
- ------ : Guanguangou drinking water FA, Shanxi province, KBD prone area
- ------: Shengyangbeizheng soil FA, Liaoning province, "disease free are

Fig 3. Photodegradation of phenanthrene in the presence of 5 mg L⁻¹ fulvic acids with different origins

at irradiation time t, k is the rate constant. This indicats also that the apparent first-order rate constant is independent of the concentration of the chemical. The first-order rate constants k for phenanthrene photodegradation were calculated from the linear regression ln (Co/Ct) vs. time (t) with all regression coefficients more than 0.9 and are summarized in Table 1. It could as well be performed to compare the rate of phenanthrene photodegradation at various conditions, and to know the effects of FAs of different origins.

It has been known that HSs influence the fate of pollutants in the environment (Suffet and MacCarthy 1989). Our results indicate that the photodegradation of phenanthrene strongly depends on the sources of fulvic acid. FAs affected the photodegradative behavior of phenanthrene. Assumably, this phenomenon is the result of differences in the structures of the FAs obtained. We did not find any significant correlation with the appearance of KBD. In a series of adsorption and complexation studies on s-triazine derivatives with HSs, Madhun (1986) reported that the interaction capability seems to be a function of the sources of HS. In numerous studies, McCarthy and Jimenez (1985), Gauthler et al. (1986), and Richnow et al. (1994) described that HSs have a large adsorption capacity for PAHs. They appear to trap or bind considerable amounts of PAHs in relative stable complexes within their macromolecular structures. Wershaw (1986) introduced a model for humic materials, which provides a means of understanding the interaction with hydrophobic pollutants. He proposed that humic materials consist of numbers of different oligomers and simple compounds resulting from the partial degradation of plant remains. These degradation products are stabilized by incorporation into humic aggregates bound together by weak bonding mechanisms, such as hydrogen bonding, π -bonding, and hydrophobic interactions. The resulting structures are similar to micelles or membranes, in which the interiors of the structures are hydrophobic and the exteriors are hydrophilic. Hydrophobic compounds will partition into the hydrophobic

Table 1. Influence of fulvic acids obtained from different sampling sites of P. R. China on apparent first-order rate constant (k) and half-life $(t_{1/2})$ for the phenanthrene photodegradation

FA source	k (hr-1)	t _{1/2} (hr)
Phenanthrene	0.236	2.94
Drinking water from Suiling	0.174	3.98
Peat from Lianjiang	0.120	5.78
Soil from Shenyang	0.535	1.30
Drinking water from Guanguangou	0.502	1.38
Drinking water from Jiangjiashan	0.214	3.24

interiors of the humic micelles. The model of Wershaw (1986) explains clearly the transport, fate and effects of the adsorbed pollutants. Since humic materials differ in molecular size, structure, acidity, lipophilicity and other properties. Therefore, the units of micelles differ too, depending on their origins and degree of transformation. This may explain that different results with the same chemicals under the same test.

In the aquatic environment, many organic compounds may in principle be transformed by sunlight as a result of either direct light absorption by these compounds or by reaction with reactive intermediates e.g. formed from humic materials on irradiation (Noont et al. 1988). Humic materials can act as photosensitizers (Skurlatov et al. 1983) or precursors for the production of reactive oxygen species such as siglet oxygen, hydroxyl radicals, peroxy radicals, hydrogen peroxide and solvated electrons (Hoigne et al. 1989; Faust and Hoigne, 1987). Two general mechanisms (Skurlatov et al. 1983) can explain the experimental results. The first mechanism involves photosensitization by HSs in water:

> $HS + light \rightarrow HS^*$ $HS^* + Phenanthrene \rightarrow products$

This mechanism could either include the direct reaction between the substrate and the electronically excited sensitizer, HS* which transfers its energy to the chemical adsorbed or the reaction between the substrate and some oxidizing species derived from HS*. A schematic representation as shown below may well describe the process:



The precise nature of the free radicals as well as their role in the photodegradation remains an important field of research.

Conclusions

The presence of humic substances in aqueous systems has significant influence on the phenanthrene photodegradation. Retardation or acceleration to phenanthrene photodegradation depends upon the origins of the HSs. In the presence of H_2O_2 , phenanthrene photodegrads very quickly, which could be an effective way for removal of PAH contaminants such as phenanthrene from natural waters. The major photoproducts identified in each experiment were 9,10,-phenanthrenquinone, a group of hydroxyphenanthrene with hydroxyl at different position (1,3,4, and 9), 2,2'-biphenyldialdehyd, 2,2'-biphenyldicarbonic acid and 2-biphenylbenzaldehyd, albeit the relative rate of their formation differed. This finding suggests the involvement of free radical mechanisms in the photodegradation of phenanthrene.

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References

Beltran, F. J., G. Ovejero and B. Acedo, 1993. Oxidation of atrazine in water by ultraviolet radiation combined with hydrogen peroxide. Water Research, 27 (6), 1013-1021

Bruccoleri, A., Bhuvan C. Pant, Devendra K. Sharma, and Cooper H. Langford, 1993. Evaluation of primary photoproduct quantum yields in fulvic acid, Environmental Science and Technology, 27 (5), 889-894.

