

## Photocatalytic Degradation of PAHs Contaminated Soil in South Pars Economic and Energy Zone with TiO<sub>2</sub> Nanocatalyst

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### Abstract

Heterogeneous photocatalytic degradation of Polynuclear Aromatic Hydrocarbons (PAHs) contaminated soil in the Pars Economic and Energy Zone was carried out under laboratory conditions to evaluate the potential use of this technology for in situ remediation. Analysis of soil samples show that contaminated soil is primarily related to the concentration of phenanthrene. Hence phenanthrene is used for photocatalytic degradation under laboratory conditions. Soil samples were spiked with two phenanthrene concentrations (50 and 100 mg kg<sup>-1</sup>), loaded with catalyst TiO<sub>2</sub> and exposed to uv light with 125 W power. Different catalyst loads (1, 2, 3 and 4 % w/w) were tested in phenanthrene contaminated soil (50 mg kg<sup>-1</sup>) for up to 16h exposure. Both the catalyst and phenanthrene concentration show no influence on the kinetics of the phenanthrene degradation. The results indicated that the optimum removal condition was at 2% w/w catalyst and 100% w/w water with 85% degradation efficiency. The degradation efficiency of other PAHs was also assessed with the optimum condition. This paper shows that photocatalytic is a particularly important methodology, in which a major process is being made in the oxidative methods for the degradation of organics such as PAHs in contaminated soil.

**Keywords:** PAHs; Soil; Photocatalysts; Titanium Dioxide

### 1- Introduction

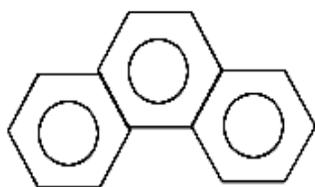
Soil and groundwater contamination has become a common problem in many locations. Many organic pollutants are hydrophobic and sparingly soluble. Polynuclear aromatic hydrocarbons (PAHs) are exemplary compounds of this type and are known components of coal tars, gasoline, and jet fuel [1,3]. Since the PAH benzo[a]pyrene is a known carcinogen and PAHs such as naphthalene and phenanthrene are priority pollutants listed by the u.s. Environmental

Protection Agency (EPA), the presence of these compounds in groundwater and soil constitutes a health hazard, and their removal from contaminated sites is desirable.

Analysis of soil samples show that contaminated soil is primarily related to phenanthrene concentration, and therefore phenanthrene is used for photocatalytic degradation under laboratory conditions. The structure of this compound is shown in Figure 1.

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**Figure 1.** Structural formula of phenanthrene

There are numerous technologies with potential application for soil remediation and deactivation processes of hazardous wastes that are focused mainly on biological and chemical treatments. However, the American Environmental Protection Agency (USEPA) has proposed in situ treatment as a potentially safe and economical method of soil cleanup [4,5]. There have been numerous studies exploring the use of soil bioremediation in situ, since it appears to have less impact on the environment. Nonetheless, considering that some waste components can be toxic to the microorganism consortium normally used in this remediation process, long periods of time may be necessary to achieve the target concentration of the contaminants in the soil. In this case, the choice of a chemical treatment based on the use of strong oxidants, such as  $H_2O_2$  and  $KMnO_4$ , may provide a suitable means of destroying xenobiotic contaminants over time periods shorter than those required for biological treatment, leaving byproducts that are ubiquitous in the environment [5,9].

Heterogeneous photocatalysis has been successfully tested as an emerging technology for the decontamination of industrial effluents [8]. Unlike non-destructive traditional methods like volatilization or adsorption onto a solid phase, this process has the advantage of destroying the organic compounds by redox reactions on the catalyst surface. The mechanisms of this process have been described in detail elsewhere [6-8].

As expected in a photon mediated process that, in this particular case, explores the use

of solar light, radiation intensity has to be considered as a key parameter when evaluating process efficiency, which means that, in tropical countries, soil remediation using photocatalysis is very dependent upon the season of the year [5,9]. Another parameter that will influence the extent of degradation is the characteristics of the soil. In this porous medium, the presence of a carrier is necessary to bring together the substrate onto the catalyst surface and this is normally achieved by increasing the amount of water in this medium. Additionally, water molecules can further react on the surface of the catalyst by oxidation in the hole ( $h^+$ ) and generate  $\cdot OH$  radicals, thus increasing the rate of degradation. The pH is another important parameter, and the presence of an alkaline coadjutant not only impacts the surface charge in the catalyst, but also determines the predominant species of the substrate, controlling the extension of adsorption, thus potentially affecting the kinetics of degradation [3].

