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ENGINEERING-SCALE EXPERIMENTS OF SOLAR PHOTOCATALYTIC OXIDATION OF TRICHLOROETHYLENE*

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ABSTRACT

A photocatalytic process is being developed to destroy organic contaminants in water. Tests with a common water pollutant, trichloroethylene (TCE), were conducted at the Solar Thermal Test Facility at Sandia with trough systems. Tests at this scale provide verification of laboratory studies and allow examination of design and operation issues that only arise in experiments on a realistic scale. The catalyst, titanium dioxide (TiO_2), is a harmless material found in paint, cosmetics and even toothpaste. We examined the effect of initial contaminant concentration and the effect of hydrogen peroxide on the photocatalytic decomposition of trichloroethylene (TCE). An aqueous solution of 5000 parts per billion (ppb) TCE with 0.1 weight% suspended titanium dioxide catalyst required approximately 4.2 minutes of exposure to destroy the TCE to a detection limit of 5 ppb. For a 300 ppb TCE solution, the time required was only 2.5 minutes to reach the same level of destruction. Adding 250 parts per million (ppm) of hydrogen peroxide reduced the time required by about 1 minute. A two parameter Langmuir Hinshelwood model was able to describe the data. A simple flow apparatus was built to test four fixed catalyst supports and to measure their pressure drop and assess their ability to withstand flow conditions typical of a full-sized system. In this paper, we summarize the engineering-scale testing and results.

BACKGROUND

Photocatalytic processes have the potential to destroy organic pollutants in large volumes of water using sunlight as the light source. Photocatalytic oxidation of dilute aqueous solutions of organic compounds has been investigated extensively for about a decade and a half [1-16]. Ollis [1] and Matthews [2] have shown that sunlight and titanium dioxide catalyst can completely oxidize organic chemicals. Examples of organic compounds that can be destroyed by this process are chlorinated solvents, polychlorinated biphenyls (PCBs), dioxins, pesticides, and dyes. This process can completely minerized these organics yielding only carbon dioxide, water, and dilute mineral acids (e.g., HCl) as the final oxidation products [1-10]. An advantage of this process over conventional treatment methods such as air stripping or carbon adsorption is that the contaminants are completely destroyed rather than transferred from one phase or medium to another.

At Sandia National Laboratories, we have demonstrated destruction of a chlorinated solvent, TCE, using titanium dioxide catalyst and concentrated sunlight as the light source reflected from a 465 m^2 trough system. With this process, water containing low concentrations (ppm range) of contaminants and the suspended semiconductor photocatalyst titanium dioxide (TiO_2) flows through a glass pipe reactor mounted at the focus of the trough. The titanium dioxide absorbs high-energy photons from the incident sunlight to produce surface holes and electrons that react with dissolved oxygen or oxidants in the water to generate hydroxyl radicals and superoxide ions [4,5].

Previous experiments with our trough system have demonstrated destruction of salicylic acid and TCE [14-16]. This paper is a continuation of that work, focusing on establishing the effects of process variables such as initial TCE concentration and hydrogen peroxide on the reaction rates. These effects were investigated to determine reaction rates over the ranges expected in actual systems. We also screened possible fixed catalyst supports by assessing their activity and pressure-drop flow characteristics. A fixed catalyst is needed to eliminate suspension, filtration and recovery of the catalyst. The goal of this work, a joint program between Sandia and the Solar Energy Research Institute, is to demonstrate and field test the technology at a remediation site.

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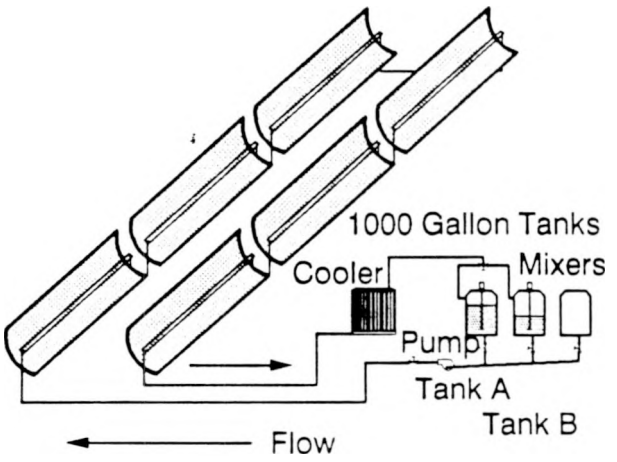

Figure 1. Large outdoor trough system (465 m^2) measuring 218 m long by 2.1 m wide with a 38 mm I.D. borosilicate glass pipe. Incident sunlight is concentrated about 50 times.

