

Removal of petroleum hydrocarbons from contaminated waters using a solar photocatalytic process

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1- Introduction

Petroleum compounds include aromatic and aliphatic hydrocarbon components. The aromatics are forms of stable, hard-biodegradable, toxic and carcinogenic complexes. Sources of oil pollution in the aquatic environment, including oil spill, refinery wastewater, the water produced in the oilfields, fuel leaks from storage tanks or pipelines balance water of oil tankers, and runoff dispersed in the surface of the gas stations. In Iran where we have 10% of the world's oil reserves, storage facilities with a capacity of 8.8 billion liters, more than 2,300 fueling stations, more than 8000 oil tankers carrying petroleum products, 82 crude oil storages, and daily distribution of over 233 million liters of petroleum products, there are always hazards of pollution to oil compounds to our water resources. Treatment of contaminated water with petroleum compounds may be done by applying absorption, filtration, membrane, coagulation, advanced oxidation, stabilization pond and anaerobic methods. Physical methods such as adsorption only transfer pollution from one phase to another phase. The efficiency of biological processes is low, but they are inexpensive whereas the efficiency of chemical methods is high while they are expensive. Among the AOPs, the heterogeneous photocatalysis process has been used extensively.

2- Experimental Program

In this method, immobilized titanium dioxide through the generation of a hydroxyl radical ($\bullet\text{OH}$) in the presence of UV light, can potentially destroy a wide range of organic complex. According to the activity of TiO_2 in the near ultraviolet region ($\lambda=400\text{-}300\text{ nm}$), this process was commonly carried out with UV-A lamps using which is costly. In addition, 5% of the solar radiation on the earth's surface is UV light 98% of which is UV-A and the radiation intensity is about $30\text{-}20\text{ Wm}^{-2}$ near the surface at noon of a sunny day. So far, the photocatalytic treatment process has been used for wastewater

treatment of paper, textile, paint industries and power plants. In a recent study, nano TiO_2 was immobilized on a light-weight concrete plate by concrete paste. Generally, the purpose is the use of UV solar light instead of UV lamps in photocatalytic process for the removal of petroleum hydrocarbons with the aim of saving energy saving and using clean energy. Removal of hydrocarbons from water contaminated synthetically with petroleum hydrocarbons was performed by TiO_2 nanoparticles coated on light-weighted concrete plates in the reactor.

The solar reactor (Figure 1) consisted of five concrete rectangular plates $24 \times 12 \times 4\text{ cm}$ at a slope of 2.50%. The weir of 5 L that has been located at the upstream of the plates distributed the flow uniformly. The reactors are covered with a 3-mm glass in order to prevent evaporation of the compounds and to ensure that the reactors remains waterproof. A storage tank with a volume of 60 L along with a floating pump circulated the flow at the rate of 200 L.hr^{-1} . An aerated pump at the rate of 270 L.hr^{-1} supplied sufficient oxygen. The slurry method was used for stabilizing the nanoparticles.



Fig. 1 The studied solar reactor

Mixing of 100 mL of two-component epoxy paste was done in 1000 mL of deionized water. After 5 min of stirring, the concrete surface was polished by applying a paint brush. The concrete plates were impregnated with a suspension of TiO_2 (12 gr TiO_2 in water-ethanol solution), then dried under ambient conditions, heated at $450\text{ }^\circ\text{C}$ for 120 min in a muffle

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furnace to enhance the stability of the coatings against mechanical attrition and washed to eliminate the excess Titanium. The photo-reactor was oriented southward at an angle of 37° with respect to the horizontal. The experimental set-up was located on the rooftop of the school of engineering of the Tarbiat Modares University. The data were registered every 30 minutes from 9 a.m. to 5 p.m. for 6 months. The operating parameters affecting the photocatalytic degradation include pH, mass loading of TiO₂ per unit area, H₂O₂ dosage, initial concentration and exposure time. Each of these factors was examined at different exposure times to reach optimal conditions. To ensure proper coating of TiO₂ on the plates, SEM images of the original and coated concrete (Figure 2) were taken and they showed that TiO₂ loading of 60 gm⁻² provides sufficient coating. Finally, the reactor was run under optimum conditions that are pH of 5, TiO₂ mass loading of 60 gm⁻², UV equivalent irradiation time of 200 min, initial concentration of 100 mgL⁻¹ and H₂O₂ dosage of 2000 mgL⁻¹.

