TiO_2 PHOTOCATALYSIS TREATMENT FOR CONTAMINATED SOIL REMEDIATION

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Abstract
Soil pollution by petroleum hydrocarbons may occur through accidental spills during refining, exploration, production, and tank leakage. Petroleum pollution can have negative impacts on local soil ecosystems and human health. Environmental weathering processes attenuate lighter and chemically simpler components of crude oil, while leaving behind heavy hydrocarbons that are generally recalcitrant to the processes. Photocatalysis is able to transform heavy hydrocarbons to more water soluble, less toxic, and more bioavailable forms. The present work shows the use of TiO_2 as a photocatalyst for either directly decrease total petroleum hydrocarbon residuals or accelerate the natural processes that do so, while combined with other processes, like bioremediation. Real contaminated soil was used. Soil samples were treated using photocatalysis with TiO_2. All experiments were done in duplicate and were exposed to lamps mimicking sunlight for 2, 4, 8, 12 and 24 hours. Hydrocarbons removal of 32% was obtained at 2 hours reaction time.

Key words: Photocatalysis, hydrocarbons, soil, TiO_2.

TRATAMIENTO DE FOTOCATÁLISIS CON TiO_2 PARA REMEDIACIÓN DE SUELOS CONTAMINADOS

Resumen
La contaminación del suelo por hidrocarburos derivados del petróleo puede ocurrir a través de derrames accidentales durante la refinación, exploración, producción y fugas en los tanques. La contaminación por petróleo puede tener impactos negativos en los ecosistemas locales del suelo y la salud humana. Los procesos de meteorización ambiental atenúan los componentes más livianos y químicamente más simples del petróleo crudo, al tiempo que dejan atrás los hidrocarburos pesados que generalmente son recalcitrantes a los procesos. La fotocatálisis es capaz de transformar hidrocarburos pesados en formas más solubles en agua, menos tóxicas y más biodisponibles. El

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presente trabajo muestra el uso de TiO_2 como fotocatalizador para disminuir directamente los residuos totales de hidrocarburos de petróleo o acelerar los procesos naturales que lo hacen, mientras se combina con otros procesos, como la biorremediación. Se utilizó suelo contaminado con hidrocarburos. Las muestras de suelo se trataron mediante fotocatálisis con TiO_2. Todos los experimentos se realizaron por duplicado y se expusieron a la luz de lámparas simulando luz solar durante 2, 4, 8, 12 y 24 horas. Se obtuvo una eliminación de hidrocarburos del 32% con tiempo de reacción de 2 horas.

Palabras clave: remediación, suelos, hidrocarburos, TiO_2, fotocatálisis.

1 Introduction

Soil pollution by petroleum hydrocarbons may occur through accidental spills, during refining, exploration, production, and tank leakage. Petroleum pollution can have negative impacts on local soil ecosystems and human health (Adeniyi and Afolabi, 2002; Das *et al.* (2010). Environmental weathering processes such as volatilization, biodegradation, and dissolution attenuate lighter and chemically simpler components of crude oil, while leaving behind heavy hydrocarbons that are generally recalcitrant to the processes due to their relatively large and complex chemical structures (i.e., these molecules are hydrophobic, poorly soluble, and poorly available to microbiological attacks). Photocatalysis, as an oxidation process, is able to transform heavy hydrocarbons to more water soluble, less toxic, and more bioavailable forms (Goi *et al.*, 2006; Rittmann *et al.*, 2002) (Fig. 1).

