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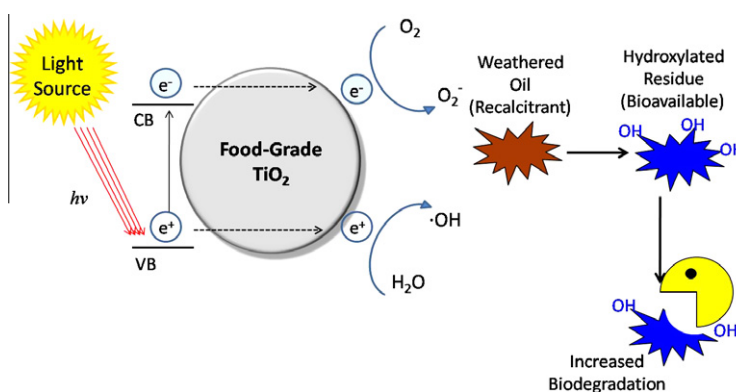
Photocatalytic pre-treatment with food-grade TiO₂ increases the bioavailability and bioremediation potential of weathered oil from the Deepwater Horizon oil spill in the Gulf of Mexico

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HIGHLIGHTS

- ▶ Food-grade TiO₂ has potential as an environmentally benign photocatalyst.
- ▶ Photocatalysis can be used to jump-start oil spill bioremediation.
- ▶ Photocatalytic pre-treatment increased weathered oil solubility and biodegradability.

GRAPHICAL ABSTRACT



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ABSTRACT

Using the 2010 Deepwater Horizon oil spill in the Gulf of Mexico as an impetus, we explored the potential for TiO₂-mediated photocatalytic reactive oxygen species (ROS) generation to increase the bioavailability (solubility) and biodegradability of weathered oil after a spill. Food grade TiO₂, which is FDA approved for use as food additive in the United States, was tested as a photocatalyst for this novel application. Photocatalytic pre-treatment (0.05 wt.% TiO₂, UV irradiation 18 W m⁻², 350–400 nm) for 24 h in a bench top photoreactor increased the soluble organic carbon content of weathered oil by 60%, and enhanced its subsequent biodegradation (measured as O₂ consumption in a respirometer) by 37%. Photocatalytic pre-treatment was also tested outdoors under sunlight illumination, but no significant increase in solubility or biodegradation was observed after 11 d of exposure. Although sunlight irradiation of food-grade TiO₂ generated ROS (assessed by the degradation of 4-chlorophenol as a probe compound), the efficacy of weathered oil pre-treatment was apparently hindered by sinking of the photocatalysts under quiescent conditions and illumination occlusion by the oil. Overall, results indicate that photocatalytic pre-treatment to stimulate bioremediation of weathered oil deserves further consideration, but controlling the buoyancy and surface hydrophobicity of the photocatalysts will be important for future efforts to enable ROS generation in proximity to the target compounds.

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1. Introduction

The oil spill in the Gulf of Mexico in the summer of 2010 was the largest accidental marine release in the petroleum era (Crone and Tolstoy, 2010). With 5 million barrels ($6 \times 10^5 \text{ m}^3$) released into the ocean, the environmental ramifications are significant and potentially long-lasting. For example, two decades after the 1989 Exxon Valdez oil spill in Alaska, some oil contamination remains in the subsurface and protected coves (Boehm et al., 2008). Recovery from such disasters can be slow and some toxic effects may linger for decades (Christen, 1999; Whitfield, 2003). Weathered oil is the non-volatile, persistent hydrocarbon fraction that remains after the light-weight alkanes and monoaromatic hydrocarbons have been biodegraded, volatilized or dispersed, usually within the first few weeks after a spill (Boehm et al., 1982). Whereas natural processes such as dilution, sedimentation, sequestration and biodegradation mitigate to varying extents the long-term effects of weathered oil on aquatic organisms, remedial action is required to alleviate environmental and economic strains in the wake of such releases.