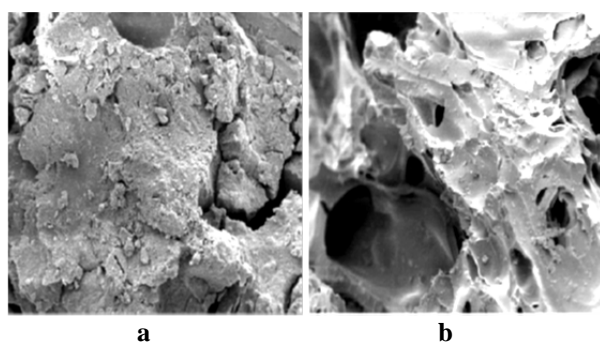


Fig. 2 SEM images of a) original b) coated concrete

3- Conclusions

The results demonstrated that under optimal conditions the removal efficiency total petroleum hydrocarbons (TPH) and poly aromatic hydrocarbons (PAHs) of chemical oxygen demand (COD) were 67.63, 84.75 and 70.48 percent, respectively (Figure 3).

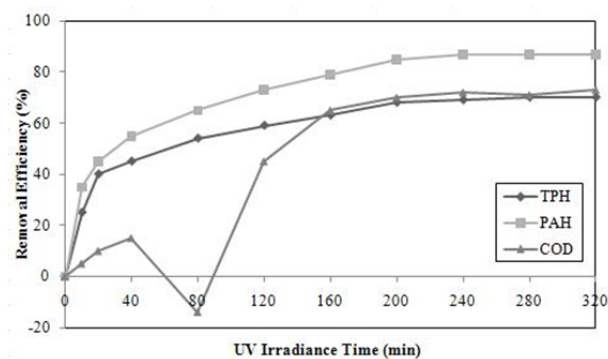


Fig. 3 Variation of TPH, PAH & COD removal efficiency at optimal conditions

The results of GC/FID analysis of wastewater

before and after the photo-degradation under optimum conditions showed that a majority of the aromatic compounds have been eliminated at relatively high efficiencies (Figure 4), and the aliphatic compounds that had remained have no toxicity.

The results showed that at low concentrations and exposure time of 200 min (solar reactor operation of 5 day) discharge standards of treated effluent can be met. Therefore, we can expect that the use of the solar photocatalytic system for treatment of wastewater of refineries and oil fields at industrial scale would be economically effective, especially in the southern region. In addition, the immobilization of the photocatalyst on the concrete surface, which is a main element of WWTPs structures will double the efficiency of this method.

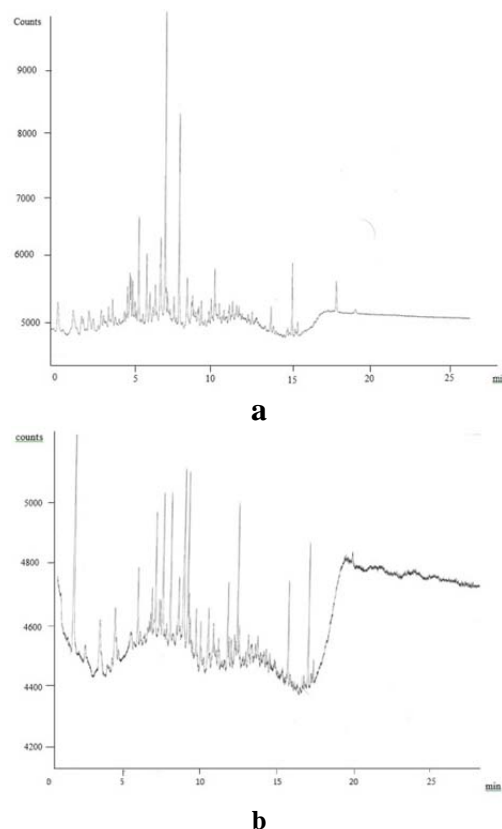


Fig. 4 The results of GC/FID analysis of wastewater a) before and b) after the photo-degradation under optimum conditions