

## APPLICATION OF UV/TiO<sub>2</sub> ADVANCED OXIDATION IN TREATING OILY COMPOST LEACHATE GENERATED DURING OILY SLUDGE COMPOSTING

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In this work, oily compost leachate (OCL) generated during oily sludge composting was treated by UV/TiO<sub>2</sub>. OCL subsamples, gathered bi-weekly from the composting process, were thoroughly mixed and then filtered to reduce the solution turbidity. The effects of initial chemical oxygen demand (COD) concentration, UV type (A and C), pH (3, 7, and 11), reaction time (30, 60, 90, and 120 min), and TiO<sub>2</sub> concentration (0.5, 1, and 2 g L<sup>-1</sup>) on the total petroleum hydrocarbons (TPH) and COD removal from OLC were examined. The results showed that the efficiency of the process improved with the increase in TiO<sub>2</sub> concentration and reaction time and the decrease in pH and pollutant concentration. In the optimal conditions (UV-C, TiO<sub>2</sub> concentration of 1 mg L<sup>-1</sup>, reaction time of 90 min, and pH of 3), 52.29% of TPH was removed. Moreover, 36.69 and 48.3% of TPH was reduced by UV-A/TiO<sub>2</sub> and UV-C/TiO<sub>2</sub>, respectively in real conditions of OCL (pH = 6.3, COD = 1501.24 mg L<sup>-1</sup>, and TPH = 170.12 mg L<sup>-1</sup>) during the 90 min reaction time. The study verified that UV/TiO<sub>2</sub> has the potential to be applied to treat OCL.

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## 1. INTRODUCTION

Storage tank bottom sludge contains huge quantities of total petroleum hydrocarbons (TPH) which severely threaten both public health and the environment [1, 2]. Hence, like any other oily sludge, it should be well purified before being discharged into the environment [3, 4]. In this regard, composting has been introduced as one of the most effective measures for treating this kind of waste [5, 6]. Nonetheless, this method is accompanied by the generation of a great deal of oily compost leachate (OCL). Since this kind of pollution can pose a major threat to both the environment and human health, it should be treated accordingly. OCL treatment is a very broad process as it contains varying amounts of petroleum compounds and other pollutants [7]. A variety of treatment methods can be used to minimize or avoid the adverse effects of this oily pollutant and, among them, advanced oxidation processes have been widely used to degrade a range of organic contaminants such as oily compounds [8-10].

Within this framework, photocatalytic oxidation by TiO<sub>2</sub> (UV/TiO<sub>2</sub>) is one of the most effective technologies [11, 12]. UV/TiO<sub>2</sub> has some prominent advantages including non-toxicity, cheapness, easy operation, and high stability [11]. Thus, many organic contaminants can be degraded via the application of TiO<sub>2</sub> in heterogeneous photocatalysis [12, 13]. In this process, pollutants are degraded through two main pathways: (1) OH radicals produced from valence holes, and (2) direct valence hole oxidation [14, 15]. Some variables like photocatalyst type, photocatalyst loading, target compound loading, initial pH value, and wavelength can highly influence the performance of the process. Hence, these variables should be taken into account seriously in studies performed regarding removal of target contaminants by this process [16].

To the best of our knowledge, limited information is available on the photocatalytic oxidation of OCL containing high levels of TPH. Therefore, we utilized the UV/TiO<sub>2</sub> process for the removal of chemical oxygen demand (COD) and TPH from OCL generated during oily sludge composting. Moreover, the effects of parameters such as UV type, TiO<sub>2</sub> loading, and pH on the performance of the process were investigated.

## 2. MATERIALS AND METHODS

### 2.1. Experimental design and operation of composting experiments

In this study, the OCL was taken from the two-phase composting systems used in our previous studies. These composting experiments were operated under different conditions being amendment type, mixing ratios, and aeration rates, all of which were reported in our previously published articles [17-22]. The compost leachate generated during the composting process was gathered bi-weekly over 16 weeks. Next, all the subsamples of equal volume (500 mL) were thoroughly mixed to form one composite mixture (pH = 6.3, COD = 1501.24 mg L<sup>-1</sup>, and TPH = 170.12 mg L<sup>-1</sup>) and then filtered to reduce the solution turbidity.

### 2.2. Chemicals and materials

Titanium dioxide (Sigma Aldrich, Germany) with a diameter of <50 nm and a purity of 99.5% was utilized as a photocatalyst (Fig.1). A stock solution was prepared and stored at 4 °C until use, with working solutions prepared daily from it.

