Merits and limitations of TiO$_2$-based photocatalytic pretreatment of soils impacted by crude oil for expediting bioremediation

Yu Yang[1], Hassan Javed[1,2], Danning Zhang[1], Deyi Li[3], Roopa Kamath[4], Kevin McVey[4], Kanwartej Sra[4], Pedro J.J. Alvarez (✉)[1]

1 Department of Civil and Environmental Engineering, Rice University, Houston, TX 77005, USA
2 Department of Chemistry, Rice University, Houston, TX 77005, USA
3 Department of Civil and Environmental Engineering, Tongji University, Shanghai 200092, China
4 Chevron Energy Technology Company, Houston, TX 77002, USA

Abstract   Heavy hydrocarbons (HHCs) in soils impacted by crude oil spills are generally recalcitrant to biodegradation due to their low bioavailability and complex chemical structure. In this study, soils were pretreated with varying concentrations of ultraviolet radiation A (UVA) or ultraviolet radiation C (UVC) activated titanium dioxide (TiO$_2$) (1%–5%) under varying moisture conditions (0%–300% water holding capacity (WHC)) to enhance biodegradation of HCCs and shorten remediation timeframes. We demonstrate that pretreatment of impacted soils with UVC-activated TiO$_2$ in soil slurries could enhance bioremediation of HHCs. Total petroleum hydrocarbon (TPH) removal after 24 h exposure to UVC (254 nm and 4.8 mW/cm^2) was (19.1±1.6)% in slurries with 300% WHC and 5 wt-% TiO$_2$. TPH removal was non-selective in the C15-C36 range and increased with moisture content and TiO$_2$ concentration. In a 10-d bioremediation test, TPH removal in treated soil increased to (26.0±0.9)%, compared to (15.4±0.8)% for controls without photocatalytic pre-treatment. Enhanced biodegradation was also confirmed by respirometry. This suggests that addition of UVC-activated TiO$_2$ to soil slurries can transform recalcitrant hydrocarbons into more bioavailable and biodegradable byproducts and increase the rate of subsequent biodegradation. However, similar results were not observed for soils pretreated with UVA activated TiO$_2$. This suggests that activation of TiO$_2$ by sunlight and direct addition of TiO$_2$ to unsaturated soils within landfarming setting may not be a feasible approach. Nevertheless, less than 1% of UVA (7.5 mW/cm^2) or UVC (1.4 mW/cm^2) penetrated beyond 0.3 cm soil depth, indicating that limited light penetration through soil would hinder the ability of TiO$_2$ to enhance soil bioremediation under land farming conditions.

Keywords   TiO$_2$ pretreatment, bioremediation, total petroleum hydrocarbons, ultraviolet

1   Introduction

In the United States, 10–25 million gallons of oil is inadvertently spilled annually during oil production, transportation and storage activities [1]. Of particular concern are on-shore oil spills that can hinder the ability of soil to sustain plant life. Thus, it is important to remediate oil spills and restore the productive capacity of impacted soils.

The lighter and more bioavailable hydrocarbons are generally removed by environmental weathering processes, such as volatilization, biodegradation and dissolution, leaving behind less bioavailable and recalcitrant heavy hydrocarbons (HHCs). Bioremediation techniques such as landfarming and slurry bioreactors are commonly used to remove HHCs in soil [2–4]. However, low bioavailability and recalcitrant chemical structure of these HHCs can result in slow degradation, with remediation timeframes of 2–6 months. Furthermore, in some cases, depending on soil conditions and the nature of the hydrocarbons, soil clean-up standards may not be achieved with bioremediation as a stand-alone technology. Integrating an advanced (photo)oxidation process with bioremediation may be an easily scalable and cost-effective approach to enhance the bioavailability of HHCs and thereby increase treatment rates and processing capacity.