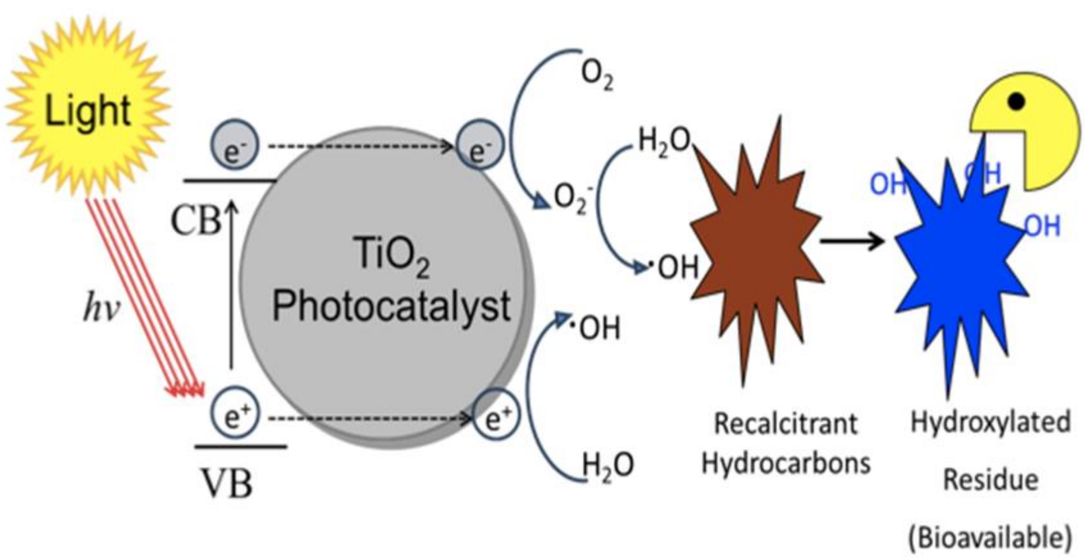

Figure 1. Degradation mechanism of TiO_2 photocatalytic oxidation (Source: Brame *et al.*, 2013)

Compared to other technologies, TiO_2 photocatalytic oxidation has several advantages:

• is an environmental friendly, health safe and cost effective material.

• is a very effective photocatalyst that can continuously produce free radicals after one addition.

• can be activated by sunlight.

• can be applied directly to soil without interfering with other bioprocesses like landfarming or composting.

The aim of the present work is to show the use of TiO_2 as a photocatalyst for either directly decrease total petroleum hydrocarbon (TPH) residuals or accelerate the natural processes that do so, while combined with other processes like bioremediation.

2 Literature review

Advanced oxidation is a promising technology to improve the bioavailability of heavy hydrocarbons in contaminated soil. Free radicals produced by advanced oxidation can attack organic molecules by introducing ·O (mainly as ·OH groups), cleaving aromatic rings, and releasing N or S from heterocyclic compounds (Scott and Ollis, 1995; Brame *et al.*, 2013; Yan *et al.*, 2013). All of these steps make the molecules simpler, more hydrophilic, and more susceptible to biodegradation.

Among all of the advanced oxidation approaches, titanium dioxide (TiO_2) photocatalysis (Fenoll *et al.*, 2013; Oyama *et al.*, 2010) shows a "green" pre-oxidation route that can use sunlight to produce reactive oxygen species with strong oxidative activity.

TiO_2 photocatalysis is very effective to produce free radicals. When illuminated by light that contains near-UV radiation (present in sunlight), TiO2 produces reactive oxygen species, such as hydroxyl radicals (·OH) and superoxide (·O2-), that can hydroxylate hydrophobic organic compounds and increase their bioavailability to the microbial community (Turchi and Ollis, 1990; D′Auria *et al.*, 2009; Brame *et al.*, 2013; Park and Choi, 2005; Lee *et al.*, 2011) (Figure 1). It is also an inexpensive and environmentally acceptable photocatalyst. TiO_2 has been widely used as a pigment in commercial products such as paper, paint and plastic, self-cleaning coatings, hair styling devices, air filtration, and environmental remediation (ERG USEPA, 2010).

3 Methodology

Preliminary work using TiO_2 for decreasing specific hydrocarbons (Model compounds) from soil samples was done. In that case we used for each experiment 5 grams of clean soil contaminated with one model compound. It was found that the best results were obtained with 50% adjusted soil with water holding capacity (WHC) with TiO_2 application on a surface of 0.418 kg/cm^2 of soil.

For the present work, the same conditions were used. The difference is that larger samples (80 g) were now used and soil was taken from an aged oil spill site. Samples were treated as follow:

Treated soil. Soil sample with TiO_2 added on the surface and exposed to sunlight.

