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Aqueous photodegradation and toxicity of the polycyclic aromatic hydrocarbons fluorene, dibenzofuran, and dibenzothiophene

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ABSTRACT

Decay kinetics resulting from the application of UV and UV/H_2O_2 to the polycyclic aromatic hydrocarbons (PAHs) fluorene, dibenzofuran and dibenzothiophene was studied. Batch experiments were conducted with both low-pressure monochromatic (253.7 nm) and medium pressure polychromatic (200–300 nm) UV sources alone or in the presence of up to 25 mg/L hydrogen peroxide, in a quasi-collimated beam apparatus. Degradation of all three PAHs, by both UV and UV/H_2O_2, exhibited pseudo-first-order reaction kinetics and low quantum yields ranging from 1.4×10^{-3} to 1.8×10^{-2} mol/E using both UV lamps. Toxicity testing using a bioluminesence inhibition bioassay was correlated to the decay in concentration of the PAHs as analyzed analytically using HPLC. Results demonstrated that treatment efficacy of oxidative PAH degradation measured by following the decay of the target compound is best complemented by also evaluating the toxicity of the treated water due to byproduct formation concerns.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic substances composed of carbon and hydrogen atoms grouped into at least two condensed aromatic ring structures. PAHs can be introduced to the environment by incomplete combustion of coal, oil, and wood, improper storage or disposal of fuels and oils, and wood treatment processes. Many of the PAHs are toxic, carcinogenic, and tend to bioaccumulate in aquatic organisms. These compounds along with their oxidation products have been identified in environmental samples (Sabaté et al., 2001) such as industrial and municipal wastewater, effluents, rainwater, and drinking water (Maier et al., 2000; Jamroz et al., 2003). In surface water the concentration of PAHs were reported to range from 0.1 to 830 ng/L (Menzie et al., 1992).

Exposure to wildlife and humans can occur in water through advective and/or diffusive transport of contaminants and microbially produced intermediates to the overlying water column, where these chemicals can be subject to photolytic attack. Microbial transformations of photoproducts can also occur through the activity of suspended or sediment bacteria. The LD_{50} in aquatic organisms varies considerably, but is generally several orders of magnitude higher than concentrations found in most heavily polluted bodies of water (Arfsten et al., 1996). Growing evidence suggests that the real hazards of PAHs to aquatic life may result from their photo-induced toxicity caused by UV radiation in sunlight (Mekenyan et al., 1994; McConkey et al., 1997; Grote et al., 2005). Photo-induced toxicity of PAHs can be driven from formation of intracellular singlet oxygen and other reactive oxygen species (ROS) that cause oxidative

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damage in biological systems (El-Alawi et al., 2002), or formation of photo-products, which exert different, often stronger, bioactivity than the parent compound (Grote et al., 2005).

Fluorene (FLU), dibenzofuran (DBF) and dibenzothiophene (DBT) are three ring PAHs largely derived from anthropogenic sources (e.g., petroleum products), although they can also form through natural processes (e.g., forest fires). These compounds share fluorene's basic molecular structure, only differing by one atom in the bridge of the furan ring: C in FLU, O in DBF, and S in DBT (Fig. 1). Like many PAHs, these compounds are sparingly soluble with low volatility and high Kow, and in soils and sediments they strongly associate with dissolved or particulate organic matter (McCarthy, 1983; Liu and Amy, 1993). Association with dissolved organic matter may significantly increase apparent solubility (Lassen and Carlsen, 1999) yet often reduce bioavailability and toxicity (Weinstein and Oris, 1999; Steinberg et al., 2000).

Bioremediation is most often the treatment used for the removal of PAHs from contaminated water and soil because it is generally found to have cost and technical advantages (Zeng et al., 2000). Advanced oxidation processes (AOPs) including ozone, hydrogen peroxide, UV irradiation, and combinations of these processes were also shown to degrade various PAHs (Beltran et al., 1996; Zeng et al., 2000; Miller and Olejnik, 2001). The highly reactive hydroxyl radicals, generated during AOPs, can lead to complete mineralization of the pollutant but most typically result in the formation of products of higher polarity and solubility in water such as phenols, quinones, and acids (Stucki and Alexander, 1987; Beltran et al., 1996). These by-products are often more bioavailable for microorganisms, increasing overall natural biodegradation (Lehto et al., 2003; Grote et al., 2005).