Photocatalysis is a well-known advanced oxidation process that has been widely reported to degrade industrial contaminants and pesticides [5,6]. Among the vast range of photocatalysts used, TiO_2 remains a popular choice as it is relatively inexpensive and earth-abundant, is non-toxic, chemically inert and is an efficient photocatalyst [7,8]. When irradiated with UV radiation ($\lambda < 387$ nm), TiO_2 produces reactive oxygen species (ROS) such as hydroxyl ($\cdot OH$) and superoxide ($\cdot O_2^-$) radicals that can attack a wide variety of organic compounds [5]. Photogenerated holes on the TiO_2 surface can also directly oxidize many types of environmental pollutants [9,10]. Thus, it is plausible that hydroxylation of hydrophobic HHCs or fragmentation into smaller molecules by photocatalytically-generated ROS and holes can increase the bioavailability of HHCs to the soil microbial community for subsequent biodegradation, as shown for many other recalcitrant organic pollutants [5,11–17]. UVC radiation (280–315 nm) is known to efficiently activate TiO_2 to degrade HHCs during advanced oxidation process [18] and can be provided in engineered reactors (e.g., soil slurries), whereas UVA (315–387 nm) constitutes about 95% of UV radiation [19] and would be more suitable for natural systems (e.g., landfarming).

This study investigates the potential for photocatalytic pre-treatment of HHC-impacted soils (using food-grade TiO_2) to enhance TPH removal under exposure to UVA or UVC. The performance of the UVC-activated TiO_2 in a slurry system was evaluated under a wide range of TiO_2 concentrations and soil moisture contents. Ten-day bioremediation experiments following photocatalytic pretreatment using UVC with TiO_2 were conducted and compared to untreated controls to assess the benefits of TiO_2 amendment. TiO_2 pretreatment was also assessed under typical landfarming conditions (60% WHC as soil moisture) using UVA (8.14–9.27 mW/cm²) which accounts for 95% of UV in sunlight and can potentially activate TiO_2 [20,21]. UV penetration through the soil vertical profile was also measured to assess this issue as a potential limiting factor for photocatalytic applications to landfarming.

2 Experimental section

2.1 Materials

Food-grade TiO_2 particles were obtained from American International Chemical. The particles had an average diameter of 328 nm and surface area of 8.88 m²/g. The TPH calibration standard, C8-C40 alkane calibration standard, and dichloromethane (DCM) were purchased from Sigma-Aldrich (St. Louis, MO). Crude-oil-impacted soils were provided by Chevron Energy Technology Company (Houston, TX). These soils were dried in a fume hood, sieved (sieve mesh No. 18) and used for all the experiments. Details on the HHC-impacted soil are

included in the SI (Table S1). Water holding capacity (WHC) of the soil was 0.35 g H_2O/g soil.

2.2 UVC photocatalytic pre-treatment experiments

2.2.1 UVC pretreatment

The photocatalytic tests were performed in a LED-L16 Photoreactor from Luzchem Research Inc. (Ottawa, Canada) equipped with fourteen 7.2 W UVC lamps (254 nm, USHIO G8T5). For these tests, 10 g of impacted soil was added to a glass beaker (250 mL) with predetermined mass of TiO_2 to achieve TiO_2 concentration of 1, 2.5 or 5 wt-%. The required amount (10.5 g) of water was added to achieve a moisture level of 300% WHC to create a slurry. Photocatalytic tests were also setup at three different soil moisture levels (0% WHC, 100% WHC and 300% WHC) for TiO_2 at 5 wt-%. The reactor constituents were mixed to achieve visually uniform distribution of TiO_2 before illuminating the reactors with UVC ((254 nm, 4.2–4.9 mW/cm²)) for 24 h. Moisture in reactors was continually lost to evaporation during photocatalytic treatment and ventilation. Therefore, moisture was adjusted in these slurry reactors every 12 h. Following UVC exposure, TPH analysis was performed by extracting 2 g of dry soil sample with 10 mL DCM as solvent. The solvent was collected after 5 min centrifugation (3000 r/min) and analyzed with GC-FID after filtration (0.2 μm membrane). Untreated soil was processed in the same way and three replicate soil samples were analyzed for each treatment.

