DETOXIFICATION OF TRICHLOROETHYLENE (TCE) USING SOLAR LIGHT/TiO₂ IN A UV CONCENTRATING RADIATION SYSTEM

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ABSTRACT

There has been considerable interest in photocatalytic oxidation of recalcitrant contaminants using titanium dioxide (TiO₂) in recent years. A solar-driven, photocatalyzed detoxification system using TiO₂ was constructed, and this system was applied for the degradation of trichloroethylene (TCE) contaminated water. The results showed that, with both UV light illumination and TiO₂ present, TCE was more effectively degraded than with either UV or TiO₂ alone. A 50ppm of TCE could be completely degraded in 3 to 4 hours of solar light illumination. Photocatalytic degradation of TCE increased linearly with increasing sunlight intensity. The degradation of TCE also increased with increasing TiO₂ dose, however, the degradation efficiency reached a plateau over 0.2 wt% of TiO₂ dose. The mass balance study showed that about 80% of chloride was recovered as TCE degradation byproducts. Finally, the experiment was performed in order to examine the deactivation of TiO₂ due to the adsorption of TCE during consecutive runs, but no reduction in the activity of TiO₂ was observed after the deionized water regeneration.

KEYWORDS

TCE, UV concentrating system, solar light, TiO₂, photocatalysis, UV, chloride

INTRODUCTION

Increasing public awareness and government regulations have fostered the need for effective and cost efficient technologies to remediate environmental pollution. Photocatalysis offers an important potential in the treatment of water and wastewaters because the process is relatively rapid, capable of simultaneously degrading a wide range of contaminants, and potentially cost competitive with existing technologies (Vidal *et al.*, 1999). TiO₂ (anatase) has an energy bandgap of 3.2 eV and is capable of activation by near UV-light with wavelengths up to 388nm. This absorption corresponds to between 3 and 4% of the solar spectrum (Raquel *et al.*, 1996). Although this is a small fraction of the spectrum, many studies have been carried out to develop an efficient method for using natural solar radiation to

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destroy toxic organic compounds (Raquel *et al.*, 1996; Vidal *et al.*, 1999) and to reduce toxic metals (Cho *et al.*, 2002).

The widespread presence of chlorinated hydrocarbons such as trichloroethylene (TCE) and perchloroethylene (PCE) in both natural and drinking waters poses a potentially serious environmental problem, since they may be carcinogenic and/or toxic. They are readily removed from groundwater using well pump in one-pass solar detoxification system (Pacheco *et al.*, 1993) and contaminated surface water can be treated in a UV concentrating radiation System (Yves *et al.*, 1996). In this process, major toxic compounds are mineralized to CO₂, H₂O and mineral acids such as HCl, instead of simply transferring them to another medium (Ahmed *et al.*, 1984; Glaze *et al.*, 1993).

The purpose of our study is to investigate the feasibility of the solar detoxification using TiO₂ for degrading TCE contaminated water. The effects of solar light intensity, TiO₂ concentration on the degradation rate of TCE, and the byproducts from the TCE degradation were examined.

MATERIALS AND METHODS

TCE (99+%) was obtained from Aldrich Chemical Co, and the TiO₂ used was Degussa P-25, which was mostly anatase and had a BET surface area of 50-m²/g and an average particle diameter of 30 nm. The extraction solvents used in this study were n-hexane (Burdick and Jackson, GC quality). pH adjustments were made using 0.1 N perchloric acid (Aldrich, 99.999+%), chosen for its low level of phosphate and iron contaminants, and 0.1N sodium hydroxide (Reagent Grade).

The solar light was used instead of artificial UV light in this study. First, we designed and constructed the 1.2-m² UV concentrating radiation systems (Figure 1). This module is 1.5m (long) x 0.8m (wide) with UV-transparent tubular receivers. The acceptance angle for the CPC is 52° either side of normal incidence. The polished aluminum was used as the reflective material because it is highly reflective in the UV range (300-380 nm) and quartz tube was used for tube receiver because it has excellent UV stability and transmissivity. Then, 8 modules are connected in series and the water flow (5L/min) directly from one to the other and finally to the reservoir tank. A rotary pump (Cole-Parmer Instrument Co.) was continuously recirculating the suspension to a batch vessel and the solar reactor by silicon pipes. Solar light intensity was measured using a Radiometer (VLX-3W Radiometer 9811-50, Cole Parmer Instrument Co.) at 365nm (UV-A region) at the same inclination angle to the plate.

All the experiments, unless specified, were performed under the circumstance of random weather conditions, between 10 a.m. and 4 p.m., at the Seoul National University campus located in Seoul, Korea (38°N latitude). The operation conditions are shown in Table 1.

Table 1. The operation conditions and analysis specifications (GC/ECD conditions)

Operation conditions	
Total sample batch volume	5L
Effect reactor volume	2.88L
Initial pH	7.0
Gas Chromatograph conditions	
Column	30m × 0.25mm × 0.25 μ m HP-2 fused-silica capillary column
Injection temperature	150 ~250°C
Column temperature	60~100 °C
Detector temperature	250 °C

At regular time intervals, the aliquots were withdrawn through the three-way valves. First, chloride ion production was monitored *in situ* with a specific chloride electrode (HNU System and Orion Model 701A pH/mV meter). The electrode was calibrated with HCl solutions to account automatically for the pH decrease from HCl formation. Before and during the reaction, the samples were withdrawn from the reactor with the spring-loaded adjustable syringe (10mL), and then immediately transferred to a 40ml EPA vials containing 5ml of cold n-hexane. After mixing with a mechanical mixer, TCE in the hexane layer was analyzed by split injection gas chromatography/electron capture detection(GC/ECD) (Hewlett-Packed HP 5890). To confirm the byproducts from TCE photocatalysis, some extract fractions were also analyzed by GC/MS (Hewlett-Packed HP 5890) operated in the electron impact mode, which used the same column and temperature program as described above Table1.