One effective strategy might be the *in situ* application of photocatalysts that can generate reactive oxygen species (ROS) with sunlight illumination to stimulate bioremediation of weathered oil. When illuminated by near-UV radiation ($<400 \text{ nm}$), TiO_2 produces ROS such as hydroxyl radicals that can hydroxylate hydrophobic weathered oil compounds and increase their solubility and bioavailability to the microbial community (Birks, 1970; Turchi and Ollis, 1990; Park and Choi, 2005; Choi et al., 2007; D'Auria et al., 2009; Lee et al., 2011; Keen et al., 2012). The hydrophobicity of weathered oil contributes to its low bioavailability, which increases the time for biodegradation and natural attenuation. Since hydroxylation is often the rate-limiting step in the biodegradation of hydrocarbons (Meng and Zhu, 2010), photocatalytic hydroxylation could increase not only the solubility (and thus bioavailability) of recalcitrant hydrocarbons, but also the rate of subsequent biodegradation and the range of contaminants degraded. Similar approaches involving advanced oxidation pre-treatment have been shown to increase the biodegradability of pharmaceuticals (Keen et al., 2012) and other recalcitrant organics (Scott and Ollis, 1995; Kitis et al., 2000; Li et al., 2011), but our proposed *in situ* application of photocatalyst as a pre-treatment to expedite bioremediation of weathered oil spills is novel.

This paper addresses the opportunities and challenges of TiO_2 addition to enhance *in situ* bioremediation of weathered oil samples from the 2010 Macondo well spill in the Gulf of Mexico. Because application and use of photocatalytic nanomaterials in a natural setting raises questions about potential health and safety risks (Klaine et al., 2008), we used food grade titanium dioxide (FG- TiO_2)—which has been approved by the US FDA as a chemical additive that is safe for human consumption—as a potential photocatalyst. The performance of FG- TiO_2 was compared to the common reference photocatalyst P25 TiO_2 . We believe this to be the first report of the use of FG- TiO_2 as an environmental photocatalytic material.

2. Experimental methods

2.1. Materials

Weathered oil from the Deepwater Horizon oil spill was collected at Barataria Bay, LA, in October of 2010. The hydrocarbon content in this material was reported as 18–30-carbon alkanes with small quantities of polyaromatics (a few $\mu\text{g g}^{-1}$; data reported by Ralph Portier, Professor of Environmental Science at LSU upon delivery of the weathered oil). Large non-oil components (twigs, grass, leaves, etc.) were removed prior to experimental use, but

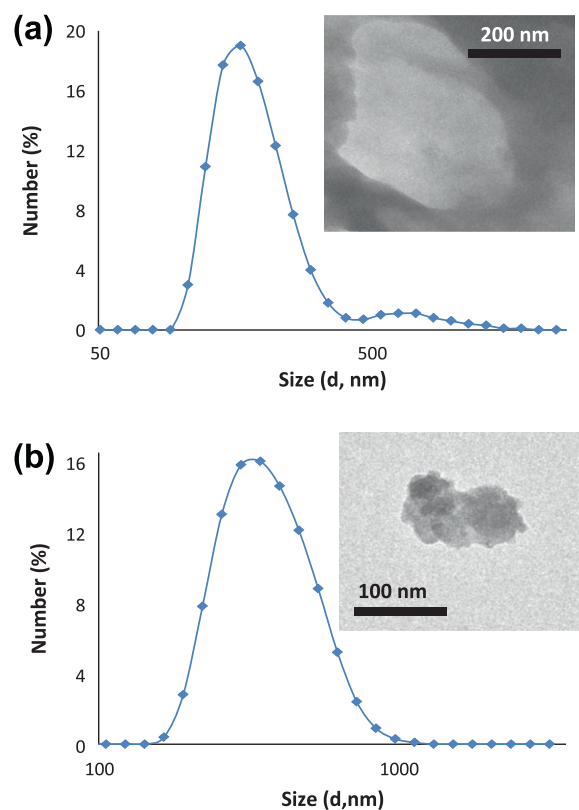


Fig. 1. TEM images of (a) P25 and (b) FG- TiO_2 . DLS and electron microscopy confirm an average particle size of 300 nm for P25 and 100 nm for FG- TiO_2 .

all samples contained some non-oil organic matter—similar to what might be encountered in a natural setting.

