

ENHANCED BIODEGRADATION OF HYDROCARBON CONTAMINANTS USING PHOTOCATALYTIC PRETREATMENT

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ABSTRACT: Photocatalysis was investigated as a pretreatment for hydrocarbon groundwater contamination at an abandoned oil field in Guadalupe, CA. A laboratory photoreactor, with a UV fluorescent lamp submerged in a suspension of TiO₂ catalyst particles, was used to determine oxidation rates and the increase in biodegradability of the hydrocarbon mixture. Chemical oxidation demand (COD) and 5-day biological oxygen demand (BOD₅) were measured as a function of exposure time using standard methods. During eight-hour photoreactor runs in a nitrogen atmosphere, the COD of diluent solutions in de-ionized water and diluent solutions in simulated groundwater both decreased by approximately 50%, while the BOD₅ increased by a factor of 2 to 3. The biodegradability quotient, BOD₅/COD, increased from initial values of between 0.03 and 0.06 up to final values of between 0.27 and 0.29 during the eight-hour photoreactor runs. Little or no decrease in the chemical oxygen demand was observed in a control with no UV light and a control with no TiO₂, confirming the role of photocatalysis in these experiments. Based on the experimental oxidation and biodegradation kinetics, design parameters for *ex-situ* and *in-situ* remediation applications are presented.

INTRODUCTION

Improper handling and disposal of hazardous wastes has led to widespread groundwater contamination at thousands of sites throughout the world (Ollis et al., 1989). Ideally, groundwater contaminants could be removed via natural attenuation processes mediated by indigenous microorganisms. Unfortunately, some contaminants are not readily biodegradable or the kinetics of biodegradation are so slow that concentration limits designated by federal and local agencies cannot be met in a reasonable time period. Thus there has been a tremendous amount of research conducted to develop technologies that accelerate natural attenuation by enhancing or augmenting biodegradation via the introduction of additional nutrients, electron acceptors, or microorganisms to the subsurface environment. A more novel approach, explored in the present research, is to increase the biodegradability of the contaminants by physical-chemical

pretreatment using photocatalysis. This approach could conceivably be applied to both above ground treatment schemes and in-situ remediation.

Photocatalysis is a promising advanced oxidation processes (AOP) that has proven useful for the oxidation of many organic hazardous waste compounds, including alkanes, alkenes, haloalkanes, haloalkenes, haloaromatics, aromatics (e.g. phenol, nitrobenzene, nitrotoluenes), surfactants, herbicides, and even some toxic metals (Ollis et al., 1989). Photocatalysis or photocatalytic oxidation (PCO) is a type of heterogeneous catalysis in which a semiconductor material is irradiated with photons of ultraviolet wavelength ($\lambda < 385$ nm), creating energetic electrons and holes on the surface of the semiconductor. In an aqueous environment, these charged carriers then react with dissolved oxygen and/or water to produce highly reactive hydroxyl radicals that readily oxidize the contaminants. PCO effectively oxidizes a wide variety of environmental contaminants, yet the most economically efficient means of remediation may be a combination of PCO and natural attenuation. Through oxidation, chemical contaminant structure is changed, often resulting in compounds that are much more biodegradable. In the present study, the feasibility of such a hybrid physical-biological treatment scheme was investigated for remediation of hydrocarbon-contaminated groundwater at a site on the central coast of California. The field site is an abandoned oil field that was contaminated by a mixture of C₁₀ to C₃₀ hydrocarbons (similar to diesel fuel), which was used as a diluent for pumping viscous crude oil. Groundwater contaminated with this diluent was collected and treated with a laboratory photoreactor using suspended TiO₂ catalyst. The kinetics of photo-oxidation and biodegradation determined in this study were then used to design potential *ex-situ* and *in-situ* hybrid remediation systems.

MATERIALS AND METHODS

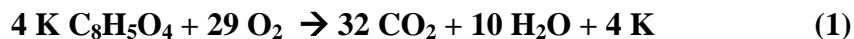
Preparation of Contaminated Water. Samples of hydrocarbon diluent were collected during groundwater sampling from the Guadalupe Dunes Oil Field. A stock solution of contaminant was prepared by continuously mixing 200 mL of raw diluent with 3 L of filtered (5 μ m) de-ionized water or simulated groundwater. Simulated groundwater contained 50 mg/L CaCl₂ (Fisher Chemical, Fisher Scientific, Fair Lawn, NJ) and 200 mg/L NaHCO₃ (Spectrum Chemical Co., Redondo Beach, CA). Contaminated water samples were allowed to come to equilibrium for 5 days before being used in the photoreactor.