### 2.3. Photocatalytic experiments

Fig. 2 presents an image of the 10-L batch photocatalytic reactor used in the present study. The reactor was equipped with two lamps being UV-A (Philips, 8 W, 352 nm) and UV-C (Philips, 8 W, 253.7 nm) which were vertically inserted at the center, placed inside a quartz tube. To mix the solution effectively, a magnetic stirrer (500 rpm) was applied. The temperature was kept at 25 °C. TiO<sub>2</sub> at concentrations of 0.5, 1, and 2 g L<sup>-1</sup> were added to the reactor containing 8 L of OCL. Next, the pH of the solution was adjusted to 3, 7, and 11 by adding H<sub>2</sub>SO<sub>4</sub> (1.0 N) and NaOH (1.0 N) as required. Moreover, the UV lamps were allowed to stabilize for at least 10 min prior to irradiation. After specific time intervals, samples were gathered from the reactor and stored at 4 °C until analysis. Prior to the analysis, the TiO<sub>2</sub> particles were separated from the reacted water through filtering of the samples.

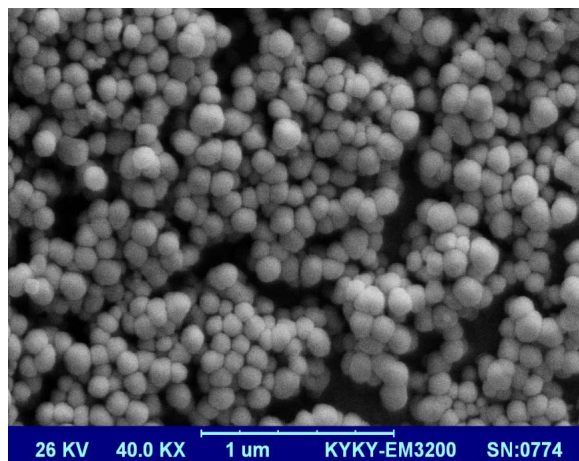


Fig.1. SEM photo of the TiO<sub>2</sub> used in the present study



Fig. 2. Experimental pilot used in the present study

#### 2.4. Analytical methods

The pH values were detected using a pH meter (JENWAY model 3510). COD was measured according to standard methods [23]. TPH was extracted with n-

pentane and quantified in a gas chromatograph (VARIAN Model CP-3800) equipped with a flame ionization detector [24] as follows: the extract was injected into a gas chromatograph to detect petroleum compounds in the range between C<sub>6</sub> and C<sub>35</sub>. A capillary column (CP-Sil 8CB) of 30 m length, 0.32 mm internal diameter, and 0.25 μm film thickness was utilized. The initial temperature was kept at 35 °C for 2 min and then increased at a rate of 10 °C min<sup>-1</sup> to reach 300 °C, then kept constant for 5 min. The final temperature was set at 325 °C for 5 min to ensure that the column was clean. The temperatures of both the detector and injection port were 325 and 280 °C, respectively. Helium was used as the carrier gas at a rate of 2.9 ml min<sup>-1</sup>. The actual pressure and split ratio were 11 psi and 25%, respectively. The flow rates of hydrogen gas, air, and makeup for FID were 40, 450, and 30 ml min<sup>-1</sup>, respectively. SPSS 19.0 and Microsoft Excel software was applied to analyze the attained data. The differences between the variables were determined by using the one-way ANOVA test (P value ≤ 0.05).

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of UV type and TiO<sub>2</sub> loading

Photocatalyst concentration can greatly affect the efficiency of the process in terms of the removal of target pollutants. In the current research, the loadings of TiO<sub>2</sub> ranged between 0.5 and 2 g L<sup>-1</sup>. The effect of UV type and TiO<sub>2</sub> loading on COD removal has been indicated in Fig. 3. When the UV-A/TiO<sub>2</sub> loading was 0.5 g L<sup>-1</sup>, 18.13% of COD was removed in 120 min. Efficiencies of 39.40 and 41.25%, respectively, were reached at concentrations of 1 and 2 mg L<sup>-1</sup> of UV-A/TiO<sub>2</sub> within 120 min. Therefore, it can be suggested that TiO<sub>2</sub> loading has a significant impact on the photocatalytic removal of COD. It was found that the performance of the process increased significantly (P < 0.05) with increasing TiO<sub>2</sub> loading between 0.5 and 1 g L<sup>-1</sup>. However, an additional increase in TiO<sub>2</sub> resulted in little elevation of the degradation rate and there was no significant difference between 1 and 2 g L<sup>-1</sup>. On the one hand, a rise in TiO<sub>2</sub> loading leads to an increase in the number of active sites, but, on the other hand, it may cause a screening effect and reduce the total available surface area of photocatalysts because of the aggregation and sedimentation of the particles of TiO<sub>2</sub> [12]. Furthermore, a gradual decline in photocatalytic performance is seen when photocatalyst loading exceeds the saturation level as a result of unfavorable light scattering and, consequently, a decrease in light penetration into the solution [11]. Thus, in using photocatalytic degradation methods, it is imperative that these processes are operated below the saturation amount of the photocatalyst. In this study, it was found that 1 g L<sup>-1</sup> of TiO<sub>2</sub> was the optimal loading. In the case of UV-C, COD removal rates were, respectively, 27.44, 56.87, and 59.56%