Untreated soil. Soil sample was only exposed to sunlight.

Dark control. Same as in Treated Soil but covered to avoid contact with sunlight.

All experiments were done in duplicate and were exposed to lamps mimicking sunlight for 2, 4, 8, 12 and 24 hours (Fig. 2). During sunlight exposition, temperature and UV were measured with a UVA/B Light Meter 850009. The UV light was 0.8 mW/cm^2 and average temperature was 30 ^{0}C.

Figure 2. Samples from real contaminated soil (from an aged oil spill site)

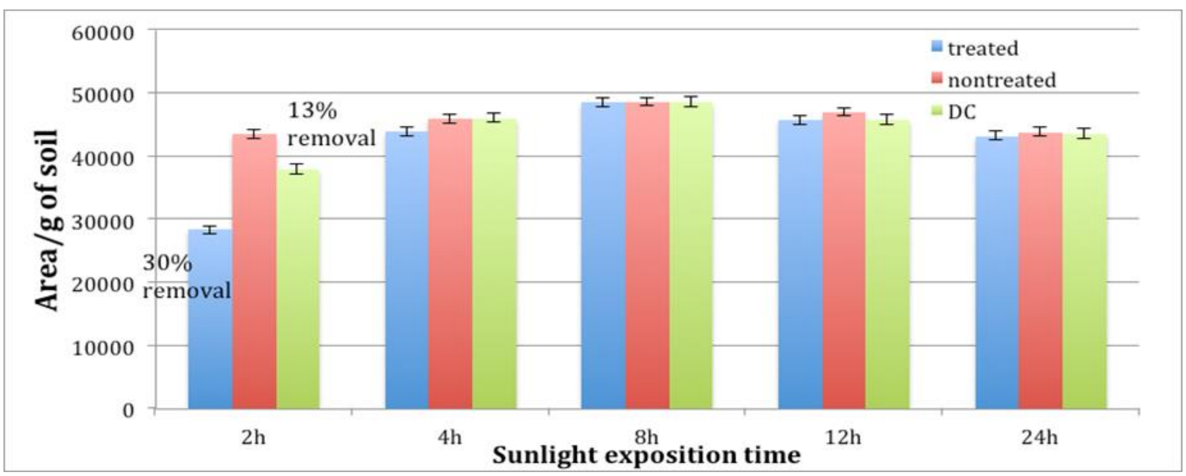

Figure 3. Total peak area for soil after different times treatment. Obtained from Gass Chromatrographic analysis

After sunlight exposition time, the explain were done using Dicloromethane (DCM) and readings were made at Gas Chromatographer (GC).

4 Results and discussions

For the present work a WHC of 50% was chosen using recommendations by Xu *et al.* (2011), who found that the most efficient degradation of pollutant occurred when the moisture content was between 30% and 50% for the diffusion of pollutants and O_2 balance. This adjustment was done at the beginning of the experiment.

Results are shown in figure 3. After 2-hour TiO_2 photocatalytic treatment, 30% of the TPH was degraded or converted. Therefore, TiO_2 photocatalysis was an effective treatment for TPH removal.

In TiO_2 dark control, about 13% of TPH was removed compared to untreated soil, indicating that TiO_2 photocatalyst adsorbed some TPH. However, the removal percentage of TPH in TiO_2 photocatalysis was much higher than in the TiO_2 dark control, demonstrating that most of TPH lost in the photocatalytic treatment was due to free radical attack.

During the following reaction times (4,8,12,24 hours) the samples were not adjusted to preserve a WHC of 50%. The removal of the hydrocarbon in the contaminated soil was not observed, this could be the result of moisture loss, which turned out to be an important factor in the removal of the contaminant and coincides with what was found by Xu *et al.* (2011) and Chang *et al.* (2011).

5 Conclusions

Using the following conditions: 50% of WHC and TiO_2 at 0.418 kg/cm^2 applied on soil surface during 2 hours reaction, TiO_2 was able to remove 30% of TPH from real contaminated soil.

Adjusting moisture in contaminated soil may result in a better percentage of hydrocarbon removal using TiO_2 photocatalysis.

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