2.2.2 Respirometry test

Oxygen consumption by indigenous soil microorganisms in photocatalytically pre-treated soil (and unamended controls) was measured to assess changes in heterotrophic activity as a result of increased HHC bioavailability. Prior to respirometry tests, 24-h pre-treatment with 1, 2.5 and 5 wt-% of TiO_2 under UVC exposure was conducted in the LED-L16 Photoreactor, and soil moisture was adjusted to 300% WHC. Water evaporated during photocatalytic pre-treatment and ventilation, resulting in a moisture content of about 5%–15% WHC. After UVC exposure, 20 g of soil with or without TiO_2 was added to a clean respirometry bottle containing one CO_2 adsorption tube (with 20 pellets of KOH) to attenuate changes in pH and pressure associated with CO_2 evolution. Nutrients (urea and triple superphosphate at 1.06 mg/g of soil and 0.56 mg/g of soil respectively) were added and the soil moisture was adjusted to 60% WHC (Table S1). The bottles were then capped and connected to a PF-8000 aerobic/anaerobic respirometer system (Respirometer Systems and Applications, LLC, Springdale, AK), and oxygen consumption was monitored continuously over 10 d. Residual TPH concentration in soil was analyzed by gas

chromatograph equipped with a flame ionization detector (GC-FID).

2.3 UVA photocatalytic pretreatment

Bioremediation experiments under landfarming conditions were conducted in the LED-L16 Photoreactor with six Hitachi (FL8BL-B) UVA lamps (8.14–9.27 mW/cm^2). Lamp intensities were similar to both measured sunlight intensities using the UVA/B light meter and representative literature values from similar UVA TiO$_2$ irradiation studies [20,22,23].

Three pans containing soil amended with TiO$_2$ at 3 wt-% and three pans with unamended soil were placed in the UV reactor for approximately 12 h each day. After 12-h of UVA exposure, these six soil pans were covered with aluminum foil and stored under ambient temperature conditions. Another set of three pans containing soil amended with TiO$_2$ at 3 wt-% and three pans that were not amended with TiO$_2$ were covered with aluminum foil and placed on bench top under ambient conditions as controls unexposed to UVA irradiation. The water content of soil was adjusted to 60% WHC (0.21 g H$_2$O/g of soil), and urea (1.06 mg/g of soil) and triple superphosphate (0.56 mg/g of soil) were added to soil as nutrients commonly used in landfarming.

In bioremediation experiments that extended for one week, the pans contained 90 g soil. In experiments that extended for eight weeks, the pans contained 100 g soil. For the one-week experiment, tilling and moisture adjustment of soil samples was conducted twice daily, once at the start of exposure and once after 6 h. Soil samples were collected on Day 0 and Day 7 and extracted for TPH analysis. Samples for the eight-week pretreated bioremediation experiment were periodically exposed to UVA (12 h/d) for 2 weeks and then covered with aluminum foil for a 6-week bioremediation period. Soil WHC and applied soil nutrient concentrations were identical to one-week experiments.

During the two-week UVA exposure period, tiling and moisture adjustment of soils was done twice daily, once after 6 h of exposure and once at the end of exposure. Tiling and moisture adjustment during the subsequent six-week bioremediation was conducted in 2–3 d intervals. The soil samples were collected on Day 0, Day 28, and Day 56 and submitted to Dr. Rosa Krajmalnik-Brown's lab in Arizona State University for external validation of TPH analyses.

2.4 Light penetration test

Experiments were conducted in the LED-L16 Photoreactor with 6 Hitachi (FL8BL-B) UVA lamps (7.5 mW/cm^2) or 6 Ushio (G8T5) UVC lamps (1.4 mW/cm^2). UVA light intensity under the dry soil was measured with UV-A/B light meter (Sper Scientific UVA/B lightmeter 850009, calibrated at 365 nm) from Sper Scientific (Scottsdale, AZ)

and UVC light intensity under dry soil was measured with UVX Digital Radiometer from UVP (Upland, CA). Soil was placed in a quartz beaker (50 mL) in lifts of 0.3 cm. Light intensity measurements in triplicate were made at 0.3 cm depth intervals. Before each measurement, the beaker was shaken to redistribute the soil and readjust the soil depths. Light intensity readings were taken following a 3-minute stabilization period. Contribution to light intensity from light penetration along the walls of the quartz beaker was determined by running blank light intensity measurements with the interior bottom surface of the beaker covered with VWR® General-Purpose Laboratory Labeling Tape from VWR International (Radnor, PA). Subsequent light intensity measurements with soils were corrected by subtracting the contribution from side-wall light penetration.