for  $\text{TiO}_2$  contents of 0.5, 1, and 2  $\text{g L}^{-1}$ . Hence, it can be said that UV-C exhibited better performance than UV-A for COD removal.

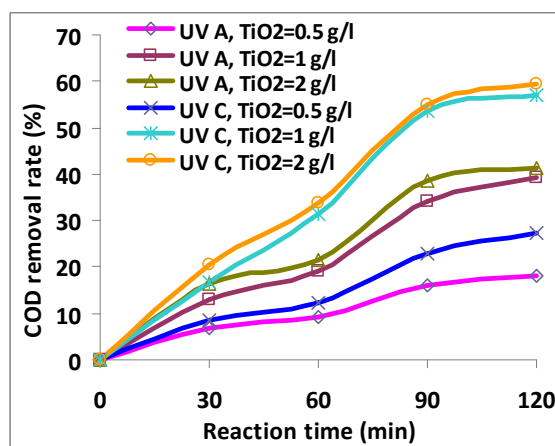


Fig. 3. Effect of UV type and  $\text{TiO}_2$  loading on the removal of COD  
initial COD concentration =  $1000 \text{ mg L}^{-1}$ ,  $\text{pH}=7$ )

### 3.2. Effect of initial pH

The efficiency of the photocatalytic process is highly influenced by the initial pH. Fig. 4 depicts the effect of the initial pH on COD removal. As presented, the highest efficiency was attained at a pH of 3. It should be pointed out that over the course of the reactions, all the initial pH values remained unchanged. At pH values of 3, 7, and 11, COD removal percentages were 42.95, 39.40, and 32.86%, respectively after 120 min. Additionally, the corresponding percentages for UV-C were found to be 62.36, 56.87, and 48.39%, respectively. Photocatalytic activity is affected by pH because the surface charge of either the photocatalyst or target pollutant, and thereby the reciprocal affinity between them, can change. In acidic conditions ( $\text{pH}<6.9$ ), the surface of  $\text{TiO}_2$  is more positively charged since the point of zero charge (PZC) of the commercial  $\text{TiO}_2$  is nearly 6.9. By contrast, in alkaline conditions ( $\text{pH}>6.9$ ), the surface of  $\text{TiO}_2$  is more negatively charged [11]. Consequently,  $\text{TiO}_2$ 's surface absorbs the target pollutant and hence enhances the direct contact between produced OH radicals and the pollutant. Other researchers have also reported similar results in terms of the effect of pH on the removal rate of target contaminants when  $\text{TiO}_2$  is used [12, 25].

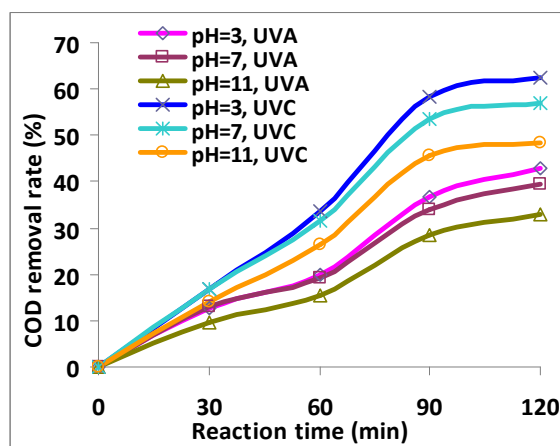


Fig. 4. Effect of pH on COD removal (initial COD concentration = 1000 mg L<sup>-1</sup>, TiO<sub>2</sub> concentration = 1 g L<sup>-1</sup>)

### 3.3. Effect of initial COD and reaction time

Reaction time is a parameter that strongly influences the performance of the UV/TiO<sub>2</sub> method. As can be clearly observed, with an increasing reaction time until 90 min, COD removal went up and then leveled off. From this point onwards, the removal rates did not rise significantly (Figs 3 and 4). Lin and Lin [11], stated that in order to reach complete decomposition of various types of organic substances with different initial contents, different irradiation times are needed. It should be further noted that initial contaminant concentration is another important variable influencing photocatalytic degradation processes.