SYSTEMS AND METHODS

Engineering Scale Parabolic Trough

Photocatalytic experiments were conducted with a system consisting of a series of six parabolic troughs with a 38 mm (1.5 in) I.D. diameter borosilicate glass pipe mounted at the focus to serve as a photoreactor. Figure 1 is a schematic of this system. The troughs have aluminized surfaces that reflect approximately 70% of the incident solar ultraviolet energy (300-400 nm) and concentrate the direct normal solar energy about fifty times. The system can be operated in either batch or single pass modes at flow rates up to 100 liters per min (25 gallons per minute) with two 4000 liter (1000 gallon) tanks used for reservoirs of test solution and one 4000 liter (1000 gallon) tank for holding clean water. The residence time for one pass is about 2.5 minutes at the maximum flow rate. The total reactor length is 218 m (720 ft) and the total aperature area of the trough is 465 m^2. Samples can be withdrawn at each 36.4-m (120 ft) section and from the tanks.

Flow Apparatus for Measuring Pressure Drop

A fixed catalyst support is necessary to eliminate the need to suspend, recover and filter the catalyst from the water. Pressure drop is a major concern (because of strength limitations of the glass) in the development of catalyst supports for solar photocatalytic systems. A water flow system was built to measure pressure drop as a function of flowrate for proposed materials and assess the ability of the materials to withstand typical flow conditions. The flow system consists of a recirculating water loop, control valve, flow indicator, and differential pressure transducer. The loop includes a 66 mm (26 in) long by 38 mm (1.5 in) diameter glass pipe (same piping used in the troughs) in which 24 inches of support material is placed for testing. With the support in place, the pressure drop across the support can be recorded for a range of flow rates from 7 to 115 liters/min (2 to 30 gpm).

Four types of fixed catalyst supports were flow tested. The four types of supports consisted of: 1) a porous reticulated alumina ceramic, 2) a helical teflon spiral wrapped with fiberglass fabric, 3) a static mixer also wrapped with fiberglass fabric and 4) a fiberglass screen coiled with spacers. The fiberglass mesh and ceramic are easily coated with TiO_2.

Materials

The TiO_2 photocatalyst (Degussa P-25, primarily anatase) had an average particle size of 30 nm. Surface analysis determined the surface area to be 53.5 m^2/gram with the majority of the area being provided by meso-pores (large pores 20 - 500 angstroms). Trichloroethylene was Fisher brand reagent grade. Hydrogen peroxide was also used as an oxidant in some tests.

Analysis

Analysis of trichloroethylene concentration was performed with a Hewlett-Packard Model-5890 gas chromatograph equipped with an automated headspace sampler (HP-19395A), tandem PID/ELCD detectors (IO Corporation), and a HP 530u series capillary column coated with an HP-1 crosslinked methyl silicone gum (30 m x 0.53 mm x 2.65 um films). The TCE detection limit for this system is approximately 5 parts per billion (ppb).

EXPERIMENTAL RESULTS

Effect of Initial TCE Concentration

The initial concentration of TCE in the water was varied from approximately 120 to 5000 ppb to assesses its effect on the reaction rate. A catalyst loading of 0.1wt% was used. The tests were run within 1.5 hours of solar noon and the direct normal insolation was above 1000 W/m^2. Results from these tests are shown in Figure 2. In these tests, no intermediates were detected.

In all cases, the curves show a change in the order of the reaction from zero-order to first order. This transition has also been seen by other researchers and can be described by Langmuir-Hinshelwood type kinetics. The formulation of the Langmuir-Hinshelwood kinetic expression is:

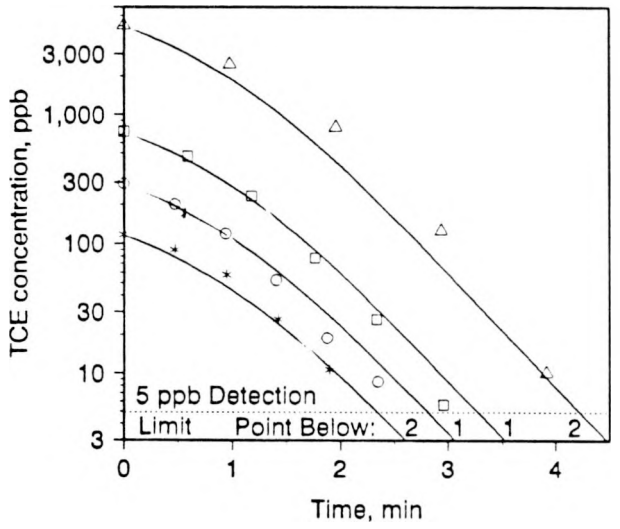

Figure 2. Destruction of TCE at various initial concentrations with 0.1 % TiO_2.

