

ENHANCING BIOREMEDIATION OF CRUDE OIL CONTAMINATED SOIL BY COMBINING WITH PHOTOCATALYTIC PROCESS USING TiO₂ AS CATALYST

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Abstract: One of the continuous environmental problems is hydrocarbon contamination caused by the activity of the petroleum industry. Although many contaminated sites were successfully cleaned up by bioremediation treatment, a number of field reports indicated that biological treatment was sometimes found to be very slow or incomplete mineralization occurred. Lack of bioavailability has been identified as one of the important factors that may inhibit a fast and complete degradation process. Enhancement of chemicals biodegradability during chemical oxidation gives a presumption to investigate the ability of combined photo-catalytic process using TiO₂ under sunlight illumination and biodegradation. This study was expected to overcome the limitation of hydrocarbon bioavailability. The experiments were conducted in a reactor made of 25 cm x 15 cm x 10 cm glass pans microcosms by varying TiO₂ concentration from 0.5, 1, 2, to 3% (w/w) and two control reactors: biostimulation and natural attenuation. During the 12-week study, several parameters were analyzed, including the main parameters: TPH gravimetric, heterotrophic bacteria, petrophylic bacteria, and other parameters, such as pH, moisture content, organic carbon, total nitrogen, and UV intensity. The results showed that the addition of photocatalyst TiO₂ was adequately significant in enhancing TPH removal rates. However, the increasing concentration of TiO₂ added to the reactors did not always show proportionality to the increasing of TPH degradation rates. TPH degradation rates were influenced by indigenous petrophylic bacteria activities and energy derived from UV light. The highest TPH degradation rate was found when 2% (w/w) of TiO₂ added.

Keywords: *Bioremediation, Biodegradation, Photocatalytic-TiO₂, TPH*

1. INTRODUCTION

Crude oil contaminated soil affects the environment negatively since hydrocarbon is classified as persistent organic pollutants (POPs) and is able to degrade soils, its ecosystems, and biodiversity. One of the biological treatments to clean up the polluted soils is bioremediation, which is widely used for the last several decades [1]-[5]. Treating oil-contaminated soil using biological process (bioremediation) is basically a matter of biological process application in a solid phase. The limitation of such a process, in most cases, is caused by poor mass transfer and poor contact between the substrate (pollutant) and biomass (bacteria). However, the low bioavailability of the contaminant, not only because of poor mixing but also due to the complexity and solubility of the contaminant resulted in a very slow process of bioremediation. It is common that a bacterial population capable of degrading specific pollutants in the environment very low in concentration. The addition of oxidants, such as hydrogen peroxide

(H₂O₂), will increase the bioavailability of oil-contaminated soil by oxidizing complex hydrocarbons into simpler forms that are going to be easily degraded by bacteria. The term bioavailability according to Maletić et al. [1] refers to the fraction of chemical compounds in the soil that can be utilized or transformed by living organisms. The level of bioavailability of a compound is defined as the ratio between mass transfer and soil biological intrinsic activity. In general, biodegradation of hydrocarbon contaminants in soils shows biphasic behavior [1], [4] which can be explained as follows. In the initial phase of hydrocarbon biodegradation, hydrocarbon removal has a high rate, but allowance is mainly limited by kinetic degradation. In the second phase, the allowance rate is low and is generally limited by slow desorption. Simultaneously, a low bioavailability fraction in hydrocarbon contamination is formed by hydrocarbons which are slowly decayed in the second phase of the bioremediation process kinetics.

Implementation of oxidation technologies in conjunction with biodegradation to degrade

contaminants in crude oil-contaminated soils has not been widely studied. Biodegradability and solubility of contaminants could increase following chemical oxidation of these contaminants such as photocatalytic oxidation [6]. For heavy fraction hydrocarbon, auto-, thermal- or photooxidation could be coupled with biodegradation since these three oxidation mechanisms could oxidize the hydrocarbon partially on the soil surface allowing its solubility in water and also its bioavailability [4].