2.5 GC-FID analysis

The solvent extract was analyzed using an Agilent 7290A gas chromatograph equipped with a flame ionization detector and a 30 m × 0.2 mm SPB™-5 column from SUPELCO (St. Louis, MO). For the oven temperature program, the initial oven temperature was 50 °C with a hold time of 1 min; the temperature was then increased to 180 °C at 15 °C/min and hold time was 0 min; then to 320 °C at 30 °C and hold time was 20 min; the total run time was 44 min. Sample injection volume was 2 μL and inlet temperature 280 °C. The carrier gas was He at 1.3 mL/min, the oxidizer was air at 400 mL/min, the fuel gas was H$_2$ at 30 mL/min and the make-up gas was He at 20 mL/min. FID detector was used and detector temperature was set at 320 °C. The TPH calibration standard and C8-C40 alkane calibration standard were applied to determine the concentrations of the total TPH and C8-C40 TPH fractions respectively. Details about TPH analysis method are provided elsewhere [24].

2.6 Statistical analysis

Two-tailed Student's t-test was used to determine whether the difference between the untreated control and the photocatalytically pre-treated samples in UVA landfarming treatments were significant at the 95% confidence level. The analysis was conducted either using SigmaPlot (Systat Software, San Jose, USA) or GraphPad (http://www.graphpad.com/quickcalcs) software.

3 Results and discussion

3.1 UVC pretreatment

3.1.1 Optimization of UVC photocatalytic treatment

Significant removal of TPH ($p < 0.05$) was observed after 24 h UVC exposure of HHC-impacted soils (with an initial

TPH concentration of 9800±474 ppm and soil moisture adjusted to 300% of WHC, representing slurry conditions) that were amended with three different TiO_2 concentrations (Fig. 1). TPH removal was (17.2±3.7)% for 1 wt-%, (18.4±0.5)% for 2.5 wt-% and (19.1±1.6)% for 5 wt-% TiO_2 concentrations. No statistically significant difference in TPH removal at the three TiO_2 concentrations was noted. UVC exposure of unamended soil alone did not significantly decrease the TPH concentration. These results indicate that amending impacted soil with 1 wt-% TiO_2 could be sufficient to partially remove HHCs in soil. However, subsequent photocatalytic treatments were conducted with 5 wt-% TiO_2 to potentially enhance the photocatalytic effect. Optimizing the dose of TiO_2 is critical: low dosages of TiO_2 cannot produce enough ROS to attack contaminants, while too much TiO_2 would block the penetration of UVC to lower depths due to inner filter effect and reduce the oxidation efficiency [5]. However, such effects were not observed at the tested TiO_2 concentrations.

Soil moisture is an important parameter that could impact the performance of TiO_2 pretreatment since water is needed to photocatalytically generate ·OH and facilitate transport [5]. Increasing soil moisture significantly improved TPH removal. Up to (8.0±1.9)% of TPH was removed within 24 h with 5% of TiO_2 in the soil with the soil moisture at 0% WHC, (11.1±0.9)% removal for 100% WHC, and (18.1±5.7)% removal for 300% of WHC.

Photooxidation using TiO_2 at 5 wt-% partially removed almost all molecular weight fractions of TPH (Fig. 2), suggesting nonselective targeting of a broad range of hydrocarbons. The removal of all molecular weight fractions of TPH increased with increasing soil moisture (Fig. S1), which is consistent with the assertion that water is required in the system to generate ·OH [5]. Whereas maintaining super-saturated moisture conditions is easily

accomplished in slurry reactors, this might be challenging under natural conditions due to water percolation and evaporation.