Cook, R.H., R.C. Pierce et al., 1983. Polycyclic aromatic hydrocarbons in the aquatic environment: formation, sources, fate and effect on aquatic biota, NRCC 18981, National Research Council of Canada, Ottawa, Ontario

Depierre, J.W. and L. Ernster, 1978. The metabolism of polycyclic hydrocarbons and its relationship to cancer, Biochim. Biophys. Acta, 473: 149-186

Evans, W. H., N. C. Thomas, M. C. Boardman, and S. J. Nash, 1993. Relationships of polycyclic aromatic hydrocarbon yields with particulate matter (water and nicotine free) yields in mainstream and sidestream cigarette smoke, The Science of the Total Environment, 136, 101-109

Faust, B. C., and J. Hoigne, 1987. Sensitized photooxidation of phenols by fulvic acid and in natural waters, Environ. Sci. Technol., 21 (10), 957-970

Fischer, A. M., and D.S. Kliger, 1985. Direct observation of phototransients in natural waters, Chemosphere, 14 (9), 1299-1306

Gauthler, T. D., E. C. Shane, W. F. Guerin, W. R. Seitz, and C. L. Grant, 1986. Fluorescence quenching method for determining equilibrium constants for polycyclic aromatic hydrocarbons binding to dissolved humic materials, Environ. Sci. Technol., 20, 1162-1166

Haag, W. R., and J. Hoigne, 1985. Photo-sensitized oxidation in natural water via .OH Radicals, Chemosphere, 14 (11/12), 1659-1671

Hoigne, J., B.C. Faust, et al., 1989. "Aquatic Humic Substances", Adv. Chem: Ser., 219, Washington D.C., Chapter 23

Huang, X. D., D. G. Dixon, and B. M. Greenberg, 1993. Impacts of UV radiation and photomodification on the toxicity of PAHs to the higher plant LEMNA GIBBA, Environmental Toxicology and Chemistry, 12 (6), 1067-1077

Kawaguchi, H., 1993. Rate of sensitized photo-oxidation of 2,4,6-trimethylphenol by humic acid, Chemosphere, 27 (11), 2177-2182

Shahamat U. K. and D. S. Gamble, 1983. Ultraviolet irradiation of an aqueous solution of prometryn in the presence of humic materials, J. Agric. Food Chem., 31, 1099-1104

McCarthy, J. F., and B. D. Jimenez, 1985. Interactions between polycyclic aromatic hydrocarbons and dissolved humic material: binding and dissociation, Environ. Sci. Technol., 19, 1072-1076

Mill, T., D.G. Hendry and H. Richardson, 1980. Free-radical oxidants in natural waters, Science 207, 886

Newsted, J. L., and J. P. Giesy, 1987. Predictive models for photoinduced acute toxicity of polycyclic aromatic hydrocarbons to Daphnia Magna, Strauss (Cladocera, Crustacea), Environmental Toxicology and Chemistry, 6, 445-461

Pahlman R., O. Pelkonen, 1987. Mutagenicity studies of different polycyclic aromatic hydrocarbons, the significance of enzymatic factors and molecular structures, Carcinogenesis 8: 773-778

Richnow, H. H., R. Seifert et al., 1994. Metabolites of xenobiotica and mineral oil constituents linked to macromolecular organic matter in polluted environments, Org. Geochem., (in press)

Simmons, M. S., and R. G. Zepp, 1986. Influence of humic substances on photolysis of nitroaromatic compounds in aqueous systems, Water Research, 20 (7), 899-904

Skurlatov, Y. I., R. G. Zepp and G. L. Baughman, 1983. Photolysis rates of (2,4,5-trichlorophenoxy) acetic acid and 4-amino-3,5,6-trichloropicolinic acid in natural waters, J. Agric. Food Chem., 31, 1065-1071

Steinberg, C. E. W., et al., 1993. Effect of dissolved humic material on bioavailability of some organic xenobiotics to Daphnia Magan, Chemical Speciation and Bioavailability, 5 (1), 1-9

Suffet, I. H., and P.MacCarthy, 1989. "Aquatic Humic Substances", Adv. Chem. Ser., 19, Washington D.C.

Van Noont, P., R. Smit, E. Zwaan, and J. Zijlstra, 1988. Pitfalls in the aquatic photochemistry testing of chlorinated aromatic compounds, Chemosphere, 17 (2), 395-398

Wang, C. X., A. Yediler, N. Hertkorn, A. Peng, and A. Kettrup, Characterization and comparison of five fulvic acid fractions from different areas in China with and without Kaschin-Beck Disease, (in press)

Wershaw, R. L., 1986. A new model for humic materials and their interactions with hydrophobic organic chemicals in soil-water or sediment-water systems, J. Contaminant Hydrology, 1, 29-45

White K.L., 1986. An overview of immunotoxicology and carcinogenic polycyclic aromatic hydrocarbons, Environ. Carcinogen Rew. C4: 163-202 Wild, S. R., K. S. Waterhouse, S. P. McGrath, and K. C. Jones, 1990. Organic contaminants in an agricultural soil with a known history of sewage sludge amendments: polynuclear aromatic hydrocarbons, Environ. Sci. Technol., 24, 1706-1711

Zepp, R. G., P.F. Schlotzhauer, and R.M. Sink, 1985. Photosensitized transformations involving electronic energy transfer in natural waters: role of humic substances, Environ. Sci. Technol., 19, 74-81

Zepp, R. G., G. L. Baughman, and P. F. Schlotzhauer, 1981. Comparison of photochemical behavior of various humic substances in water:2. photosensitized oxygenations, Chemosphere, 10, 119-126

Zika, R. G., and W.J. Cooper eds., 1987. "Photo-Chemistry of Environmental Aquatic Chemistry", ACS Symp. Ser. 327