The enhancement of biodegradability and solubility during chemical oxidation gives a presumption to investigate the ability of combined photocatalytic TiO₂ and biodegradation to overcome the limitation of hydrocarbon bioavailability to indigenous microbes and to enhance TPH removal rates in crude oil contaminated soil bioremediation using landfarming technique. The acceleration of chemical transformation by the presence of a light (light) catalyst is called photocatalysis. The catalyst can accelerate photoreaction through interaction with the substrate during excited conditions. The catalyst will not change at the end of each cycle of catalysis.

In the process of heterogeneous photocatalysis, the catalyst acts as a solid phase and is usually a semiconductor. Semiconductors have a band structure, namely valence band (VB) and conduction band (CB) that have bandgap energy transition (E_{bg}) [7]. The principle of heterogeneous photocatalysis is based on the activation of semiconductor particulate material (CdS, TiO₂, ZnO, etc.) by radiation at the appropriate wavelength (hν). This activation is obtained by the absorption of photons by semiconductor particles that have enough energy (hν ≥ E_{bg}) to conduct conduction or electron migration (e⁻) from VB to CB, forming holes in valence band (h⁺) which will act as an oxidizing place (oxidizing sites) and electrons in the conduction band [7], [8].

The energy produced by UV light is needed by heterogeneous photocatalysis to take place. Without the presence of UV light, photocatalytic oxidation cannot occur. The UV intensity level can have a linear relationship with the rate of degradation because a higher intensity produces more photons and is associated with a higher rate of degradation. However, this correlation is highly dependent on pollutant chemical compounds [9]. According to Fujishima et al. [10], an important aspect of TiO₂ photocatalysis depends on photon energy, but not the intensity. Thus, some photons with sufficient energy can induce a photocatalytic reaction, ie with an intensity of ~ 1 μW/cm² at energies greater than TiO₂ energy band gap.

The kinetic study of the enhanced bioremediation process by combining with photocatalytic process is based on two approaches: (1) the first approach relates

to the factors that influence the number of transformed compounds over a period of time, and (2) an approach that looks for the most appropriate curve to describe and describe compound degradation by microbial culture in laboratory microcosm or in the field [1]. In experiments with samples taken over a sufficient period of time for bioremediation of hydrocarbons, first-order kinetics are used to describe the kinetics of substrate degradation and show the performance of microbes in the soil [1], [3], [11], [12].

2. MATERIALS AND METHODS

2.1 Soil Sample

Soil samples were taken from Minas Oilfields in Sumatra Island wherein crude oil-contaminated soils occurred. The crude oil from Minas Oilfields could be characterized as light oil with API gravity number nearly 34^o. Three locations of crude oil contaminated soil were sampled of which had the same sandy texture based on USDA classification.

2.2 Titanium Dioxide Catalyst

The titanium dioxide catalyst (TiO₂) was a technical grade powder produced by PT. Brataco. TiO₂ had fulfilled USP NF 19 requirement with 99.76% purity.

2.3 Soil Amendment

Some chemicals were added as a soil amendment to increase nutrient concentrations and adjust pH to maintain it at a neutral level. The nutrients used were urea (46% N) and TSP fertilizers (21.52% P) while the pH adjustment used lime (Ca(OH)₂) and dolomite (CaMg(CO₃)₂).

2.4 Experimental Designs in Soil Microcosms

Initial physical, chemical, and biological soil characteristics were conducted following the standard methods as described below. Soil preparation was initiated by air-drying the soil without subjected it directly to sunlight exposure for several days. The aggregated soils were crushed to improve the drying process. Disturbing materials, such as wood branch, stone, and leaves were removed. After being dried, the soils were passed to 2-mm sieves. The retained soils were crushed more and sieved again. Then, the soils were homogenized by mixing them until petroleum hydrocarbons were assumed to have the same concentration within the soils. The prepared soil samples were shown in figure 1.



Fig 1. Prepared Soil Samples

For each of the three soil samples as replication, 1000 g was placed into a 25 cm x 15 cm x 10 cm glass pan as a landfarming batch reactor. Soil microcosms in the pans were covered to prevent volatilization and contamination and were kept in room temperature. However, this soil preparation might alter the initial soil characteristics as shown in Table 2. Therefore, the TPH concentration showing in the result part was the TPH concentration after soil preparation (t_0).