3.1.2 Bioremediation of photocatalytically-pretreated impacted soil

Respirometry tests after photocatalytic pre-treatment showed an increase in oxygen consumption by indigenous microorganisms with increasing (UV-activated) TiO_2 concentration (Fig. 3), indicating greater heterotrophic activity and improved biodegradability. Compared to unamended controls (UVC-irradiated with 0% TiO_2), oxygen consumption after 10 days increased by (36.0±14.1)% for 1% TiO_2, by (43.9±7.9)% for 2.5% TiO_2, by (68.1.0±12.3)% for 5% TiO_2, possibly due to higher biodegradability and greater microbial activity. This suggests that recalcitrant hydrocarbons were transformed into more bioavailable and biodegradable products that are more readily consumed by soil microorganisms. We also quantified residual TPH levels after 10-day of bioremediation, and observed that (26.0±0.9)% of TPH was removed in 5 wt-% TiO_2-amended soil compared to (15.4±0.8)% in the unamended control (Fig. 4). Improved biodegradability was also observed in UVC-exposed unamended soil controls, possibly due to some photolytic transformation of HHCs as observed for other hydrophobic compounds [25]. These results suggest that sequential coupling TiO_2 photocatalysis with bioremediation may improve the removal of HHC from Impacted soils.

Optimizing strategies to combine TiO_2 treatment and bioremediation is important for field application. High concentrations of TiO_2 (e.g., > 1 %) could result in extensive TPH removal, but might exert a negative effect on microbial activity in soil [26]. Lower TiO_2 doses may be preferable since the risk to soil microbial activity is
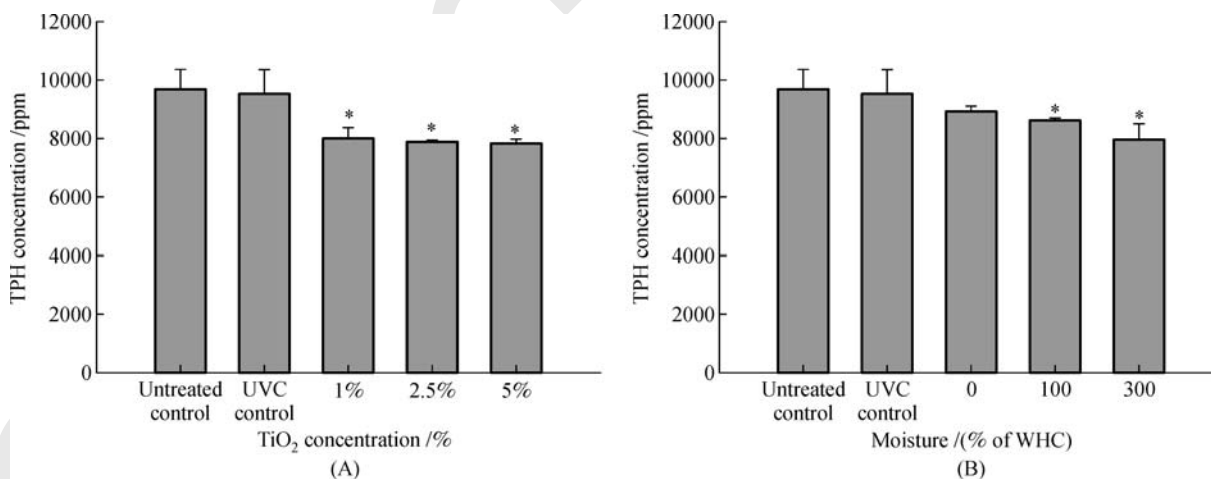