$$\frac{d(C/C_o)}{dt} = \frac{-k\ K\ C/C_o}{1 + K\ C/C_o} \quad (1)$$

where C is the concentration of the reactant (trichloroethylene), k is the reaction rate constant and K is the equilibrium coefficient. Integration of equation 1 yields:

$$\ln(C/C_o) + K(C/C_o - 1) = -kKt \quad (2)$$

which is an implicit function of concentration and represents a sum of zero- and first-order terms. All the data in Figure 2 can be described by equation (2) with two parameters. The values of these two parameters, k and K, are 1.3 min^{-1} and 1.5 (unitless), respectively.

Several physical interpretations which give rise to the Langmuir-Hinshelwood type formulation are possible. In one case adsorption and desorption of the TCE to produce a surface intermediate important in the path way from dissolved TCE to final products is possible. This explanation has been used by other researchers [13]. Another possibility is that preadsorption of the sites by the reactant or involvement of an unseen dissolved or surface intermediate may be responsible. In the tank prior to exposure to sunlight, the reactant could saturate sites on the catalyst. As the solution enters the reactor, the adsorbed species must be oxidized before first-order reaction can take over. More laboratory research is necessary to pinpoint the actual cause for the observed TCE profiles.

Despite the complexities of the kinetics, an important parameter in the design of a solar photocatalytic

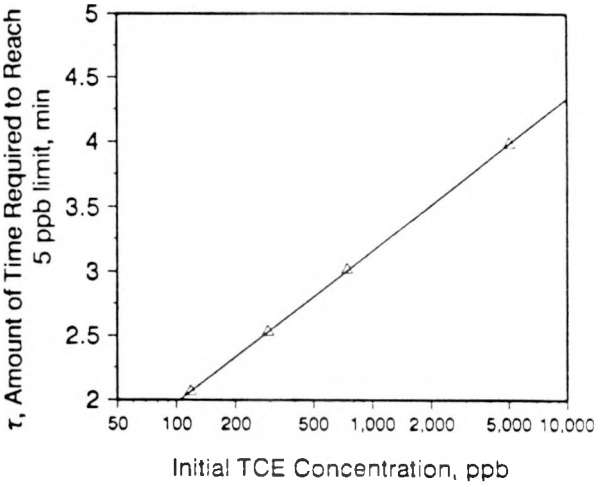

Figure 3. Amount of time required to reach EPA regulated (and detection) limit of 5 ppb for various initial concentrations. Trough aperature: 2.1 m.

water treatment system is the amount of time required to achieve a certain level of destruction given the initial concentration of the contaminant. Figure 3 is a plot of the amount of time required to reach the Environmental Protection Agency's regulated effluent limit of 5 ppb which is also the detection limit of our gas chromatograph versus the initial TCE concentration. As can be seen from equation (2) and the figure, the amount of time required is a weak empirical function of initial TCE concentration.

Effect of Hydrogen Peroxide on the Destruction of Trichloroethylene

The effect of hydrogen peroxide on the destruction TCE was evaluated at a TCE concentration of about 2000 ppb. Hydrogen peroxide has been shown in the literature to enhance the photocatalytic destruction of TCE with illuminated TiO_2 [12]. This effect is being investigated to assess its potential to increase the throughput of the system.

Figure 4 shows runs with 0.1 wt% TiO_2 alone and with 250 ppm hydrogen peroxide. As can be seen from the results, hydrogen peroxide tended to increase the decomposition rate of TCE and yielded first-order kinetic behavior from the onset. With hydrogen peroxide, the initial zero-order transient period is not seen. If peroxide accelerates the oxidation of the adsorbed species, this would lend support to the argument that the inhibition is due to preadsorption of TCE. This is collaborated by the fact that in both runs the final slope is approximately the same.