Three types of treatment with 3 (three) replicates were carried out where the water content was maintained at 40-80% water holding capacity [13]. The treatments were shown in figure 2 and could be described in the following procedures:

- Natural attenuation: the utilized natural ability of soil to degrade contaminant. There was no nutrient and catalyst applied, but tilled once a week and added water if required. This treatment behaved as a control reactor.
- Biostimulation: nutrients were added to enhance natural biodegradation. C/N ratio was maintained at the optimum condition of 100-300:10 during the study [3]. The soils were tilled twice a week and the initial pH was adjusted to an optimum range of pH 6-8. This reactor also served as a control reactor.
- Combined biodegradation and photocatalytic using TiO_2 as a catalyst: at the beginning of experiments (T_0), nutrients at the same concentration as above and varying TiO_2 concentration from 0,5, 1, 2, and 3 % wt. were added to each pan. The soils were illuminated under sunlight in sunny days to activate the catalyst. After that, each reactor was covered so that there was no other light penetrated to the pans. The soils were aerated by tilling them two to three times a week. Levels of pH and nutrients were also maintained during the experiments.

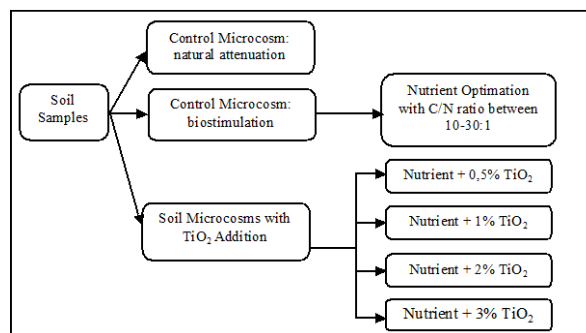


Fig 2. Soil Microcosms Treatment

2.5 Analytical Methods

Monitoring throughout the study was conducted to ensure bioremediation performance. The analytical and instrumental methods used are shown in Table 1. The soil sample was collected compositely in five different points (random sampling) using a spatula to reach the bottom part of each reactor.

Table 1 Analytical and instrumental methods

Parameter	Analytical / Instrumental Methods
Temperature	Thermometer
pH	EPA Method 9045D: soil dan waste pH
Water content	SNI 03-1965-1990
NO ₂ -N	EPA Method 354.1: Diazotasi Reaction Method – Spectrophotometry
NO ₃ -N	EPA Method 352.1: Brusin Method – Spectrophotometry
Total Nitrogen Kjeldahl = N-organic + NH ₃	APHA Method 4500-N _{org} : Macro-Kjeldahl Method
Total phosphorus (P)	APHA Method 4500-P: Stannous Chloride Method
C-organic	Walkley & Black Method
Total Petroleum Hydrocarbon (TPH) - Gravimetric	EPA SW-846 Method 9071B; followed by APHA Method 5520: Hydrocarbon
Heterotrophic bacteria	EPA <i>Standard Method</i> 9215B: <i>Heterotrophic Plate Count</i> (HPC) or <i>Total Plate Count</i> (TPC)
Petrophilic bacteria	Modified EPA <i>Standard Method</i> 9215B
UV intensity	UVX Radiometer
Particle size distribution	Sieve analysis

Parameter	Analytical / Instrumental Methods
Water-holding capacity (WHC)	Water was added to saturate soil samples and left for 24 hours until drained. The remained water was measured as WHC

3. RESULTS AND DISCUSSION

3.1 Soil Characterization

Table 2 shows the initial hydrocarbon contaminated soil characteristics used in the study. According to particle size distribution (PSD) analysis, all the soil samples could be classified as sandy soil. All these three soils were poorly-graded ($C_u < 6$) indicated that the soils had quite low permeability. Permeability refers to the ease of water to flow in porous media. The higher the permeability of the soil, it can be expected that the higher amount of water will be retained. Therefore, the water-holding capacity of the soil decreases.

Based on these soil characteristics, the TPH concentration of the soil samples varied from 2.6 – 5.2%. The populations of indigenous heterotrophic and petrophylic bacteria were less than 10^4 CFU/gram that indicated the number of the bacterial consortium were low since the environment condition was not favorable for growth. Slightly acidic pH, low water content, and low concentrations of N and P were other possible environmental factors affecting a low number of bacteria in the soils.