FG- TiO_2 was donated by Sensient Technologies (Milwaukee, WI) and used as-provided. P25- TiO_2 for comparison was obtained from Degussa (Parsippany, NJ). Dynamic light scattering (DLS) measurements showed that P25 had an average particle diameter of 220 nm in the aqueous conditions described hereafter, while FG- TiO_2 was slightly larger at 377 nm. These values were confirmed through TEM imaging (Fig. 1) and corresponded to BET surface areas of $3.0 \text{ m}^2 \text{ g}^{-1}$ (P25) and $8.9 \text{ m}^2 \text{ g}^{-1}$ (FG- TiO_2). While the primary particle size for P25 often reported in the literature is smaller (30 nm with $50 \text{ m}^2 \text{ g}^{-1}$ BET surface area (Fan et al., 2011)), unsonicated TiO_2 forms large particles (100–300 nm) made up of smaller ($\sim 30 \text{ nm}$) crystallites (Nair et al., 1993). Materials in this work were used without sonication, hence the larger particle size.

2.2. Photocatalytic tests

Initial photocatalytic tests were performed in a bench-top photoreactor with six 4 W UV lamps (350–400 nm at 18 W m^{-2} , Philips TL4W; see (Lee et al., 2010a)) arranged around a stir plate used to mix samples. For photoreactor tests, 2 g of weathered oil were placed in a quartz reactor vessel with 40 mL Milli-Q water and FG- TiO_2 photocatalyst (0.5 wt.% concentration). These samples were exposed for 24 h to UV irradiation in the photoreactor. After UV exposure, 2-mL aliquots were removed from the water fraction and filtered (Whatman 40 filter paper followed by 0.2- μm PES syringe filter) for dissolved total organic carbon (DOC) analysis. The remainder of the sample was diluted to 100 mL total volume with Milli-Q water and combined with 75 mL activated sludge (obtained from Houston, TX 69th Street wastewater treatment plant) for respirometry analysis.

Additional tests were performed using the same oil and photocatalyst concentrations in uncovered, wide-mouth glass jars under

solar illumination at Rice University (Houston, TX: 29°43'N, 95°23'W). The samples were exposed to sunlight for 11 d to simulate a longer exposure time *in situ*. Irradiation intensity was measured in the visible and UV range (visible: 700–850 W m⁻² [Daystar intensity meter, Las Cruces NM], UV: 12–18 W m⁻² [Fisher UV meter, Fischer Scientific, Waltham MA]). Water was added twice daily to replenish evaporation. Samples were placed on an orbital shaker at 20 rpm to provide slight agitation simulating wave motion in a natural environment. After 11 d samples were removed and DOC/respirometer measurements were made as described above.

2.3. Controls

In addition to dark and no catalyst controls, tests were run to determine the production of ROS under solar irradiation in the absence of weathered oil. Controls were prepared with 50 mL total volume (Milli-Q water, probe compound and scavenger compound, 0.5% photocatalyst), and exposed to sunlight for 1 d (6 h of direct sunlight) under the same conditions as the sunlight test described above. ROS production was measured using 0.1 mM 4-chlorophenol (4CP) as a probe compound and isopropyl alcohol (10% v/v) as an [•]OH scavenger (Sakhivel et al., 2004; Lee et al., 2010b).

2.4. Analytical methods

DOC content of the water fraction was measured to evaluate the ability of photocatalytic pre-treatment to increase weathered oil solubility, and hence bioavailability. DOC was quantified using a Shimadzu TOC-V analyzer (Shimadzu Scientific Instruments, Columbia, MD). To assess the increase in biodegradability, respirometry tests were performed using a PF-8000 respirometer (Respirometry Systems and Applications, Springdale AR). Oxygen consumption was measured as a function of time in continuously stirred, sealed jars held at 25 °C in a water bath with KOH plugs in each sample jar to trap the evolved CO₂ and control pH (Moon and Young, 2005).

3. Results and discussion

3.1. ROS generation activity

Under UV light, both FG-TiO₂ and Degussa P25 TiO₂ degraded 4CP (a hydroxyl radical-sensitive probe compound) equally well, with first-order reaction rate coefficients of 0.06 ± 0.01 (FG-TiO₂),

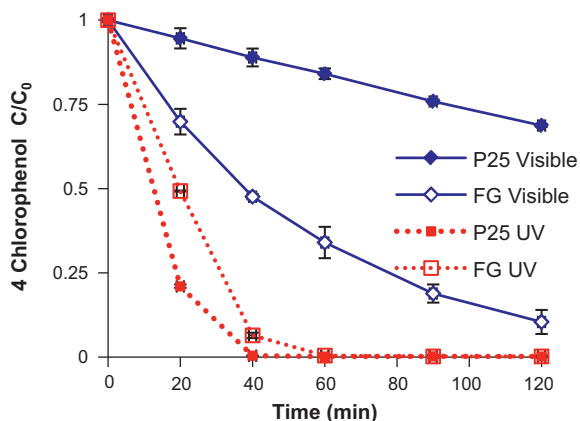


Fig. 2. Comparison of research-grade (P25) and food-grade (FG) nano TiO₂ in degradation of 4-chlorophenol (commonly used as a [•]OH probe, C₀ = 100 μM). Irradiation: visible (400–650 nm) or UV (350–400 nm) in photoreactor. Error bars represent ± one standard error.