Photoreactor Apparatus. The photoreactor used for these experiments was an annular re-circulating batch reactor as previously described (Turchi and Ollis, 1989). Briefly, the system is modular in design, with a pump, a slurry vessel and an annular flow tube. The slurry vessel is a 2 L, jacketed, round bottom flask with three threaded sampling ports. The annular reactor column is composed of two 18-inch long concentric Pyrex® tubes 30 mm and 54 mm in diameter. Within the inner concentric tube was an 18-inch, 15-watt fluorescent ultraviolet lamp ($\lambda \approx 365$ nm, Visual Effects, Inc., New York, NY). Slurry flow was maintained at 6.4 L/min using a 2.3 amp sealed bearing centrifugal pump (March Mfg, Inc., Glenview, CA). The temperature of the photoreactor was kept at 25°C by

pumping ice water into the jacket of the slurry vessel using a 1-100 rpm adjustable peristaltic pump (Cole Parmer, Chicago, IL). Experiments were conducted with either air or nitrogen sparging (A & R Welding, San Luis Obispo, CA) through a porous stone into the reaction vessel.

Photoreactor Operation and Sampling. Prior to the photoreactor runs, titanium dioxide (P25, Degussa Corp.) was added to the contaminated water at a concentration of 1 g/L and manually stirred. Once the TiO₂ was thoroughly mixed with the contaminated water, it was poured into the reaction vessel. 40 mL samples were collected at 1 hr intervals and filtered through a 0.45 μm Nylon membrane (Whatman, Maidstone, England, Cat. No. 7404002) into collection vials.

Chemical Oxygen Demand (COD) Analysis. COD was analyzed using the Accutest mercury-free Micro-COD System® (Bioscience, Inc., Bethlehem, PA). Potassium biphthalate (KHP) (Spectrum Chemical Co., Redondo Beach, CA), was used as a COD standard. Absorbance of KHP standards of known concentrations were measured and the COD in mg O₂/L was calculated using the stoichiometric relation between KHP and oxygen (Eqn. 1). A calibration curve was prepared to determine COD levels in the samples taken from the reactor.



Biological Oxygen Demand (BOD) Analysis. The initial microbial seed for BOD analyses was prepared using Polyseed® BOD Seed Inoculum (Interbio, Woodland, TX). An enrichment culture acclimated to growth on diluent was prepared from Polyseed® and used as the seed for all BOD measurements. Each 60 mL BOD bottle (Wheaton, Millville, NJ) contained 10 mL of reactor effluent sample, 2 mL acclimated seed inoculum, 12 μL of concentrated buffered mineral solution (Hach, Loveland, CO) and dilution water. The dissolved oxygen (DO) concentration in each bottle was measured using a portable DO meter with a self-stirring, polarometric DO probe (YSI, Yellow Springs, OH). The BOD bottles were incubated at 20°C for five days. DO measurements were repeated every twenty-four hours for five days, and the BOD₅ was calculated from the observed O₂ depletion.

RESULTS

To investigate the effectiveness of photocatalysis as a pretreatment to biodegradation, photoreactor experiments were run for eight hours, analyzing COD and BOD₅ of reactor effluent at 1 hr intervals. The feed used in the photoreactor experiments was either de-ionized water saturated with diluent or simulated groundwater saturated with diluent. Diluent-saturated de-ionized water was tested to evaluate the effect of photocatalysis on biodegradability without the influence of common inorganic ions. Simulated groundwater was tested to determine if common groundwater ions, particularly bicarbonate ions, had any

adverse effects on the rate of photocatalytic oxidation of diluent. The ratio of BOD₅/COD was used as a measure of the biodegradability of the photooxidized oxidized diluent. Preliminary experiments indicated that photocatalysis rates were 50% lower with nitrogen sparging compared to air sparging (data not shown). This agrees with a previous study that investigated the effects of dissolved oxygen on photocatalytic reaction rates (Hsiao et al., 1983). Although photocatalysis was slower under a nitrogen atmosphere, these results indicate that oxygen is not absolutely necessary for photocatalysis under these conditions. Since groundwater conditions are likely to be anoxic, all subsequent experiments were conducted with nitrogen sparging.

For diluent dissolved in de-ionized water, the COD of the photoreactor effluent decreased significantly (Figure 1) while the BOD₅ increased significantly (Figure 2) over the course of the eight-hour experiments. The BOD₅/COD ratio increased substantially over the eight-hour photoreactor run (Figure 3). Results for diluent in simulated groundwater were similar to the de-ionized water experiments, with COD of the photoreactor effluent decreasing significantly (Figure 1) and the BOD₅ increasing significantly (Figure 2). For the simulated groundwater experiment, the BOD₅/COD ratio increased linearly to over 9 times its initial value (Figure 3).

