



Effects of oil dispersants on photodegradation of pyrene in marine water



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H I G H L I G H T S

- Oil dispersant enhances pyrene photodegradation in seawater.
- Oil dispersant increases formation of superoxide radicals.
- Pyrene photodegradation shows a two-stage kinetics and follows first-order rate law.
- Pyrene is degraded mainly through electron transfer from excited pyrene to oxygen.
- Higher ionic strength and temperature and lower HA favor pyrene photodegradation.

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This work investigated effects of a popular oil dispersant (Corexit EC9500A) on UV- or sunlight-mediated photodegradation of pyrene (a model polycyclic aromatic hydrocarbon) in seawater. The presence of 18 and 180 mg/L of the dispersant increased the first-order photodegradation rate by 5.5% and 16.7%, respectively, and reduced or ceased pyrene volatilization. By combining individual first-order rate laws for volatilization and photodegradation, we proposed an integrated kinetic model that can adequately predict the overall dissipation of pyrene from seawater. Mechanistic studies indicated that superoxide radicals played a predominant role in pyrene photodegradation, and the dispersant enhanced formation of superoxide radicals. 1-Hydroxypyrene was the main intermediate regardless of the dispersant, suggesting that electrons were transferred from excited pyrene to oxygen. In the presence of 18 mg/L of the dispersant, the photodegradation rate increased with increasing ionic strength and temperature, but decreased with increasing HA concentration, and remained independent of solution pH. The results are important in understanding roles of oil dispersants on environmental fate of persistent oil components in natural and engineered systems.

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1. Introduction

The 2010 Deepwater Horizon (DWH) oil spill released an estimated 731 million liters of crude oil into the Gulf of Mexico [1]. In response to the incident, approximately 7.9 million liters of chemical dispersants Corexit EC9500A (6.8 million liters) and Corexit 9527A (1.1 million liters) were applied on the sea surface and at the wellhead [2].

Polycyclic aromatic hydrocarbons (PAHs) are a class of important oil-associated contaminants that are of great environmental

concern due to their potential toxicity and environmental persistence [3]. The BP's Macondo well oil contained approximated 3.9% of PAHs by weight. The DWH oil spill released approximately 2.1×10^7 kg of PAHs into the Gulf of Mexico [4].

In the marine environment, PAHs undergo a number of physical and chemical processes, such as dissolution and volatilization [5], adsorption [6], bioaccumulation [7], biodegradation [7], and photodegradation [8]. Volatilization and photodegradation are important processes affecting the environmental fate and transport of PAHs. Since PAHs can strongly absorb light in the ultraviolet region, photochemical reactions are considered a major abiotic mechanism in degrading PAHs [9]. Zhang et al. [10] found that benzo[a]pyrene can be photodegraded in the presence of TiO₂. Beltran et al. [11] studied the direct UV-photolysis of fluorene,

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phenanthrene, and acenaphthene, and found that the PAHs were completely degraded within 20 min. An and Carraway [12] reported that direct UV-photolysis of phenanthrene and pyrene followed a first-order rate law.

Three primary mechanisms have been proposed for photodegradation of PAHs: (1) direct photoionization or photolysis; (2) energy transfer from an excited PAH triplet state to molecular oxygen; and (3) charge or electron transfer from an excited singlet or triplet PAH state to molecular oxygen [13,14]. Fasnacht and Blough [14] examined the role of oxygen, photoionization, and PAH cation radicals in the photodegradation of nine PAHs, and concluded that the photodegradation proceeded primarily through reaction of O₂ with both excited singlet and triplet states of the PAHs.

Dissolved organic matter (DOM)/humic acid (HA), ionic strength (IS), and pH are known to impact photodegradation of PAHs [15,16]. DOM can influence photodegradation of PAHs in two contrasting ways: accelerating the reaction by stimulating production of hydroxyl radicals or inhibiting the degradation due to the competition of the matrix components for absorption of the radiation [13,16]. de Bruyn et al. [17] observed that the photodegradation rate of phenanthrene decreased by a factor of 5 in the presence of 10 mg/L of HA as TOC (total organic carbon). In contrast, Fasnacht and Blough's [13] reported that photodegradation of anthracene increased by 70% by 5 mg/L of Suwannee River fulvic acid. Clark et al. [15] reported that photodegradation of pyrene doubled as IS increased from 0.001 to 0.1 M.

Corexit EC9500A consists of three nonionic surfactants, namely, sorbitan monooleate (Span 80), sorbitan monooleate polyethoxylate (Tween 80), and sorbitan trioleate polyethoxylate (Tween 85), and an anionic surfactant, sodium dioctyl sulfosuccinate (SDSS) dissolved in a mixture of 1-(2-butoxy-1-methylethoxy)-2-propanol, 1,2-propanediol, and hydrotreated light distillates (petroleum) [18,19]. Researchers have investigated effects of individual surfactants on photodegradation of PAHs. An and Carraway [12] observed enhanced pyrene photolysis and retarded phenanthrene photolysis in a micellar ammonium perfluorooctanoate solution relative to water. Sigman et al. [20] reported that photodegradation of pyrene was inhibited in Brij35 micellar media, where the photolysis quantum yield was halved. However, little is known on the effects of oil dispersants on the photodegradation kinetics, mechanisms, and pathways of PAHs. Moreover, the influences of other factors such as IS, HA, pH, and temperature on PAHs degradation in the presence of oil dispersant have not yet been explored.