The feasibility of using heterogeneous photocatalysis in the treatment of highly contaminated soil was recently demonstrated [3].

The present paper describes the investigation of some key parameters such as the amount of catalyst and moisture that can alter the degradation rate of PAHs in contaminated soils when using a photocatalytic treatment combining  $TiO_2$  and solar light.

PAHs adhere strongly to soils; this action decreases their transport rate and increases the time required for the remediation of contaminated soils [2,3]. The study zones in this paper were the mangrove forest in the Pars Energy and Economic Zone in the south of Iran. Investigation of soil samples in this zone show that the soil samples were contaminated with PAHs and widespread contamination of soil with PAHs has resulted from the operation of a natural gas plant and fallout from the burning of Kuwait's oil fields in 1991.

The results of photocatalytic degradation of

PAHs contaminated soil for the set of experiments are discussed. The results were also analyzed in kinetic terms: for example percentage of degradation, degradation constant, and half life of each analyzed in different conditions.

## **2- Experimental**

### **2-1- Materials**

Titanium dioxide (Degussa, P25, nanoporous, 80:20% anatase:rutile mixture) with a Brunaur–Emmett–Teller (BET) surface area of  $50 \pm 15 \text{ m}^2/\text{g}$ , and an average particle size of 21 nm was used as received. Pure phenanthrene was used. Acetonitrile (HPLC<sup>1</sup> grade), a Merck product, was used in the mobile phase in HPLC. Dichloromethane, (95%) an Aldrich product, was used as solvent. Sandy soil was sieved (2 mm), collected and brought from the Pars Energy and Economic Zone in south Iran.

### **2-2- Soil contamination and irradiation**

The experiments were carried out on a laboratory scale, where 200g of soil contained in petri dishes were contaminated with phenanthrene. The plate was exposed to uv light with 125 W power, normally from 8 a.m. to 24 p.m. for 16h. To follow phenanthrene degradation, 30-40g samples of soil were collected after each 4h of irradiation and analyzed for phenanthrene. The catalyst load was achieved by adding the desired amount of TiO<sub>2</sub> in the soil samples, followed by manual shaking for 30 min in a 500 ml closed stainless steel reactor. To study the optimum concentration of the catalyst in the destruction of the phenanthrene, five plates were prepared with contaminated soil ( $50 \text{ mgKg}^{-1}$ ). In each plate 0, 1, 2, 3 and 4% of TiO<sub>2</sub> (w/w) were incorporated into the soil and submitted to the treatment. The influence of phenanthrene concentration was also assessed through the contamination of three soil samples with 10,

50 and  $100 \text{ mgKg}^{-1}$  of the phenanthrene, followed by the incorporation of 2% (w/w) of the TiO<sub>2</sub> catalyst.

The influence of humidity in the photocatalytic degradation was also assessed through the contaminated soil sample with 0, 50 and 100% (w/w) of water, followed by the incorporation of 2% (w/w) of catalyst.

To study the photocatalytic remediation in other PAHs compounds, the same experiments using contaminated soil with other PAHs was assessed with 2% (w/w) of the catalyst and 100% (w/w) of the water. The experiments using covered plates containing contaminated soil and TiO<sub>2</sub> showed that degradation did not exceed 15% of the total amount of contaminant present in the soil after 16h, confirming that destruction is photo dependent.

### **2-3- Soil extraction and HPLC analysis**

An aliquot of 30-40g of exposed soil was extracted with 60 ml of dichloromethane for 6h. The extracts were filtered using a 0.45  $\mu\text{m}$  Millipore syringe filter and analyzed using a Waters 1880 HPLC set with a two-channel uv-visible light absorption detector set at 254 nm absorbance for PAHs detection. A Novapack 150 mm x 39 mm ID C18 column was used, and the applied mobile phase was  $2 \text{ ml}\cdot\text{min}^{-1}$  of gradient chromatography grade acetonitril (Merck).

