

APPLICATION OF UV/TiO₂ 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/TiO₂. 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 TiO₂ concentration (0.5, 1, and 2 g L⁻¹) 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 TiO₂ concentration and reaction time and the decrease in pH and pollutant concentration. In the optimal conditions (UV-C, TiO₂ concentration of 1 mg L⁻¹, 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/TiO₂ and UV-C/TiO₂, respectively in real conditions of OCL (pH = 6.3, COD = 1501.24 mg L⁻¹, and TPH = 170.12 mg L⁻¹) during the 90 min reaction time. The study verified that UV/TiO₂ 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 TiO₂ (UV/TiO₂) is one of the most effective technologies [11, 12]. UV/TiO₂ 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 TiO₂ 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/TiO₂ 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, TiO₂ 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⁻¹, and TPH = 170.12 mg L⁻¹) 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. TiO₂ at concentrations of 0.5, 1, and 2 g L⁻¹ 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 H₂SO₄ (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 TiO₂ particles were separated from the reacted water through filtering of the samples.

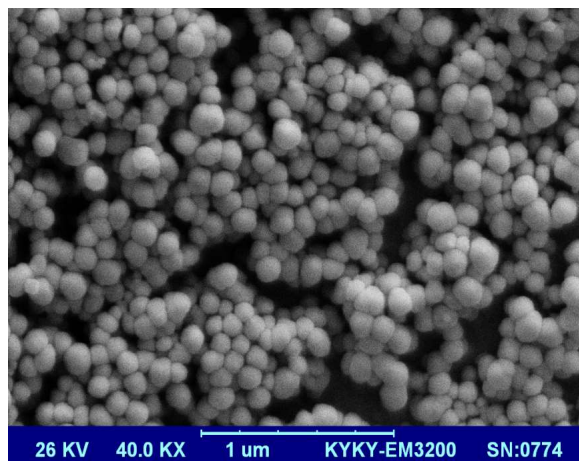


Fig.1. SEM photo of the TiO₂ used in the present study



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 C₆ and C₃₅. 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⁻¹ 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⁻¹. 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⁻¹, 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 TiO₂ 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 TiO₂ ranged between 0.5 and 2 g L⁻¹. The effect of UV type and TiO₂ loading on COD removal has been indicated in Fig. 3. When the UV-A/TiO₂ loading was 0.5 g L⁻¹, 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⁻¹ of UV-A/TiO₂ within 120 min. Therefore, it can be suggested that TiO₂ 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 TiO₂ loading between 0.5 and 1 g L⁻¹. However, an additional increase in TiO₂ resulted in little elevation of the degradation rate and there was no significant difference between 1 and 2 g L⁻¹. On the one hand, a rise in TiO₂ 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 TiO₂ [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⁻¹ of TiO₂ was the optimal loading. In the case of UV-C, COD removal rates were, respectively, 27.44, 56.87, and 59.56%

for TiO_2 contents of 0.5, 1, and 2 g L^{-1} . Hence, it can be said that UV-C exhibited better performance than UV-A for COD removal.

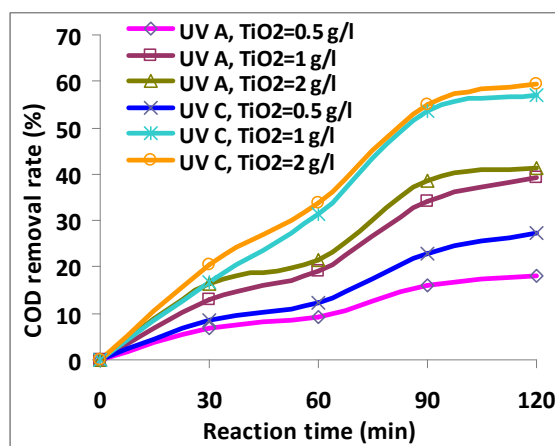


Fig. 3. Effect of UV type and TiO_2 loading on the removal of COD
initial COD concentration = 1000 mg L^{-1} , pH=7)

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 TiO_2 is more positively charged since the point of zero charge (PZC) of the commercial TiO_2 is nearly 6.9. By contrast, in alkaline conditions ($\text{pH} > 6.9$), the surface of TiO_2 is more negatively charged [11]. Consequently, 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 TiO_2 is used [12, 25].