The overall goal of this study was to determine effects of a stereotype oil dispersant (Corexit EC9500A) on the volatilization and photochemical degradation rates of pyrene in seawater. The specific objectives were to: (1) investigate effects of the dispersant on the volatilization rate of pyrene in seawater; (2) compare dispersant effects on photodegradation of pyrene under UV and sunlight irradiations; (3) formulate an integrated model to simulate effects of the dispersant on the overall dissipation (volatilization and photodegradation) rate of pyrene; (4) elucidate the mechanisms and pathways of pyrene photodegradation in the presence of the dispersant; and (5) examine effects of IS (or salinity), HA, pH, and temperature on photodegradation of pyrene in dispersant solutions.

2. Materials and methods

2.1. Materials

Seawater was collected from the top 30 cm of the water column at 30.37926/88.30684 (latitudes/longitudes) from Grand Bay, AL, USA in December, 2010. The seawater sample was stored in sealed containers at 4 °C. Before use, the seawater was first

passed through 0.45 μm membrane filters to remove suspended solids, and then sterilized at 121 °C for 35 min via autoclaving. Detailed properties of the seawater have been described elsewhere [21]. In brief, DOM in the seawater was 0.43 mg/L as TOC, and IS was 0.7 M. Six PAHs were detected in the filtered seawater, namely, naphthalene = 0.0019 μg/L, phenanthrene = 0.0029 μg/L, pyrene = 0.0028 μg/L, benzo(b)fluoranthene = 0.0028 μg/L, benzo(a)pyrene = 0.0014 μg/L, and benzo(ghi)perylene = 0.0012 μg/L.

All chemicals used in this study were of analytical grade or higher. Pyrene, 1,4-benzoquinone, *tert*-butanol, and methanol were purchased from Alfa Aesar (Ward Hill, MA, USA). Sodium azide (NaN₃), NaOH, and NaCl were obtained from Fisher Scientific (Fair Lawn, NJ, USA). Acetonitrile (HPLC grade) was purchased from EMD Millipore Corporation (Billerica, MA, USA). HCl was acquired from BDH Aristar (West Chester, PA, USA). Humic acid (sodium salt, 50–60% as HA) was procured from Acros Organics (Morris Plains, NJ, USA). Corexit EC9500A was acquired through the courtesy of Nalco Company (Naperville, IL, USA).

2.2. Experimental apparatus

Batch degradation kinetic tests were carried out in a well controlled glass photo-reactor with a surface area of 78 cm² and a volume of 650 mL. Two types of light sources were employed: (a) UV irradiation using a 4 W UV lamp operated at a wavelength of 253.7 nm; and (b) simulated sunlight using an Oriel Sol1A solar simulator (Newport Corporation, Irvine, CA, USA) with an additional air mass 1.5 global filter installed in the radiation beam to match the spectrum of the 450 W Xenon lamp with the typical solar spectrum. The light intensity was determined to be 7.7 and 257.7 W/m² for UV light and sunlight, respectively, by an optical power meter Model 1916-R. The total UV irradiation intensity was designed to be equal for both light sources, though the UV intensity in the sunlight represents the sum of UVA, UVB, and UVC (wavelength 100–400 nm), whereas the UV light is fixed at 253.7 nm. The light dose is also in accord with the actual solar irradiation (208 W/m²) in the Grand Bay area [22]. Fig. 1 shows the schematic of the experimental set-up. Before each experiment, the lamps were warmed up for 15 min to ensure stable output. A quartz plate was used as the cover without blocking the light.

2.3. Effects of dispersant on volatilization and photodegradation of pyrene

Batch kinetic tests were carried out with the reactor open to the atmosphere under UV or solar irradiation. In each batch, the reactor was filled with 300 mL of a seawater solution (pyrene = 60 μg/L), and stirred gently with a magnetic stirrer to simulate ocean wave actions and maintain uniform pyrene distribution. Control tests (carried out in a closed system in dark) indicated that pyrene loss due to sorption to the reactor walls was negligible. To determine the volatilization rate of pyrene, parallel tests were carried out in dark under otherwise identical conditions. To explore the net photodegradation rates, kinetic tests were also conducted under UV or sunlight with the reactor sealed (no volatilization). During the tests, 1 mL each of the solution was sampled at predetermined times and analyzed for pyrene remaining. To investigate the effects of the dispersant, the tests were conducted in the presence of 0, 18, and 180 mg/L of Corexit EC9500A. All experiments were conducted in duplicate at 22 ± 1 °C.

2.4. Roles of radicals in UV-mediated degradation of pyrene

The formation of oxidative species, such as singlet oxygen (¹O₂), superoxide (O₂^{•-}), and hydroxyl radicals ([•]OH), and their roles in the pyrene degradation processes were investigated in the absence

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