## **3- Results and Discussion**

Figure 2 shows the results obtained for the degradation of the target compound when the concentration of phenanthrene spiked in the soil varied between 10, 50 and  $100 \text{ mgKg}^{-1}$  using 2%(w/w) of TiO<sub>2</sub>, 100%(w/w) humidity and exposed to uv light. Degradation is independent of the three different phenanthrene concentrations. The results also allow the conclusion that, at these levels of contamination, loading with 2% (w/w) of TiO<sub>2</sub> was enough to reach efficiencies above 85% for the degradation.

When the phenanthrene concentration in the

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1- High Performance Liquid Chromatography

soil was fixed at  $50\text{mgKg}^{-1}$ , changes in the concentration of  $\text{TiO}_2$  from 2 to 4% (w/w) have no significant effect in the rate of phenanthrene degradation, as presented in Figure 3. The results also show that the degradation efficiency of phenanthrene with 1% (w/w) catalyst is about 70% and therefore the optimum catalyst concentration is 2% (w/w) of  $\text{TiO}_2$ .

The humidity effect in the photo degradation of contaminated soil is clearly shown in

Figure 4. The humidity varied between 0, 50 and 100% (w/w) when the phenanthrene concentration in the soil was fixed at  $50\text{mgKg}^{-1}$  using 2% (w/w) of  $\text{TiO}_2$ . In the absence of humidity, only 3-4% of the contaminated soil has degraded after 16h of uv light concentration, and 100% (w/w) of the water is used in the photoremediation process. On the other hand, when the humidity increases, the degradation rate also increases.

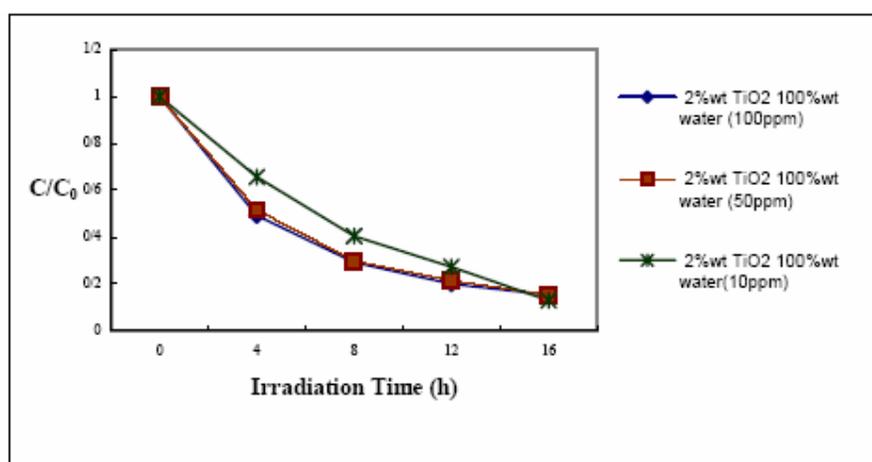


Figure 2. Influence of phenanthrene concentration on the photocatalyst degradation in soil in presence of  $\text{TiO}_2$