Table 2 Initial Soil Characteristics

Parameter	Soil Samples
Particle size distribution	Sandy Soil
Uniformity coefficient, C_u	2.623-5.567
pH	4.93-5.96
Temperature, °C	26
Water holding capacity (%)	26-30
Water content (%)	0.64-1.76
C-organic (mg/kg)	24084.21-34494.02
Total N (mg/kg)	903.83-1042.04
Total P (mg/kg)	5.14-7.11
C:N:P ratio	3638:137:1 - 6711:194:1
TPH gravimetric (% , w/w)	2.6 – 5.2
Heterotrophic bacteria (CFU/g)	$36 \times 10^1 - 45 \times 10^2$
Petrophylic bacteria (CFU/g)	$49 \times 10^1 - 11 \times 10^2$

3.2 TPH Degradation in Soil Microcosms

Enhancing the bioremediation of crude oil contaminated soil was done by the combination of biodegradation and photocatalytic TiO_2 . In this study, the experiment was applied and observed for 12 weeks. The average TPH removal for all treatments in soil microcosm reactors is shown in Figure 3. It can be seen that primarily TPH degradation in all soil microcosms occurred significantly in the first 3 weeks of which soil microcosms containing TiO_2 demonstrated a better removal rate when compared to natural attenuation and bioaugmentation.

Soil microcosms with TiO_2 content of 0.5% and 2% were found to have the best removal efficiency in the first week as demonstrated in one of the soil microcosm replications that TPH was reduced from 5.1% to 1.7% and 4.1% to 1.7% respectively (67% and 59% removal efficiency). This phenomenon might indicate that the photocatalytic process occurred first and subsequently was continued by TPH utilization by microorganisms as a carbon and energy source for growth. The photocatalytic process increased significantly dissolved organic carbon content and subsequent biodegradation [6].

The decreasing of photocatalytic rates after a few weeks were influenced by relative humidity in which water molecule may compete with contaminant particles to be absorbed to photocatalysts surface when the water content is excessive [14]. Excessive water content might increase the thickness of the water interface on the catalysts surface preventing the contact between contaminants and TiO_2 .

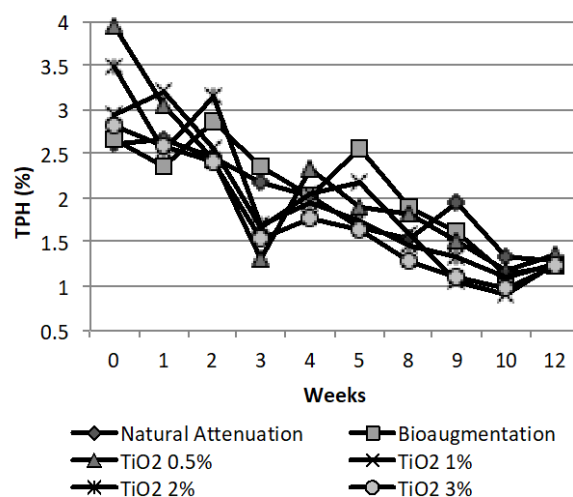


Fig. 3 Average of TPH degradation pattern in soil microcosm reactor

3.3 Effects of Catalysts Concentration

Kinetic modeling was performed to estimate the rates of photocatalytic and biodegradation processes in the studied systems. The experimental results of this study followed pseudo-first-order kinetics as also described by other authors [1], [3], [7], [12], [15]. TPH removal rates r and half-life $t_{1/2}$ of these three replicates of soil microcosms are shown in Table 3. It was found that the highest TPH degradation rate, r (%.week⁻¹) was approximately 0.114±0.023%/week and occurred when 2% (w/w) of TiO₂ was added. Although the portion of TPH degradation due to the photocatalytic process could not be identified in this study, it was definitely proved that the addition of TiO₂ as a catalyst would increase the overall degradation rate.