Commonly the efficiency of AOPs is determined by following kinetics of decay of a target compound. In other cases byproducts, formed during oxidation, are identified. For example, Rivas et al. (2006) proposed a detailed mechanism of oxidation of FLU by hydroxyl radicals at which 9-fluorenone, 9-fluorenol, and DBF were formed in the first stage of the reaction. Further oxidation of these products proceeded via hydroxylation and cleavage of the fluorene-ring. Yet, too often the ecological or human health threat is assumed to be relieved upon degradation of a parent compound and the fate of the oxidation byproducts is overlooked. A different approach suggests that chemical analysis should be complemented by the application of bioassays to give an integrated measure of toxicity along with the chemical analysis data. Non-target pollutants as well as reduced availability of toxicants, antagonistic or synergistic interactions are all considered when using a biological test system (Loibner et al., 2004). Toxicity bioassays can be used not only to evaluate efficiency of oxidation processes but also to study the fate of the parent compounds as well as the byproducts formed during oxidation. Traditionally, crustaceans, fish and algae are used for aquatic toxicity measurement. Tests based on these organisms require long exposure times and large sample volume. Thus, toxicity measurements based on microorganisms which are rapid, cost effective and reproducible are being used extensively (Parvez et al., 2006). Luminescent bacteria have been found to be particularly useful in evaluating toxicant impacts (El-Alawi et al., 2002) and provide a measure of sub-lethal response for pollutants.

In this research, degradation kinetics and quantum yield were established for treating FLU ($C_{13}H_{10}$), DBF ($C_{13}H_{10}O$), and DBT ($C_{13}H_{10}S$) by UV and UV/H_2O_2 processes at wavelengths ranging from 200 to 300 nm, applicable for engineered treatment processes rather than naturally occurring sunlight-based environmental processes. Toxicity testing using a bioluminesence inhibition bioassay was conducted for each compound and further correlated with the decay of the PAHs as analyzed analytically using HPLC.

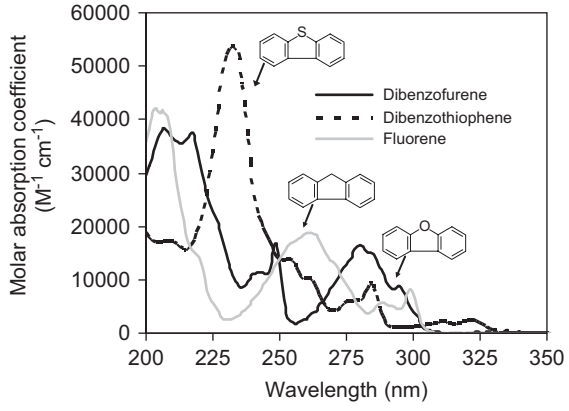

Fig. 1 – Molar absorbance of DBF, FLU, and DBT in aqueous solution.

2. Materials and methods

2.1. Materials

FLU and DBF (98% purity) were purchased from Alfa Aesar (MA, USA), DBT (98% purity) from Aldrich (MO, USA); molinate from Chem Service Inc. (PA, USA); hydrogen peroxide (30% w/w) and HPLC grade acetonitrile from Fisher Chemicals (NJ, USA); HPLC grade water from Acros (Geel, Belgium). All chemicals were used as received and all solutions were prepared with de-ionized (DI) water.

2.2. Photolysis experimental setup

Photolysis was carried out with low (LP) Hg vapor germicidal UV lamps (ozone-free, General Electric # G15T8) emitting essentially monochromatic UV light at 254 nm and a polychromatic (200–300 nm) medium-pressure (MP) (Hanovia Co., Union, NJ) Hg vapor lamp in a quasi-collimated beam apparatus. Emission spectrum of the UV lamps is shown elsewhere (Shemer et al., 2006a). In order to overcome the low solubility of the PAHs, methanolic stock solutions of the PAHs were placed in a glass vessel, the methanol was evaporated with a gentle stream of N_2, after which 20 mM phosphate buffer solution at pH 7 was added and the solution was covered and stirred overnight to dissolve the chemicals. A 100 mL sample was irradiated with gentle stirring in a 70×50 mm crystallization dish (34.2 cm^2 surface area,