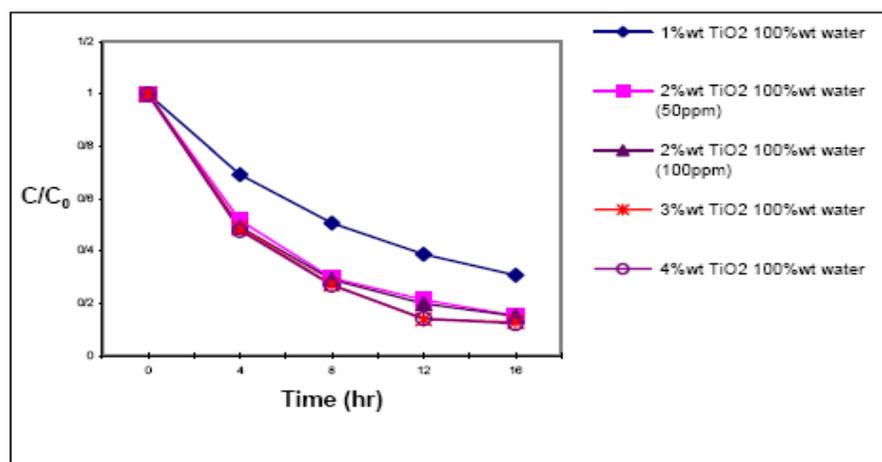
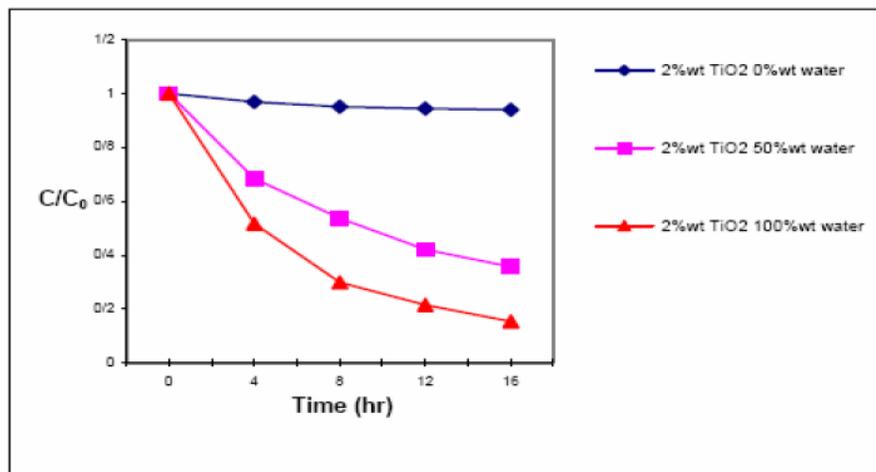


Figure 3. Influence of  $\text{TiO}_2$  load on the photodegradation of phenanthrene ( $50\text{mgKg}^{-1}$ ) in soil



**Figure 4.** Influence of humidity on the photocatalytic degradation of phenanthrene in soil in presence of TiO<sub>2</sub>.

Several experimental results indicated that the photodegradation rates of various organic contaminants fitted the Langmuir–Hinshelwood model [10,11]. The Langmuir–Hinshelwood rate form is

$$r_R = \frac{-dC_R}{dt} = \frac{k_r K C_R}{1 + K C_R} \quad (1)$$

Where  $r_R$  is the reaction rate of the reactant,  $C_R$  the concentration of the reactant,  $t$  the illumination time,  $k_r$  the reaction rate constant, and  $K$  the adsorption coefficient. Integration of Eq. (1) yield Eq. (2):

$$-\ln\left(\frac{C_R}{C_{R0}}\right) + K(C_{R0} - C_R) = k_r K t \quad (2)$$

When the initial concentration  $C_{R0}$  is low,

Eq. (2) is altered to Eq. (3):

$$-\ln\left(\frac{C_R}{C_{R0}}\right) = k_{app} t \quad (3)$$

which express pseudo-first-order reactions, where  $k_{app}$  is the apparent photo degradation rate constant. The photo degradation kinetic curves of the phenanthrene under uv light irradiation are presented in Figure 5.

The values of  $k_{app}$  and the linear regression coefficients for the pseudo-first-order kinetics of the phenanthrene degradation are listed in Table 1. According to these results, the photodegradation kinetics phenanthrene follows a pseudo-first-order degradation curve, which is consistent with the Langmuir–Hinshelwood model.