Fig. 1 TPH concentrations under (A) 1 to 5 wt-% of TiO_2 (at 300% of WHC) and at (B) soil moisture with 0%–300% of WHC (5 wt-% of TiO_2) under UVC exposure. Asterisks (*) indicate significant removal compared to the dark control ($p < 0.05$). Error bars represent ± one standard deviation from the mean of triplicate measurements
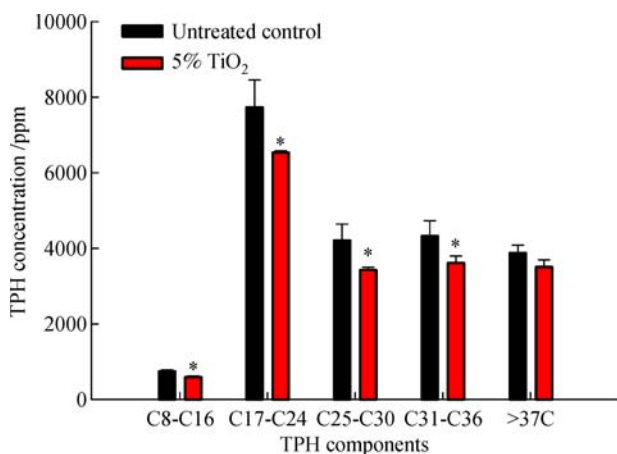
Fig. 2 Different molecular weight fractions of TPH with and without 24-h pretreatment with 5 wt-% TiO₂ under slurry conditions (300% WHC). Asterisks (*) indicate significant increases compared to the control ($p < 0.05$). Error bars represent ±one standard deviation from the mean of triplicate measurements
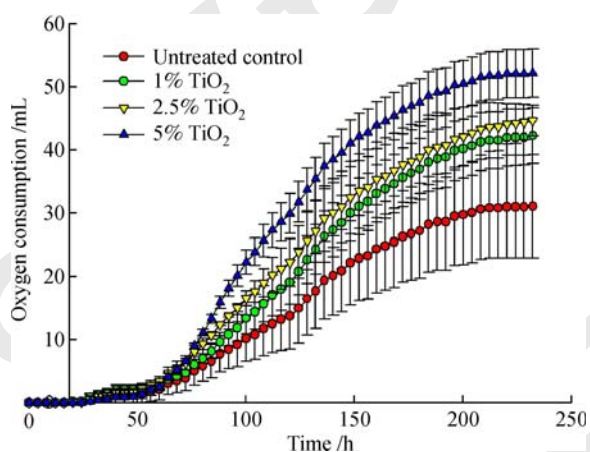

Fig. 4 TPH concentration in untreated control, UVC-irradiated control and UVC-activated TiO₂ in slurries after 10-d bioremediation. UVC irradiation was at 254 nm, 4.2–4.9 mW/cm² for 24 h. Asterisks (*) indicate significant increases compared to the control ($p < 0.05$). Error bars represent ± one standard deviation from the mean of triplicate measurements

Fig. 3 Oxygen consumption in blank and UVC activated TiO₂ pre-treated slurries (1 to 5 wt-%). Error bars represent ± one standard deviation from the mean of triplicate measurements

Fig. 5 TPH removal in 1-week, 4-week and 8-week pan studies

decreased [27,28], and repeated amendment could be applied to enhance TPH removal efficiency. To reduce the cost and balance the benefits of both increased photoactivity without potentially hindering microbial activity, a concentration of 3% TiO₂ was used under simulated landfarming conditions.

3.2 Landfarming conditions

In contrast to the UVC-irradiated slurry treatments, UVA-activated TiO₂ amendment did not significantly remove TPH in soil after one-week of pretreatment under UVA exposure (Fig. 5). Higher photocatalytic activity of TiO₂ under UVC irradiation than UVA has been widely observed [29–31]. Since the one-week experiments may
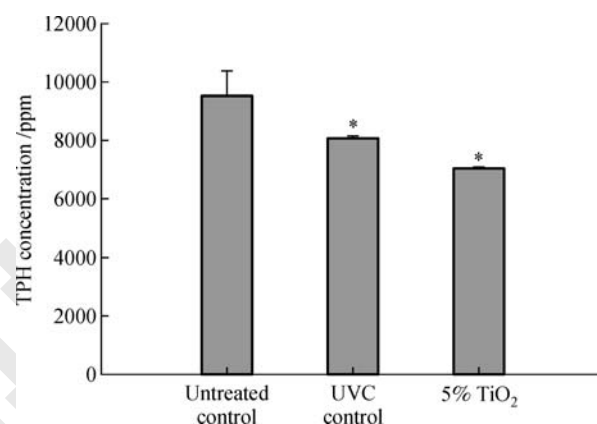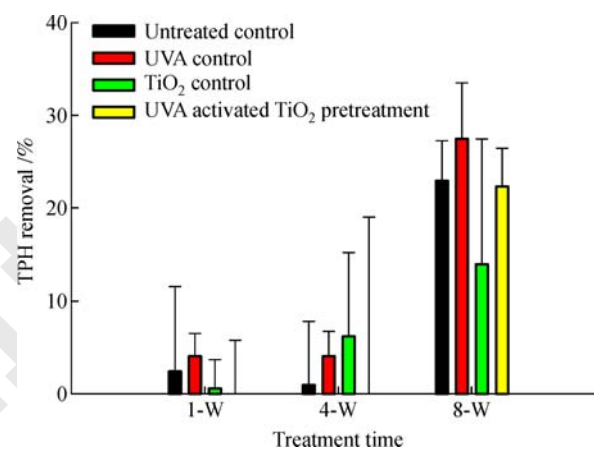
not have provided sufficient time for TiO₂ and bacteria to degrade HHCs, we extended the incubation time and conducted an 8-week pan study (i.e., 2-week 12 h/d UVA exposure followed by a 6-week bioremediation period). However, no statistically significant TPH removal was observed relative to unamended controls, suggesting that landfarming without proper irradiation might not be amenable to photocatalytic enhancement for faster remediation of oil-impacted soil.