and 0.05 ± 0.02 min⁻¹ (P25) (Fig. 2), indicating significant ROS generation. Under visible light (fluorescent lamps with 400 nm cutoff filter) the FG-TiO₂ was significantly (*p* < 0.05) more effective than P25 (first-order rate constants *k*_{FG} = 0.02 ± 2 × 10⁻⁴ versus *k*_{P25} = 0.003 ± 6 × 10⁻⁵ min⁻¹). Degradation of CP in the presence of TiO₂ irradiated by visible light is possible through complexation of the phenols onto the TiO₂ surface followed by direct electron transfer from the phenol to the conduction band of TiO₂, with degradation rates proportional to surface area (Kim and Choi, 2005). However, a comparison of surface area-normalized degradation rate coefficients suggests that other factors, such as differences in phase composition, contributed to the higher visible light efficiency of FG-TiO₂. The surface area-normalized degradation rate coefficient (*k*_i/SA) for FG-TiO₂ was lower than that for P25 when exposed to UV light (*k*_{FG}/SA = 0.68 × 10⁻² min⁻¹ m⁻² versus *k*_{P25}/SA = 1.7 × 10⁻² min⁻¹ m⁻²), but higher than P25 when exposed to visible light (*k*_{FG}/SA = 2.3 × 10⁻³ min⁻¹ m⁻² and *k*_{P25}/SA = 1.0 × 10⁻³ min⁻¹ m⁻²). This discrepancy likely reflects the higher rutile content of FG-TiO₂ (i.e., P25 anatase:rutile = 75:25; FG-TiO₂ anatase:rutile = 60:40 w:w). Although anatase TiO₂ is more photocatalytically active, mixed phases are usually more efficient because they inhibit charge recombination and can extend the excitation wavelength range (Zhang et al., 2010; Shen et al., 2011). Since the bandgap of rutile TiO₂ is 3.1 eV (corresponding to excitation wavelength of 400 nm) while the bandgap of anatase is 3.3 eV (corresponding to excitation wavelength of 375 nm (Linsebigler et al., 1995)), the larger fraction of rutile combined with larger surface area are consistent with the observed higher activity of FG-TiO₂ under visible light irradiation.

3.2. Effect of photocatalytic pre-treatment in photoreactor

A significant increase (*p* < 0.05) in DOC was observed under UV exposure (24 h) in photocatalyst-treated samples relative to controls (Fig. 3a). UV light alone produced a small increase in DOC (from 37 ± 1 to 47 ± 1 mg L⁻¹, a 27% increase), whereas the UV/photocatalyst treatment produced a 125% increase (from 36 ± 1 to 81 ± 1 mg L⁻¹). The photocatalytic treatment resulted in 60% higher DOC than UV alone, indicating that solubility (and bioavailability) of hydrophobic oil compounds could be significantly increased through this approach.

Respirometry tests showed an initial biological response to both UV exposure and photocatalytic treatment. Both samples that were exposed to UV light (with and without FG-TiO₂ photocatalyst) had rapid initial oxygen consumption (first 25 h) compared to dark controls (Fig. 3b). We postulate that this was the result of enhanced solubilization due to photolytic transformation of hydrophobic organics (Plata et al., 2008), as indicated by the increase in DOC in both samples exposed to UV light. BOD exertion after 25 h (Fig. 3b inset) shows biodegradation of the treated sample and the controls over 150 h. The total BOD exerted by the photocatalyst-treated sample was 37% greater than that for the UV-only control. This suggests that photocatalytic pre-treatment was effective at hydroxylating some components of the weathered oil and thereby enhancing their subsequent biodegradability (Turchi and Ollis, 1990; Keen et al., 2012).