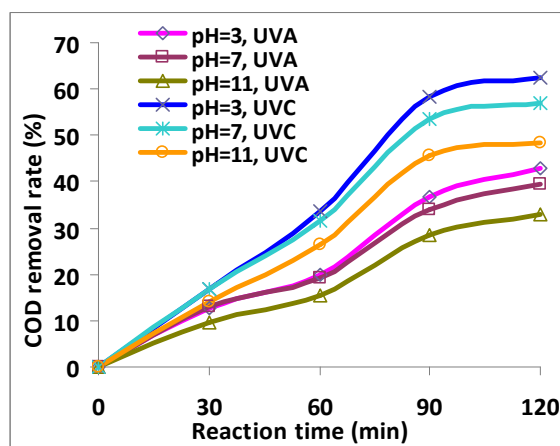


Fig. 4. Effect of pH on COD removal (initial COD concentration = 1000 mg L⁻¹, TiO₂ concentration = 1 g L⁻¹)

3.3. Effect of initial COD and reaction time

Reaction time is a parameter that strongly influences the performance of the UV/TiO₂ 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.

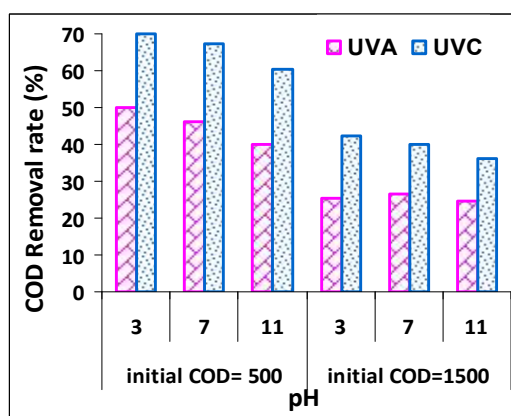


Fig. 5. Effect of initial COD concentration on its removal rate (Reaction time= 90 min, TiO₂ concentration= 1 g L⁻¹)

Fig. 5 compares the COD degradation percentages attained by UV-A/TiO₂ and UV-C/TiO₂ processes at three pHs (3, 7, and 11) and two initial COD concentrations (500 and 1500 mg L⁻¹). The findings illustrated that at an initial concentration of 500 mg L⁻¹, the efficiencies were higher. Moreover, the performance declined when the initial COD concentration was raised between 500 and 1500 mg L⁻¹. 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/TiO₂

The experiments were also performed for TPH removal both under the optimized conditions (pH of 3 and TiO₂ concentration of 1 g L⁻¹) and the real conditions of the OCL (pH of 6.3 and TiO₂ concentration of 1 g L⁻¹). 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/TiO₂ and UV-C/TiO₂ processes, respectively. Thus, it can be claimed that UV-C/TiO₂ is also more efficient than UV-A/TiO₂ in TPH removal from OCL. The low removal rate of TPH by UV/TiO₂ could be attributed to the high initial concentration of TPH (170 mg L⁻¹) and, to some extent, the high turbidity of the OCL which can prevent UV transmittance through the solution.