First order kinetics accurately modeled the COD data for both the de-ionized water and simulated groundwater experiments ($R^2 = 0.93$, $p < 0.0001$), while zero order kinetics more accurately modeled the BOD₅ data measured during the first 5 days ($R^2 = 0.85$, $p < 0.0004$) for each of the experiments. Table 1 summarizes the first order and zero order rate constants from the COD and BOD₅ analyses of the photoreactor runs. COD rate constants from a control without UV light and a control without TiO₂ are also shown for comparison. The rate constants from the controls are very low compared to the rate constants from the photoreactor experiments with both UV and TiO₂. BOD₅/COD data followed zero order kinetics ($R^2 = 0.95$, $p < 0.00001$). The zero order BOD₅/COD rate constant for diluent in simulated groundwater was slightly higher than that for diluent in de-ionized water, indicating that the common inorganic ions present in the simulated groundwater had no detrimental effect on the rate of photocatalytic oxidation. These rate constants are also given in Table 1.

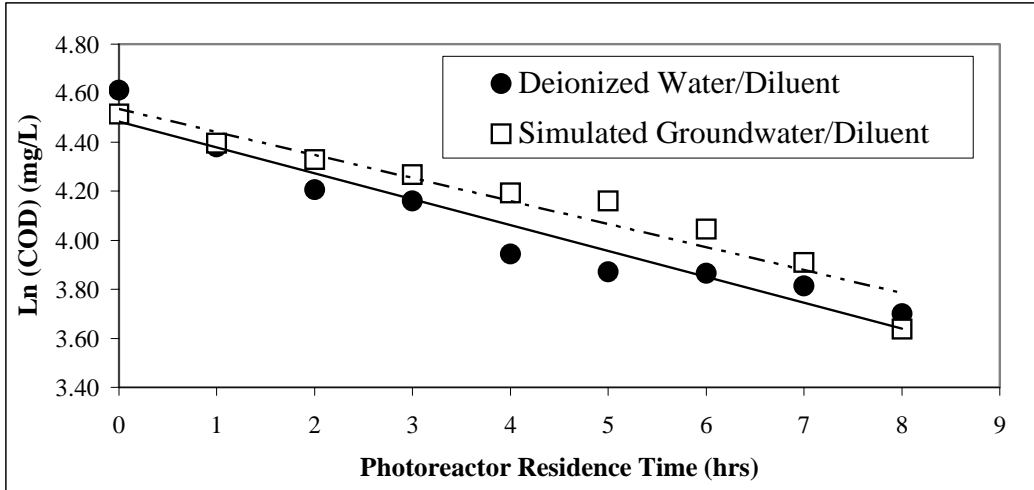


FIGURE 1. COD of photoreactor effluent for experiments with diluent in deionized water and simulated groundwater. Note the log scale for COD. These semi-log plots were used for the determination of first order rate constants.

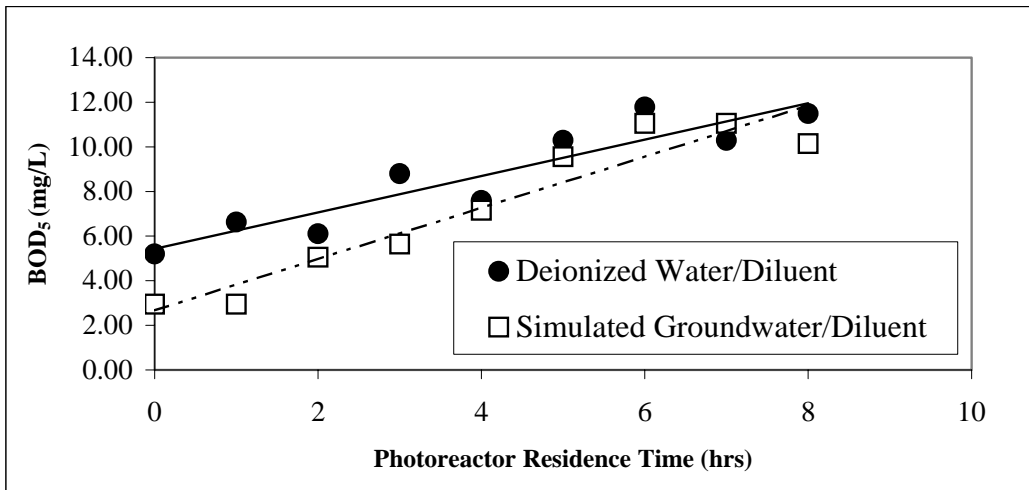


FIGURE 2. BOD₅ Analysis of Photoreactor Effluent from Diluent Saturated De-ionized Water and Simulated Groundwater Experiments.