The total mass of the oil compounds removed in these short-term experiments was difficult to assess because of the relatively small change in mass and the tendency of the oil to stick to containers, stir bars and other system components. However the DOC increase indicates that the 24-h photocatalytic pre-treatment increased the soluble carbon content by 30–50 mg L⁻¹, which represents a total increase of 0.1–0.2% (1–2 mg soluble carbon g⁻¹ of oil), underscoring the importance of addressing mass-transfer limitations that hinder the bioavailability and biodegradability of weathered oil. Further research is required to determine whether

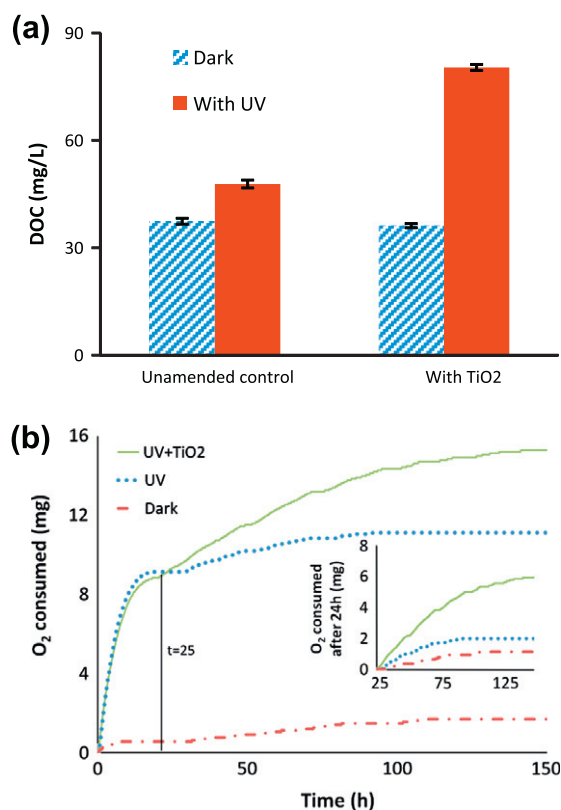


Fig. 3. Photodegradation (a) and subsequent biodegradation (b) of weathered oil samples in a photoreactor (with FG-TiO₂). Respirometry (b) showed significant subsequent biodegradation (per O₂ consumption) in the first 25 h of those samples exposed to UV, followed by increased long-term degradation of the sample treated with UV and FG-TiO₂ (inset, after 25 h). Error bars represent ± one standard error.

the overall increase in biodegradability under similar conditions might be significantly increased if pre-treatment time were increased. For example, assuming an average daily increase in exerted BOD of 0.1% for each day of exposure, this would extrapolate to 36% more BOD exerted (and thus 36% more oil removed) over a 1-yr photocatalytic contact time. This could significantly reduce the duration and cost of bioremediation of weathered oil spills, especially since the photocatalyst is an industrially available food-grade product that could be used in large quantities at relatively low cost and minimal perceived environmental impact.

3.3. Effect of photocatalytic pre-treatment under sunlight

Photocatalytic pre-treatment with FG-TiO₂ for 11 d under sunlight exposure did not significantly increase DOC relative to treatments with visible illumination alone (Fig. 4a). Respirometry tests corroborated no significant difference in biodegradability (Fig. 4b). Insufficient illumination was ruled out as the cause of this lack of enhancement because controls with photocatalyst but without oil efficiently generated ROS (assessed by the degradation of 4-CP as a probe compound) with the same irradiation conditions. Furthermore, ROS generation was extinguished with the addition of a [•]OH-quenching compound (1 mM isopropanol, Fig. 5), indicating that the photocatalyst did produce ROS under solar irradiation.

One probable reason for the inefficacy of these tests was the method of mixing, which affected catalyst sinking and the ability of the generated ROS to interact with floating oil. Unlike the photoreactor tests that were conducted on a stir plate (which provided rapid mixing of the water, photocatalysts and floating oil), less vigorous mixing was used under sunlight exposure (orbital shaker at