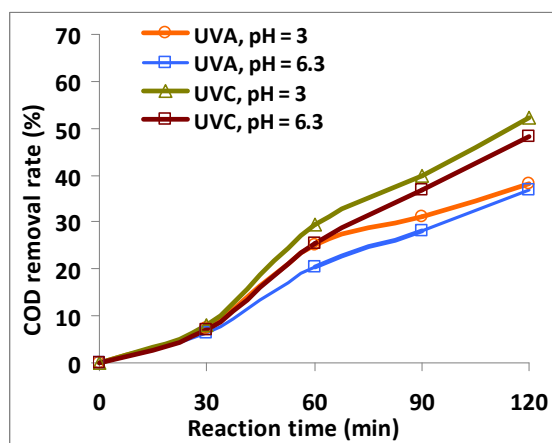


Fig. 6. Effect of UV/TiO₂ on TPH removal (TPH= 170.12 mg L⁻¹, TiO₂ concentration= 1 g L⁻¹)

4. CONCLUSION

The feasibility of using UV/TiO₂ for removal of COD and TPH from OCL was investigated in the present research. The efficiency of the process with the increase in TiO₂ 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, TiO₂ concentration of 1 g L⁻¹, 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/TiO₂ and UV-C/TiO₂, respectively after a reaction time of 90 min. This study found that photocatalytic oxidation by UV/TiO₂ is effective in OCL treatment.

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REFERENCES

1. Hu, G, Li, J and Zeng, G 2013. Recent development in the treatment of oily sludge from the petroleum industry: a review, *Journal of Hazardous Materials*, 261, 470-490.
2. Taiwo, A, Gbadebo, A, Oyedepo, J, Ojekunle, Z, Alo, O, Oyeniran, A, Onalaja, O, Ogunjimi, D and Taiwo, O 2016. Bioremediation of industrially contaminated soil using compost and plant technology, *Journal of Hazardous Materials*, 304, 166-172.
3. Suja, F, Rahim, F, Taha, MR, Hambali, N, Razali, MR, Khalid, A and Hamzah, A 2014. Effects of local microbial bioaugmentation and biostimulation on the bioremediation of total petroleum hydrocarbons (TPH) in crude oil contaminated soil based on laboratory and field observations, *International Biodeterioration & Biodegradation*, 90, 115-122.
4. Wang, ZH, Zhang, L, Li, JX and Zhong, H 2015. Disposal of oily sludge, *Petroleum Science and Technology*, 33, 9, 1045-1052.
5. Chen, M, Xu, P, Zeng, G, Yang, C, Huang, D and Zhang, J 2015. Bioremediation of soils contaminated with polycyclic aromatic hydrocarbons, petroleum, pesticides, chlorophenols, and heavy metals by composting: Applications, microbes, and future research needs, *Biotechnology Advances*, 33, 6, 745-755.
6. Zhang, Y, Guan, Y and Shi, Q 2015. Simulating the dynamics of polycyclic aromatic hydrocarbon (PAH) in contaminated soil through composting by