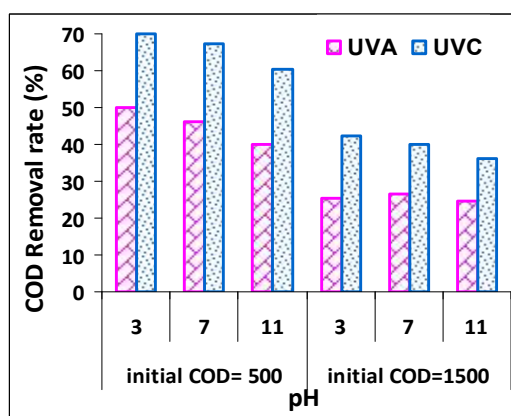


Fig. 5. Effect of initial COD concentration on its removal rate (Reaction time= 90 min, TiO<sub>2</sub> concentration= 1 g L<sup>-1</sup>)

Fig. 5 compares the COD degradation percentages attained by UV-A/TiO<sub>2</sub> and UV-C/TiO<sub>2</sub> processes at three pHs (3, 7, and 11) and two initial COD concentrations (500 and 1500 mg L<sup>-1</sup>). The findings illustrated that at an initial concentration of 500 mg L<sup>-1</sup>, the efficiencies were higher. Moreover, the performance declined when the initial COD concentration was raised between 500 and 1500 mg L<sup>-1</sup>. In accordance with our study, other researchers have claimed that photocatalytic oxidation is a contaminant concentration-dependent process [11, 12, 25].

### 3.4. TPH removal by UV/TiO<sub>2</sub>

The experiments were also performed for TPH removal both under the optimized conditions (pH of 3 and TiO<sub>2</sub> concentration of 1 g L<sup>-1</sup>) and the real conditions of the OCL (pH of 6.3 and TiO<sub>2</sub> concentration of 1 g L<sup>-1</sup>). As can be seen from Fig. 6, the highest removal efficiency (52.29%) was obtained at the optimum conditions of UV-C. But, in the case of the real conditions of OCL, only 36.69 and 48.3% of TPH were removed by means of the UV-A/TiO<sub>2</sub> and UV-C/TiO<sub>2</sub> processes, respectively. Thus, it can be claimed that UV-C/TiO<sub>2</sub> is also more efficient than UV-A/TiO<sub>2</sub> in TPH removal from OCL. The low removal rate of TPH by UV/TiO<sub>2</sub> could be attributed to the high initial concentration of TPH (170 mg L<sup>-1</sup>) and, to some extent, the high turbidity of the OCL which can prevent UV transmittance through the solution.

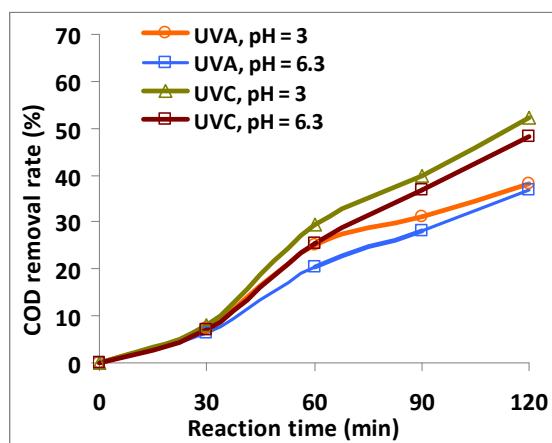


Fig. 6. Effect of UV/TiO<sub>2</sub> on TPH removal (TPH= 170.12 mg L<sup>-1</sup>, TiO<sub>2</sub> concentration= 1 g L<sup>-1</sup>)



#### 4. CONCLUSION

The feasibility of using UV/TiO<sub>2</sub> for removal of COD and TPH from OCL was investigated in the present research. The efficiency of the process with the increase in TiO<sub>2</sub> concentration and reaction time and decrease in pH and pollutant concentration. Application of UV-C presented higher efficiencies than UV-A. The optimal conditions for the process were found to be as follows: pH of 3, TiO<sub>2</sub> concentration of 1 g L<sup>-1</sup>, and reaction time of 90 min. At these optimal conditions, 52.29% of TPH was removed from OCL. In the real conditions of OCL, 36.69 and 48.3% of TPH were reduced by UV-A/TiO<sub>2</sub> and UV-C/TiO<sub>2</sub>, respectively after a reaction time of 90 min. This study found that photocatalytic oxidation by UV/TiO<sub>2</sub> is effective in OCL treatment.

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