Pressure Drop of Potential Fixed Supports

The pressure drop of a catalyst support plays an important part in the configuration of a trough

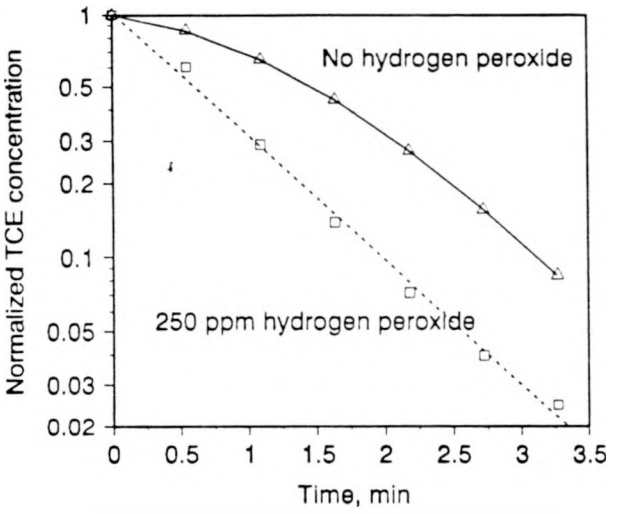

Figure 4. Effect of hydrogen peroxide on the destruction of trichloroethylene with 0.1wt% TiO_2.

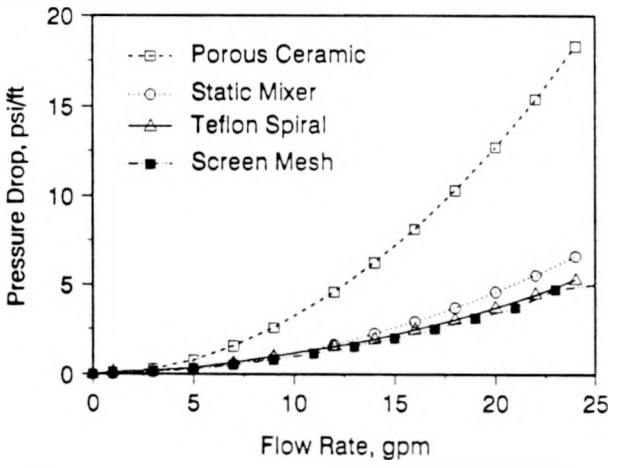

Figure 5. Pressure drop across four catalyst support materials as described in the text.

system because the strength of the glass piping limits the maximum pressure of the system. For example, the glass piping used in the trough system can withstand a maximum pressure of approximately 60 psi which presents a constraint on the length and flow capacity of the reactor.

Four potential catalyst supports were flow tested to determine the pressure drop across the supports. The four supports were: 1) a porous reticulated alumina ceramic, 2) a helical teflon spiral wrapped with fiberglass fabric, 3) a static mixer also wrapped with fiberglass fabric and 4) a fiberglass screen coiled with spacers. The pressure drops for the supports are shown in Figure 5. As can be seen from the figure, the screen mesh has the lowest flow resistance followed closely by the teflon spiral and the static mixer. The porous alumina ceramic had the highest pressure drop. Even for the support with the lowest flow resistance, the pressure drop limits the length and flow rate of the system. As a example of this limitation, using a static mixer configuration and one section of trough 36.3 m (120 ft) long, the maximum flow rate is approximately 23 liters per minute (6 gallons per minute) for glass that can operate at a maximum pressure of 60 psi. Provided that the flow rate can be controlled to allow the necessary residence time (as dictated by the kinetic data), the configuration would be suitable and desired throughput would determine the number of troughs required.

In addition to pressure drop constraints, a fixed catalyst support must have sufficient mass transfer characteristics and suitable optical properties to allow light to penetrate into the support. A volumetric support which also enables intimate contact of the solution with the catalyst or a support that forces the flow through the illuminated catalyst (such as the static mixer/catalyst coated fiberglass mesh) is most desirable.

CONCLUSION

We have examined the effect of initial reactant concentration and the effect of hydrogen peroxide on the photocatalytic decomposition of TCE. We found that the amount of time required to achieve a destruction to the regulated limit is a weak function of the initial TCE concentration. We also found that hydrogen peroxide can reduce the time required to reach a desired level of destruction.

Four potential catalyst supports were flow tested to measure their pressure drop and assess their ability to withstand flow conditions typical of a full-sized system. Three of the supports can yield acceptable pressure drop characteristics by arranging the troughs in a parallel rather than series configuration.

We plan to address a number of additional issues before this process is field tested. Catalyst immobilization (eliminating the suspension and removal of the catalyst particles), catalyst deactivation and regeneration, catalyst enhancements, reactor design, the effect of minerals found in ground water, optimal residence times and thus flow rates, the control requirements for a solar detoxification system, and optimal solar concentrations must be addressed to assess their effectiveness on the process and its economics. Also, experiments with real contaminated water must be conducted to assess the performance of the process under life-like conditions.

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