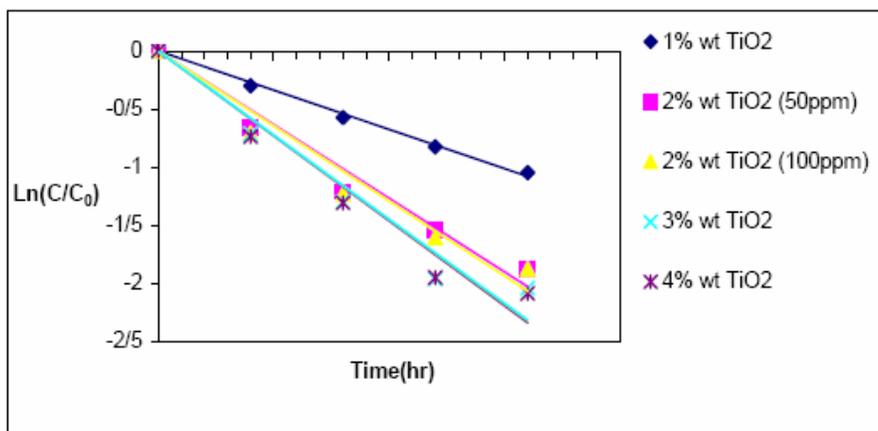


Figure 5. the photodegradation kinetic curves of the phenanthrene in presence of  $\text{TiO}_2$  under uv light irradiation

Table 1. Kinetic parameters for photodegradation of phenanthrene in presence of  $\text{TiO}_2$  under irradiation of uv light

| Photoreactive conditions               | $k_{\text{app}}$<br>( $\text{hr}^{-1}$ ) | $R$    | $t_{1/2}$<br>(hr) |
|--|--|--------|-------------------|
| 1%(w/w) $\text{TiO}_2$ (50mg/kg soil)  | 0.0772                                   | 0.987  | 9                 |
| 2%(w/w) $\text{TiO}_2$ (50mg/kg soil)  | 0.1268                                   | 0.9609 | 5.5               |
| 2%(w/w) $\text{TiO}_2$ (100mg/kg soil) | 0.1292                                   | 0.9483 | 5.4               |
| 3%(w/w) $\text{TiO}_2$ (50mg/kg soil)  | 0.1448                                   | 0.9443 | 4.79              |
| 4%(w/w) $\text{TiO}_2$ (50 mg/kg soil) | 0.1462                                   | 0.952  | 4.74              |

The photodegradation of other PAHs components such as pyrene, flouranthene, and anthracene that have the same structure type as phenanthrene show that these

components were undergoing degradation in the presence of 2% (w/w)  $\text{TiO}_2$  and 100% (w/w) humidity. (Figure 6).

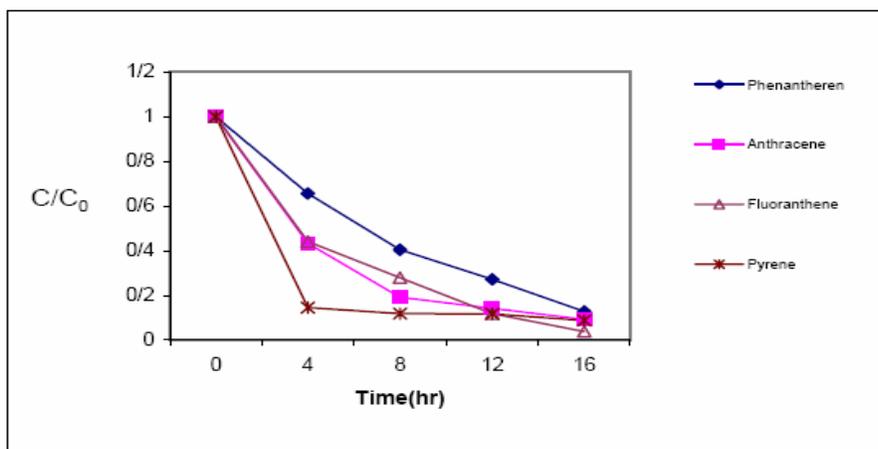


Figure 6. the photodegradation of other PAHs components in the presence of  $\text{TiO}_2$  and humidity

#### **4- Conclusion**

The combination of TiO<sub>2</sub> with uv light can destroy the PAHs components in soil. The process with phenanthrene as a contaminant is fast and the phenanthrene degradation half-life rarely 5.5h under optimized conditions. As expected, the catalyst concentration was an important parameter to control the degradation, and the higher the soil humidity, the better the destruction yield. In addition, the photodegradation kinetics phenanthrene follows a pseudo-first-order degradation curve, which is consistent with the Langmuir–Hinshelwood model.

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