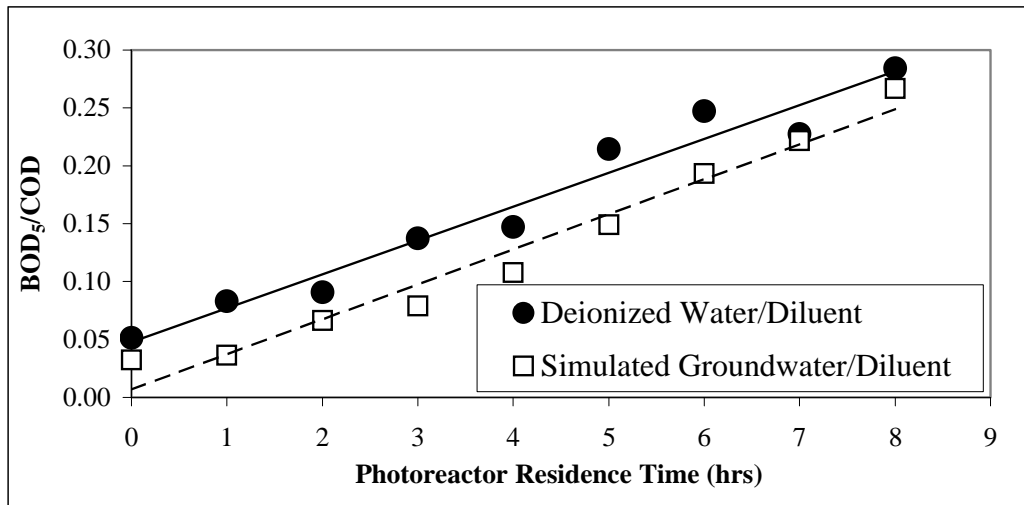


FIGURE 3. BOD₅/COD Analysis of Photoreactor Effluent from Diluent Saturated De-ionized Water and Simulated Groundwater Experiments.

TABLE 1. Summary of COD, BOD₅ and BOD₅/COD Rate Constants for Each Photoreactor Experiment.

Photoreactor Experiment with Diluent Saturated Water	COD First Order Rate Constants (mg/L*hr)	BOD ₅ Zero Order Rate Constants (mg/L*hr)	BOD ₅ /COD Zero Order Rate Constants (1/hr)
De-ionized Water	0.1053	0.818	0.0292
Simulated Groundwater	0.094	1.15	0.0303
No UV Control	0.0261	-----	-----
No TiO ₂ Control	0.0125	-----	-----

DISCUSSION

Gilbert (1987) studied the effect of prior ozonation on the biodegradability of twenty-eight organic compounds and concluded that oxidation was sufficient for rapid biodegradation when the BOD₅/COD quotient reached at least 0.4. Thus, an optimally designed photocatalytic pretreatment would utilize a reaction time capable of increasing the BOD₅/COD ratio to 0.4. In the current study, the BOD₅/COD ratio for the diluent increased five fold over the eight-hour experiment, but only reached a maximum of 0.3 during this time frame. Using the kinetic parameters obtained in this study, the data were extrapolated and it was estimated that it would take approximately 12 hours to reach a BOD₅/COD ratio of 0.4 under these conditions.

Results of the photocatalysis experiments are encouraging because they indicate that the process is feasible under typical groundwater conditions. The observation that photocatalysis is only inhibited by 50% under nitrogen compared to air is an indication that the process is viable even under the anoxic conditions that exist in the subsurface. Also, it is apparent that groundwater ions, such as

bicarbonate, do not inhibit the photocatalytic degradation of hydrocarbon contaminants present in diluent contaminated groundwater, as confirmed with the simulated groundwater experiment. In fact, the photocatalysis rates and final biodegradability quotient (BOD_5/COD) were higher for the simulated groundwater than for diluent dissolved in de-ionized water.

It is important to note that these experiments were carried out in a slurry reactor with TiO_2 particles in suspension. In such a reactor, the overall reaction rate is limited by surface transformations and not mass transfer. In other reactor configurations or in an *in-situ* treatment application, reaction rates may be limited by mass transfer and, thus the time required to reach a BOD_5/COD ratio of 0.4 could be higher.