Table 3 The value of r (%.week⁻¹) and $t_{1/2}$ (week) of soil microcosms

Variation	Kinetics	
	r	$t_{1/2}$
Natural attenuation	0.055±0.005	12.73±0.98
Biostimulation	0.067±0.010	10.50±1.39
Nutrient + TiO ₂ 0.5 %	0.088±0.010	6.70±2.26
Nutrient + TiO ₂ 1 %	0.108±0.032	6.77±1.79
Nutrient + TiO ₂ 2 %	0.114±0.023	6.20±1.13
Nutrient + TiO ₂ 3 %	0.096±0.018	7.37±1.40

It can be seen From Table 3 that the addition of nutrients solely in biostimulation did not significantly enhance the removal rates of TPH compared to natural attenuation. On the other hand, the addition of photocatalyst in all soils with various TiO₂ concentrations were able to enhance TPH removal rates adequately significant and reached as twice as the rates in biostimulation. Interestingly, the variation of TiO₂ concentration from 0.5 to 3% (w/w) did not always show proportionality to TPH degradation rates. This fact was not in agreement with Chien et al. [16] stating that photocatalytic degradation of organic contaminants was improved as TiO₂ concentration increased, which was likely due to the increase of active sites for photocatalysis. According to Haque et al. [7], in the beginning, photocatalysis rate was proportional to photocatalyst concentration, yet at a certain level of concentration, the rates would decline and become independent of the concentration. The proportionality of TiO₂ concentration to the TPH degradation rate was only valid until particular concentration and might be slowing down in higher concentration [17], [18].

3.4 Microbial Populations vs TPH Degradation

The microbial growth pattern indicated that microbes are able to utilize hydrocarbon as an energy source and carbon source. Figure 4 shows the correlation between TPH and microorganisms in soil microcosms at the optimum TPH that occurred when 2% of TiO₂ were added. The lag phase was occurred very rapidly, continued by the exponential phase, stationer phase (which also took place very quickly), and followed by the death phase within 12 weeks. Nutrients addition at the beginning of experiments and routine tilling and also watering had stimulated the microbial growth. However, the increase of microbial populations should not be only directly related to a significant decrease in TPH concentrations. The decreased of microbial populations during the study was affected by environmental factors, such as pH, nutrient limiting, or the presence of toxic metabolite products that inhibit the growth.

As explained above, the highest TPH removal was demonstrated in soil microcosm where 2% TiO₂ added. It gave high TPH removal in the first week despite the fact that petrophylic bacteria just started growing from 10⁴ to 10⁶ CFU/g. This indicated that photocatalytic reactions occurred dominantly. As time went by, the catalyst surface became saturated, both by water and contaminant particles. As a result, the TPH degradation seemed to be dominated by the ability of bacteria petrophylic consortium to utilize TPH as a carbon source for growth as shown in Figure 4.

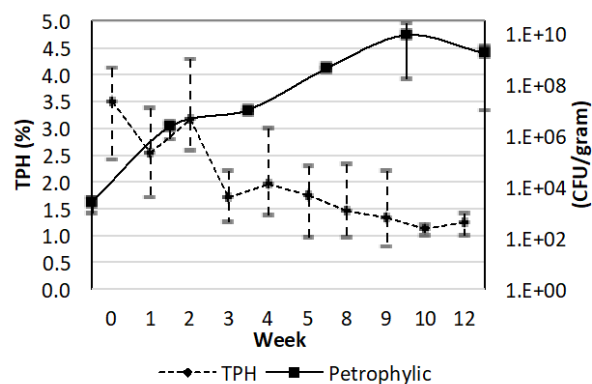


Fig. 4 Correlation between TPH and petrophylic bacteria in soil microcosm with 2% TiO₂

The growth of bacteria reached its peak in week 12 and followed by insignificant TPH reduction. This was due to the lack of contaminant bioavailability and the toxic residues of contaminants after the previous degradation. The lack of bioavailability might be affected by the weathered soils and, therefore, influences the sorption-desorption process.

Contaminants molecule might become smaller than bacteria sizes after being attacked by photocatalyst, and thus, were absorbed to inaccessible regions [19]. In general, the results demonstrated the ability of consortium indigenous petrophilic bacteria to degrade TPH (in conjunction with photocatalysis) as indicated by their presence and growth in soil microcosms.