- COP-Compost model, *Environmental Science and Pollution Research*, 22, 4, 3004-3012.
7. Yu, L, Han, M and He, F 2017. A review of treating oily wastewater, *Arabian journal of chemistry*, 10, S1913-S1922.
 8. Jamaly, S, Giwa, A and Hasan, SW 2015. Recent improvements in oily wastewater treatment: Progress, challenges, and future opportunities, *Journal of Environmental Sciences*, 37, 15-30.
 9. Turek, A and Włodarczyk-Makula, M 2016. Catalytic Oxidation of Pahs in Wastewater (*Katalityczne Utlenianie WWA w Ściekach*), *Civil and Environmental Engineering Reports*, 20, 1, 179-191.
 10. Włodarczyk-Makula, M, Wiśniowska, E and Popena, A 2018. Biotic and abiotic decomposition of Indeno-Pyrene and Benzo (GHI) perylene in sewage sludge under various light conditions, *Civil and Environmental Engineering Reports*, 28, 4, 116-128.
 11. Lin, HHH and Lin, AYC 2018. Photocatalytic oxidation of 5-fluorouracil and cyclophosphamide via UV/TiO₂ in an aqueous environment, *Water Research*, 48, 559-568.
 12. Lai, WWP, Lin, HHH and Lin AYC 2015. TiO₂ photocatalytic degradation and transformation of oxazaphosphorine drugs in an aqueous environment, *Journal of Hazardous Materials*, 287, 133-141.
 13. Lai, WWP, Hsu, MH and Lin, AYC 2017 The role of bicarbonate anions in methotrexate degradation via UV/TiO₂: mechanisms, reactivity, and increased toxicity, *Water Research*, 112, 157-166.
 14. Cao, H, Lin, X, Zhan, H, Zhang, H and Lin, J 2013. Photocatalytic degradation kinetics and mechanism of phenobarbital in TiO₂ aqueous solution, *Chemosphere*, 90, 4, 1514-1519.
 15. Zhang, N, Hu, K and Shan, B 2014. Ballast water treatment using UV/TiO₂ advanced oxidation processes: an approach to invasive species prevention, *Chemical Engineering Journal*, 243, 7-13.
 16. Jefferson, B, Jarvis, P, Bhagianathan, GK, Smith, H, Autin, O, Goslan, EH, MacAdam, J and Carra, I 2016. Effect of elevated UV dose and alkalinity on metaldehyde removal and THM formation with UV/TiO₂ and UV/H₂O₂, *Chemical Engineering Journal*, 288, 359-367.
 17. Koolivand, A, Rajaei, MS, Ghanadzadeh, MJ, Saeedi, R, Abtahi, H and Godini, K 2017. Bioremediation of storage tank bottom sludge by using a two-stage composting system: Effect of mixing ratio and nutrients addition, *Bioresource technology*, 235, 240-249.
 18. Koolivand, A, Naddafi, K, Nabizadeh, R, Jafari, A, Nasserri, S, Yunesian, M, Yaghmaeian, K and Alimohammadi, M 2014. Application of hydrogen peroxide and fenton as pre-and post-treatment steps for composting of bottom

- sludge from crude oil storage tanks, *Petroleum Science and Technology*, 32, 13, 1562-1568.
19. Koolivand, A, Naddafi, K, Nabizadeh, R, Nasseri, S, Jafari, AJ, Yunesian, M and Yaghmaeian, K 2013. *Degradation of petroleum hydrocarbons from bottom sludge of crude oil storage tanks using in-vessel composting followed by oxidation with hydrogen peroxide and Fenton*, *Journal of Material Cycles and Waste Management*, 15, 3, 321-327.
 20. Koolivand, A, Naddafi, K, Nabizadeh, R, Nasseri, S, Jafari, AJ, Yunesian, M, Yaghmaeian, K and Nazmara, S 2013. Biodegradation of petroleum hydrocarbons of bottom sludge from crude oil storage tanks by in-vessel composting, *Toxicological & Environmental Chemistry*, 95, 1, 101-109.
 21. Koolivand, A, Naddafi, K, Nabizadeh, R and Saeedi R 2018. Optimization of combined in-vessel composting process and chemical oxidation for remediation of bottom sludge of crude oil storage tanks, *Environmental technology*, 39, 20, 2597-2603.
 22. Koolivand, A, Godini, K, Saeedi, R, Abtahi, H and Ghamari, F 2019. *Oily sludge biodegradation using a new two-phase composting method: Kinetics studies and effect of aeration rate and mode*, *Process Biochemistry*, 79, 127-134. <https://doi.org/10.1016/j.procbio.2018.12.003>
 23. APHA (American Public Health Association): *Standard methods for the examination of water and wastewater*. Washington, DC, USA APHA-AWWA-WEF 2011.
 24. TNRCC: Total petroleum hydrocarbons. Method 1005. *Texas natural resource conservation commission 2001*.
 25. Lin, L, Xie, M, Liang, Y, He, Y, Chan, GYS and Luan, T 2012. *Degradation of cypermethrin, malathion, and dichlorovos in water and on tea leaves with O₃/UV/TiO₂ treatment*, *Food control*, 28, 2 (2012) 374-379.

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