Insufficient light penetration was an apparent limiting factor hindering the benefits of TiO₂ pretreatment under landfarming conditions. At a soil depth of 0.3 cm, UVA light intensity decreased by 99.8%, from 7511 to 14 μW/cm², indicating poor UVA light penetration (Figs. 6(A) and 6(C)). Low sensitivity of the photometer at low intensities and small variations in light intensity of lamps after they are turned on/off may account for large error bars. Limited penetration through soil was also
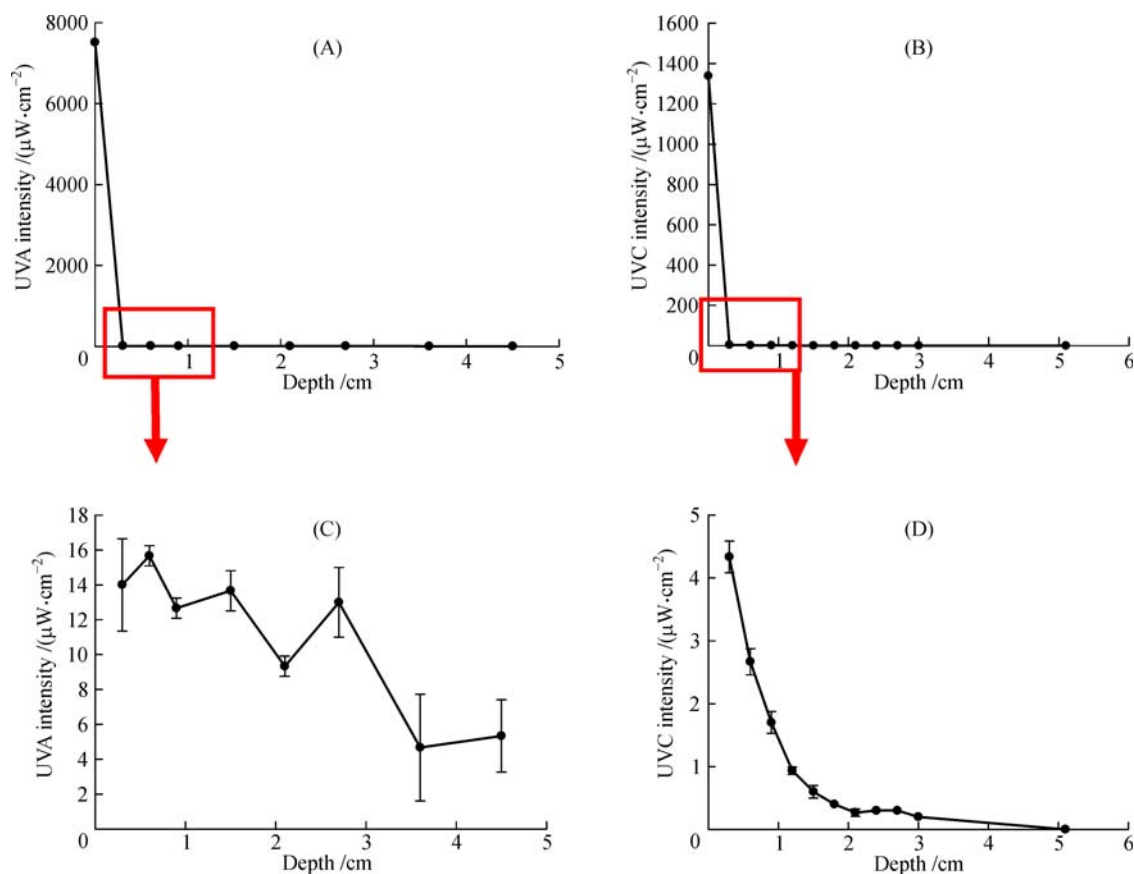
Fig. 6 Penetration of UVA (A and C) or UVC light (B and D) through different depths of dry soil. Irradiation intensities were 7.5 mW/cm^2 for UVA and 1.4 mW/cm^2 for UVC. Error bars represent±one standard deviation from the mean of triplicate measurements