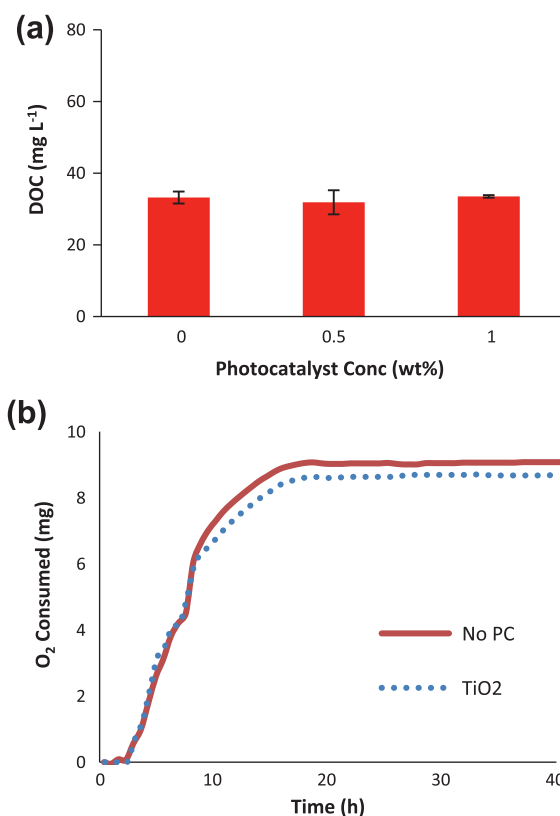


Fig. 4. Lack of enhanced oil solubilization (a) or subsequent biodegradation (b) of weathered oil samples exposed to FG-TiO₂ under sunlight for 11 d. Error bars represent ± one standard error.

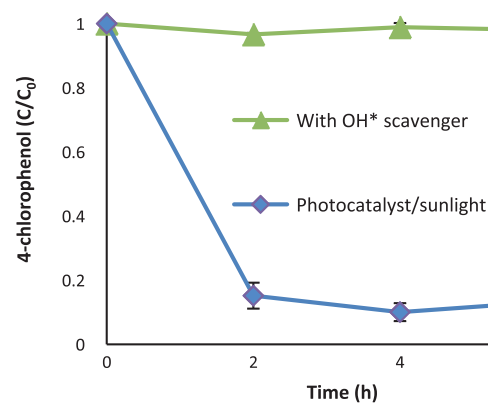


Fig. 5. Demonstration of photo-excitation of FG-TiO₂ photocatalyst under solar radiation. Graph shows the degradation of 4-chlorophenol (C₀ = 100 μM) by FG-TiO₂. Isopropanol (an OH^{*} scavenger) quenched the degradation of the probe compound (no loss due to sorption). Error bars represent ± one standard error.

20 rpm, designed to simulate natural conditions), which resulted in the photocatalysts sinking to the bottom of the reaction vessel. Apparently, any ROS generated by the sinking TiO₂ photocatalyst were too short-lived to diffuse beyond a typical interaction distance of ~1 μm (Tachikawa and Majima, 2009) and react with the oil compounds which were floating on the water surface. This shortcoming suggests the potential benefit of engineering photocatalysts or heterogeneous substrate/photocatalyst systems that are sufficiently buoyant to maintain close proximity with floating oil, while sufficiently hydrophobic to act at the oil–water interface to facilitate interaction with the generated ROS. Such material modifications may be particularly important in saline environments where

high ionic strength could promote coagulation and precipitation of the photocatalyst. For example, photocatalysts modified with hydrophobic coatings remain dispersed within organic target materials and do not lose photo-degradation efficiency after salt addition (Sunada and Heller, 1998).

Overall, this negative result helps delineate potential limitations for *in situ* application of nano-photocatalysts, and provides insight to guide future material development effort (e.g., controlling the buoyancy, hydrophobicity and other surface properties (Duncan et al., 2008) of the photocatalysts) to enable ROS generation in proximity to light hydrophobic compounds. The positive results obtained under better controlled exposure conditions (Fig. 3) encourage further consideration of photocatalytic pre-treatment for enhancing the bioavailability and removal efficiency of hydrophobic organic pollutants in biological treatment reactors.

4. Conclusions

FG TiO₂ nanoparticles were smaller and generated ROS equally or more efficiently than P25 under UV and visible light irradiation. Photocatalytic pre-treatment of weathered oil samples from the Gulf of Mexico using this food grade material in a photoreactor significantly increased dissolved organic carbon content (presumably through hydrocarbon hydroxylation by the generated ROS) and subsequent biodegradation. This dual-step remediation approach may be particularly beneficial for scenarios where the proximity between generated ROS and target organic compounds can be better controlled, as may be the case in modular engineered systems where photoreactors are placed upstream of bioreactors to enhance biodegradation of recalcitrant constituents. Thus, the novel application of a food grade environmental photocatalyst deserves further consideration.

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