Natural and engineered weathering of spilled oil: Roles of photodegradation, surface ozonation and effects of dispersants

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This presentation summarizes our findings on effects of oil dispersants on the photochemical degradation of oil hydrocarbons, role of natural ozonation in weathering of spilled oil, and engineered photodegradation of dispersed oil.

Large quantities of oil dispersants were applied during the 2010 Deepwater Horizon (DwH) oil spill. This study investigated the effects of Corexit EC9500A on the simulated sunlight-facilitated photodegradation of pyrene (a model oil PAH). The presence of 18 mg/L of Corexit EC9500A increased the first-order reaction rate constant of pyrene from 0.0022 min^{-1} to 0.0063 min^{-1}. The surfactants Span 80 and Tween 85 in Corexit EC9500A were found to play critical roles in facilitating the photodegradation of pyrene. These oil-based surfactants tend to render a vertical concentration gradient in the water column, with the higher concentration in the upper layer. In addition, the surfactants also facilitate production of more reactive radicals and greater light absorption. GC-MS analysis indicated that 1-hydroxypyrene and pyreneuinones are the major photodegradation by-products. Furthermore, the dispersant itself was found to be subject to photodegradation. The information is helpful for assessing the dispersant effects on the photochemical weathering of oil and the environmental fate of oil dispersants.

Ozone is a strong oxidant for oil hydrocarbons, and atmospheric ozone in the Gulf Coast environment is known to affect the health of the ecological systems. However, effects of atmospheric ozone on weathering of spilled oil remained unknown. Using phenanthrene, pyrene, 1-methyfluorene and 9,10-dimethylanthracene as model oil polycyclic aromatic hydrocarbons (PAHs), this work investigated ozonation rates and extents of the PAHs in seawater under simulated atmospheric ozone, and examined effects of an oil dispersant (Corexit EC9500A) on the ozonation process. In all cases, fairly rapid oxidation of the PAHs was observed. For instance, at an air phase ozone concentration of 86 ppb, 200 ppb of 1-methylfluorene or 40 ppb of 10-dimethylanthracene was completely degraded in 22 days. In general, the degradation kinetics followed a two-stage pseudo-first order rate profile, with a slower initial stage followed by a much faster stage. The presence of 18 and 180 mg/L of the dispersant inhibited the phenanthrene and pyrene degradation rates, but enhanced the degradation rates of the methylated PAHs. The ozonation rates decreased with increasing solution pH and temperature, but remained independent of ionic strength. Rapid ozonation rates were also observed for total petroleum hydrocarbons (TPHs) and *n*-alkanes. The results indicate that atmospheric ozonation plays an important role in oil weathering and should be taken into account in assessing fate and environmental impacts of oil spill, and oil dispersants may have complex impacts on the ozonation rate and extent.

To facilitate rapid destruction of persistent oil components (PAHs and large a-alkanes), we prepared a novel composite material, referred to as activated charcoal

supported titanate nanotubes (TNTs@AC), for highly efficient adsorption and photodegradation of oil hydrocarbons. TNTs@AC was prepared through a simple one-step hydrothermal method, and is composed of a hydrophobic core (modified activated charcoal) and a hydrophilic shell (TNTs). The new material showed not only very high adsorption capacity for phenanthrene (a model PAH), but also great photocatalytic activity under UV light, allowing for highly efficient adsorption and photo-degradation of PAHs. TNTs@AC offered a maximum Langmuir adsorption capacity of 12136 μg/g for phenanthrene, which is ~6.7 times higher than that of the parent activated charcoal. Batch kinetic tests showed that >92% of phenanthrene ($C0$=500 μg/L) was rapidly (within 60 min) concentrated on the material at a material dosage of 0.5 g/L, and subsequently, the sorbed PAH was completely photodegraded under UV light within 2 hours, which also serves as a highly efficient regeneration process. The photo-regenerated TNTs@AC can then be reused for another adsorption-photodegradation cycle without significant capacity loss. TNTs@AC performed well over a wide range of pH, ionic strength, and dissolved organic matter. Mechanistically, the enhanced adsorption capacity results from the heterogeneous structure of TNTs@AC and micro-carbon sites on TNTs. Transfer of excited electrons by AC leads to inhibition of recombination of electron-hole pairs excited on the TNTs. The combined high adsorption capacity, photocatalytic activity and regenerability/reusability merit TNTs@AC a very attractive material for concentrating and degrading a host of micro-pollutants, including PAHs, pharmaceuticals and other emerging contaminants.