observed for UVC (Figs. 6(B) and 6(D)), and less than 1% of UVC penetrated beyond 0.3 cm soil depth. Note that TiO$_2$ has been reported to photocatalytically degrade a film of hydrocarbons under as little as 1 μW/cm^2 illumination, at a rate of 1 μm/h [32]. Nevertheless, whereas TiO$_2$ can be activated at low UV intensities, insufficient sunlight penetration would likely limit the amount and depth of photocatalytically-treated soil by landfarming.

Photocatalytic pretreatment (using solar irradiation) of soil amended with TiO$_2$ for subsequent soil bioremediation may offer only marginal benefits under landfarming conditions. First, UV light (< 387 nm) constitutes only 4%–5% of the solar spectrum (Fig. 7), and thus light utilization efficiency from solar irradiation is low. Impurity doping, immobilization, surface modification and sensitization have resulted in varying levels of success in enhancing TiO$_2$ activation into the visible-light region [33–35]. Second, only the TiO$_2$ particles that are near the soil surface would be activated by sunlight, so photocatalytic pre-treatment would be effective only in the uppermost layer of the soil [36]. High soil moisture can increase the radiation absorbance and UV utilization in the soil [37]. Frequency of tilling may also be helpful to improve light penetration and enhance the benefits of photocatalytic pre-treatment.
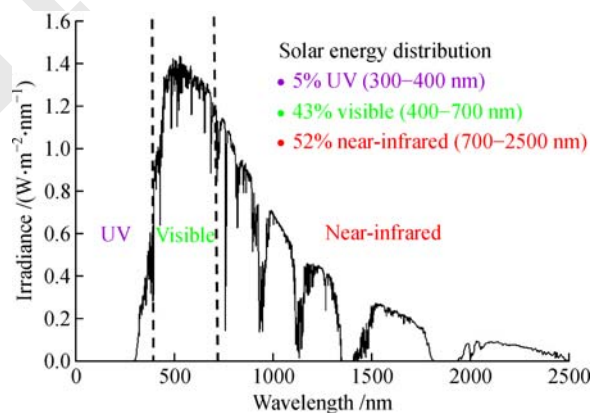

Fig. 7 Solar radiation spectrum. The data were obtained from the National Renewable Energy Laboratory website (http://rredc.nrel.gov/solar/spectra/am1.5/)

4   Conclusions

Sequential coupling of photocatalytic treatment with TiO$_2$ and bioremediation holds promise to effectively remove TPH in impacted soil, if adequate light penetration is achieved. Whereas this might be accomplished in properly

irradiated slurry reactors, insufficient light penetration can be a major limiting factor under landfarming conditions. In our UVC-irradiated slurry reactor, reliable photocatalyzed degradation of TPH (17.2%–19.1%) was achieved and lighter petroleum hydrocarbon molecular weight fractions ($<$ C37) of TPH were significantly reduced within 24 h at all TiO$_2$ concentrations tested. TiO$_2$ photocatalytic activity was improved with increasing soil moisture, possibly reflecting the requirement for increased soil moisture content to generate sufficient hydroxyl radicals and enhance irradiation utilization efficiency. An increase in oxygen consumption by soil slurries after photocatalytic pre-treatment with UVC-activated TiO$_2$ suggests improved TPH biodegradability versus untreated controls. Overall, this study illustrates the potential merits of TiO$_2$ pretreatment in UVC-irradiated slurry reactors to degrade HHCs and enhance subsequent bioremediation, while minimal UVA penetration through soil may preclude the benefits of TiO$_2$ pretreatment under natural (sunlight-irradiated) landfarming conditions.

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