RESULTS AND DISCUSSIONS

First, the control experiments were carried out in order to examine the effect of dark reaction (the effect of adsorption of TCE on the TiO₂ powder), as well as the photolysis of TCE by solar radiation only in the absence of TiO₂. Figure 2 showed the degradation ratio of TCE as the function of exposed time for the control experiments (solar light alone and TiO₂ alone).

Figure 1. Schematic diagram of photocatalytic solar reactor

The dark reaction was initially carried out by injecting a sampling of TCE into the slurry of TiO_2 to given a final solution of 50 ppm TCE. The run in the dark condition (TiO_2 alone) showed about 20% of TCE degradation after 6 hours, but no chloride was produced. This result indicates that a portion of TCE was not degraded, but adsorbed onto TiO_2 particles. As another control experiment, a 50ppm TCE solution was circulated in a TiO_2 -free reactor, which was exposed to solar light. The reaction was run from 10 a.m. to 4 p.m., on a sunny day. Under this condition, the TCE removal efficiency was found to be about 15%, and about 5ppm of chloride (10% of initial amount of chloride in TCE) was produced. This result implicates that TCE undergoes photolysis, but not significantly.

Next, a 50-ppm TCE solution was circulated in the solar reactor, with TiO_2 , and exposed to sunlight on a clear day, to examine the effect of TiO_2 photocatalysis. Figure 2 also shows the degradation of the TCE with TiO_2 photocatalysis. It was shown that the TCE was completely removed within 5 hours, with a chloride production yield of approximately 85%. The result means that the major fate of TCE is to undergo the mineralization, due to the loss of chloride from the TCE molecule.

Figure 2. The effect of control conditions (solar light only and TiO_2 only), and photocatalytic condition on the degradation of TCE and chloride production (as HCl) (Experimental conditions; 50 ppm TCE, pH 7, Flow rate = 5L/min, 0.1 wt% TiO_2).

Effect of the TiO_2 regeneration

We conducted an experiment that used TiO_2 particle at the end of a single day runs, which was filtered out using an aspirator, washed with 1 liter of deionized water, and reused in the subsequent run. This procedure was repeated during consecutive runs. As shown in Figure 3(a), the weather conditions were consistently clear (sunny day), with the exception of December 9 (partly cloudy). Under these weather conditions, Figure 3(b) shows that more than a 90% TCE degradation was achieved after 4 to 5 hours during the runs, with a chloride yield of 80~85%, which remained constant during all experiments. On December 9th, the TCE degradation and chloride production showed slower reactions than under the other conditions, which is probably due to the partly cloudy weather conditions. This result implicates

that activity of the TiO_2 used in the system was maintained following deionized water regeneration.

Figure 3. The effect of TiO_2 regeneration; (a) UV intensity at 365 nm during the test days (b) exposed time (min) vs. TCE degradation ratio and chloride production (Experimental conditions; 50 ppm TCE, pH 7, Flow rate = 5L/min, 0.1wt% TiO_2).

Effect of TiO_2 dosage

The six different TiO_2 dose concentrations (0.1, 0.15, 0.2, 0.3, 0.4 and 0.5 wt%) were applied to the solar reactor on different days. During these runs, the weather was consistently clear, and the light intensity changed from 0.6 to 1.75 mW/cm² at UV_{365nm} between 10 a.m. and 4 p.m. We measured the pseudo-first order rate constant values of the TCE degradation, with the changes in the TiO_2 concentration using linear regression analysis, and the result are shown in Figure 3(a). We found that, at low loading from 0 to 0.2wt%, the degradation rate increased linearly with TiO_2 concentration, but there was no difference in reaction rate constant for TiO_2 loadings over 0.2 wt % loading.

Figure 4. The effect of TiO_2 on the TCE degradation and chloride production (a) plot of pseudo first order rate constant, k_{obs} , vs. TiO_2 dosage. (b) plot of the percent production of chloride vs. TiO_2 dosage.

These results indicate that a 0.2 wt% TiO₂ loading is sufficient to harvest all the incident light, and that there is no advantage to a loading above this value. Additionally, the chloride conversion of 75-85% was observed over a period of 360min in every TiO₂ concentration, as shown in Figure 4(b).

Finally, three chlorinated byproducts from the degradation of TCE were qualitatively identified from GC/MS analysis; and were dichloroacetic acid (DCAA), the methyl esters of dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA), respectively. They were confirmed by comparison of mass spectra and retention time with the library standards. The production of methyl esters from DCAA, and TCAA looks to be from the use of methanol solvent for dissolving TCE into the water.

CONCLUSION

The results indicated that the solar light/TiO₂ system could effectively treat TCE contaminated waters, and can save the cost of the electricity in the treatment system, and using no artificial UV light. One potential application of such a solar outdoor system might be for the *ex-situ* remediation of TCE contaminated groundwater or industrial waste streams.

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