The kinetic data obtained in these experiments can be used to estimate design parameters for *ex-situ* (pump and treat) and *in-situ* remediation applications. An *ex-situ* system can be envisioned that consists of a packed-bed solar array photoreactor followed by an attached-film bioreactor for final biodegradation of the hydrocarbon contaminant. The proposed photoreactor is a fixed-bed reactor packed with TiO_2 coated silica gel, as described previously (Crittenden et al., 1996). The UV flux in such a system is about 600 times greater than that employed in these laboratory experiments. Based on this UV flux and first-order COD kinetics from the simulated groundwater experiments, the photoreactor retention time required to increase the BOD_5/COD ratio to 0.4 would be 1.4 min (based on an initial BOD_5/COD ratio of 0.03). Thus, for example, a pump and treat system for groundwater saturated with diluent and operating at a flow rate of 20 L/min would require an effective photoreactor volume of 28 L. The bioreactor stage can be designed based on the experimentally observed first order BOD degradation kinetics ($k = 0.096$ mg/L-day). Assuming a maximum biomass concentration of 14 g/L (Shieh and Keenan, 1986), the bioreactor retention time required to reduce the contaminant concentration below 5 ppb would be 6 hr. Thus the example design flow rate of 20 L/min would require a bioreactor volume of 7200 L.

In-situ application of this hybrid technology would require bringing contaminated water into contact with UV light in the saturated zone of the contaminated aquifer. One way to accomplish this would be to bury fiber optic cables coated with TiO_2 in a subsurface reactive barrier as described by Peill and Hoffmann (Peill and Hoffmann, 1995). The required thickness of this reactive barrier will depend on photocatalysis kinetics and groundwater velocity. For a groundwater velocity of 50 m/yr (as observed at the field site), the required barrier thickness would be extremely thin (approx. 0.1 cm) based on the calculated retention time. However, a practical design would have to account for the lack of solar radiation for up to 16 hrs/day. Thus, a prudent design would employ a retention time of 16 hrs, increasing the required barrier thickness to 8 cm for this site. A practical remediation scheme could use a funnel and gate system with impermeable barriers funneling contaminated groundwater into the photoreactive barrier. Subsequent biodegradation of oxidized contaminant would be mediated by natural soil microbes down-gradient from the reactive barrier. Based on BOD degradation rates observed in the laboratory, the 50 m/yr groundwater velocity,

and a soil microorganism concentration of 1 g/L soil, the distance required to reach 5 ppb would be only 40 cm. Of course, actual biodegradation rates will be considerably slower in the anaerobic groundwater environment. These illustrative calculations are very approximate, but indicate that the proposed hybrid treatment system is potentially feasible for both *ex-situ* and *in-situ* remediation.

CONCLUSIONS

The objective of this project was to determine the feasibility of a hybrid photocatalysis/biodegradation treatment approach to remediating groundwater contaminated with hydrocarbon diluent. Results indicated that photocatalytic pretreatment was successful in increasing the biodegradability of the hydrocarbon diluent in contaminated de-ionized water and in contaminated simulated groundwater. Chemical oxygen demand of the photoreactor effluent decreased by an average of 50% over the course of the eight-hour experiments, while the biological oxygen demand of the effluent rose by 2-3 times its original value for both deionized water and simulated groundwater experiments. The BOD₅/COD ratio, which was used as a measure of biodegradability, increased linearly from initial values of 0.03 and 0.06 to final values after eight hours of 0.27 and 0.29 for the simulated groundwater and de-ionized water experiments, respectively. Extrapolation of the linear regression equation was used to estimate the reaction time required to reach a BOD₅/COD ratio of 0.4. It was estimated that a ratio of 0.4 would be reached after a photoreactor retention time of 12-13 hours. It is at this point that biodegradability is considered acceptable for bioremediation. Additional control experiments were done without titanium dioxide and without ultraviolet light. As expected, contaminant oxidation was very slow in these experiments, confirming that the observed reductions in COD were the result of TiO₂-catalyzed photo-oxidation.

Photo-oxidation rates with nitrogen sparging were 50% lower than rates observed with air sparging. Although this reduction in rate is significant, these results indicate that photocatalytic oxidation under anoxic groundwater conditions is possible. Furthermore, dissolved ions at concentrations typical in groundwater did not inhibit photocatalytic oxidation. The success of these experiments indicates that *in situ* groundwater treatment using photocatalysis could be accomplished without the need for air sparging of the groundwater.

Finally, potential *ex-situ* and *in-situ* remediation designs were presented based on the observed photocatalysis and biodegradation kinetics. While these designs are preliminary, they indicate that photocatalysis pretreatment has potential in both scenarios, thus warranting further research in the application of this hybrid technology.

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