3.5 Effect Of C/N Ratio

Nutrients commonly added to soil in the bioremediation process are nitrogen and phosphorus because the amount of these substances is usually limited in the TPH contaminated soil. Many bioremediation processes show that the addition of nitrogen and phosphorus can stimulate biodegradation. The amount added to the soil is usually referred to as C-N ratio. Zhou and Crawford [19] reported that the optimum C-N ratio at a value of 50:1 for biodegradation of oil in clay soil. Meanwhile, United State Environmental Protection Agency (USEPA) [20] suggested a C-N ratio in the range of 10:1 to 100:1 for bioremediation of petroleum hydrocarbons from leakage underground storage tanks (UST).

Basing nitrogen augmentation in hydrocarbon contaminated soils solely on C:N ratios is problematic. Because optimal C:N ratios are dependent on contaminant concentrations, their use can lead to over-fertilization in heavily contaminated soils [21]. Figure 5 shows that during the bioremediation process in soil microcosms, the C/N ratio could be maintained under optimum condition between 10:1 to 25:1. Since the carbon source used for petrophilic growth was from TPH, the decrease of TPH resulted in the reduction of C/N ratio. The addition of TiO₂ had no direct effect on the C/N ratio in soil microcosms, but for some extent, the presence of TiO₂ might involve in the nitrogen fixation process [22]. This process might result in readily available nitrogen for bacterial growth.

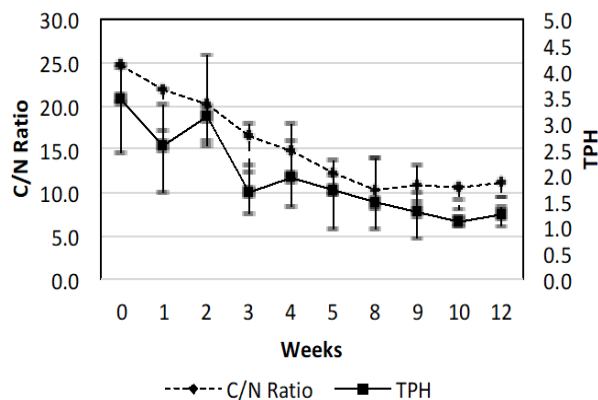


Fig. 5 Correlation between TPH Degradation and C/N Ratio in soil microcosm with 2% TiO₂

3.6 Profile Of Soil pH

As a semiconductor, TiO₂ has amphoteric properties. It can be protonated (becomes positively charged) in acidic pH < 6.8 and deprotonated (becomes negatively charged) in alkaline pH > 6.8 [7], [16]. One essential parameter that contributes to surface-charge in photocatalysis is pH. Zhang et al. [23] stated that because of the amphoteric behavior of most semiconductor oxides, an important parameter in the reaction taking place on semiconductor particle surfaces is the pH of the dispersions since it influences the surface charge properties of the photocatalyst. The TiO₂ surface is positively charged in acidic media (pH<6.8) whereas it is negatively charged under alkaline conditions (pH>6.8) as evidenced by zeta potential measurements [23].

In this combined system, pH played an important role because it also supports indigenous bacterial growth. The correlation between pH level and TPH reduction during the experiments is shown in Figure 6. The average pH level in soil microcosm with TiO₂ 2% was around 6.6-7.9. The pH level of each soil is able to support both bacterial growth and degradation, though several treatments have a pH more than the maximum of optimal range 5.5-8.8 for growth and 6.5-8.0 for hydrocarbon biodegradation [13].

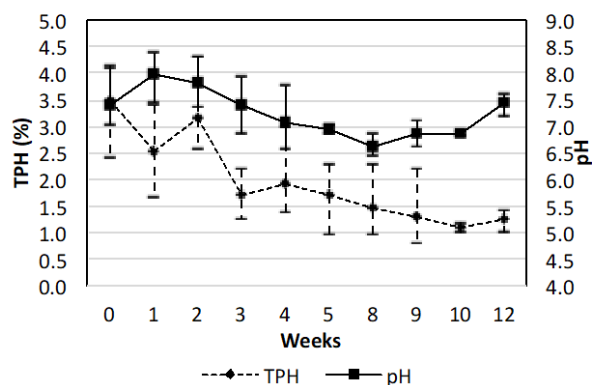


Fig. 6 Correlation between TPH Degradation and pH in soil microcosm with 2% TiO₂

As mentioned before that it was most likely that photocatalytic dominated the process in the first week when the pH of soil microcosm was above 7.0. Degradation rates in acidic or alkaline pH levels can be attributed to the orientation of molecular structure which is more preferable to be attacked by photocatalyst. The preferential pH level of the photocatalytic process of hydrocarbon in the

treatments which gave high TPH degradation rates and removal was found under alkaline condition ($\text{pH} > 6.8$). According to Ahmed et al. [24], pH can influence the formation of radical hydroxyls by the reaction between hydroxide ions and holes on the surface of TiO_2 . Hydroxyl radical is a species that is dominant at neutral pH or higher. Thus, a higher pH value results in higher degradation efficiency. The decreasing pH level during the study indicated the occurring biodegradation by producing carboxylic acid [4] making TPH degradation slowed down afterward.

3.7 Effects Of Sunlight Irradiation

In this study, sunlight was used as a UV source to activate TiO_2 . It was based on the fact that sunlight produces UV-A and UV-B that can reach the earth atmosphere and have wavelength λ at around 400-320 nm and 320-290 nm, consecutively. The effect of UV intensity on TPH removal efficiency in this study is shown in Figure 5. TiO_2 is activated by the energy of 3.2 eV or at the wavelength < 387 nm with a minimal intensity of $\sim 1 \mu\text{W}/\text{cm}^2$ [10]. Therefore, the sunlight irradiation which had occurred for 12 weeks (24 sunny days) with a total of 72 hours exposure with the average intensity of $109 \mu\text{W}/\text{cm}^2$ at $\lambda = 365$ nm was able to activate TiO_2 . Therefore, these measurement results indicated the occurrence of photocatalytic reaction in soil microcosm.

For some extent, it could be seen that UV light played an important role in activating TiO_2 and thus enhanced TPH removal. As shown in Figure 7, however, UV intensity level at a certain wavelength measured did not significantly affect TPH removal because TiO_2 can only be activated to produce hydroxyl radical with enough energy [25].

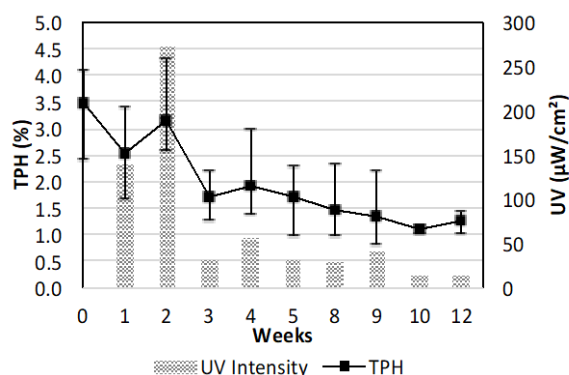


Fig. 7 Correlation between TPH Degradation and UV Intensity in soil microcosm with 2% TiO_2

Since the soil microcosm reactor was aimed to mimic the landfarming process, the soil depth was maintained at around 8-10 cm. Hamerski et al. [17] stated that systematic tilling and humidification could distribute the photocatalyst evenly in the soil. However, the photocatalytic only took place in the soil surface due to the inability of sunlight to penetrate further to soil depth. Osborn [9] also stated that the correlation between UV intensity and degradation rate also depended on pollutant chemicals.

4. CONCLUSION

This study demonstrated a possibility of combining chemical oxidation (photocatalytic TiO_2 under sunlight irradiation) and biodegradation to improve TPH degradation in crude oil contaminated soil bioremediation using landfarming technique. The results indicated that the addition of photocatalyst was able to enhance TPH removal rates compared to biostimulation solely. However, the increasing rates were not always proportional to the increase in TiO_2 concentration. The degradation process was influenced by the indigenous microbial activity and energy derived from UV light but was not affected significantly by UV intensity. The highest TPH degradation rate was given by soil microcosm where 2% TiO_2 concentration was added.

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