

Counter-Flow Silica-Titania Reactor for the Simultaneous Treatment of Air and Water Contaminated with VOCs

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ABSTRACT

The photocatalytic oxidation of VOCs was investigated using a novel countercurrent flow reactor designed to enable the treatment of toluene present in the gas and the aqueous phases simultaneously. The reactor was packed with silica-titania composites commingled with plastic pall rings. Using this mixed packing style was advantageous as it resulted in a higher UV penetration throughout the reactor. The average UV intensity in the reactor was determined to be 220 $\mu\text{W/g}$ irradiated TiO_2 . It was found that under dry conditions, the STCs had a high adsorption capacity for toluene; however, this adsorption was completely hindered by the wetting of the STCs when the two phases were flowing simultaneously. The destruction of toluene in the aqueous phase was determined to follow a linear trend as a function of the contaminant concentration. In the presence of both phases, toluene destruction was only observed under conditions in which the solution was initially supersaturated with respect to the gas phase. Under these conditions, the net destruction of toluene in the system reached a maximum of 68%. For the most part, the destruction occurred in the aqueous phase, and it was observed that high gas phase flowrates could be detrimental to the toluene destruction in the two phase reactor. The operating conditions in the system could be optimized to achieve improved destruction in the presence of both phases compared to the aqueous phase only.

INTRODUCTION

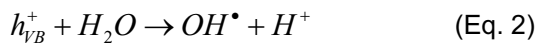
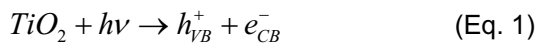
Many volatile organic compounds (VOCs) are currently regulated as water and air contaminants because of the threat they pose to human health and the environment

(USEPA, 2007). Common treatment technologies to remove VOCs from air or water are often mass transfer processes that do not eliminate the contaminants completely, but rather transfer them to another phase. Heterogeneous photocatalysis using titanium dioxide (TiO_2) irradiated with UV light can mineralize VOCs to CO_2 and water (Alberci and Jardim, 1997). Toluene was selected as the target compound for this study since it is representative of many volatile compounds because of its moderately high Henry's constant and it has been shown to be less reactive during photocatalysis with TiO_2 compared to other regulated VOCs (Blount et al., 2001). Despite its potential for eliminating contaminants, the feasibility for implementing this technology in large scale systems, particularly those that treat both air and water phases, has not been successfully demonstrated. A full size practical reactor configuration and catalyst support for such reactor to implement this technology have not been developed. The reactor needs to be both efficient at achieving the required removal and cost effective compared to currently available technologies. Several factors have impeded the design of effective photocatalytic reactors. Since heterogeneous photocatalysis requires UV irradiation to initiate the reactions, sufficient distribution of UV radiation inside the reactor that will activate most of the catalyst is of utmost importance. Another barrier to the development of the photocatalytic reactor is the incorporation of the catalyst inside the reactor. Several configurations, such as thin film coatings for the gas phase and slurries for the aqueous phase, have been used in lab-scale experiments, but most of them are usually inconvenient and expensive when considered for large scale systems (Crittenden et al., 1997; Maira et al., 2001). Finally, the reactor must be able to handle fluctuations in flowrates and concentrations that are typical in full-scale

applications (Ray, 1999). Accordingly, this work focused on the development and testing of a reactor designed with a twofold purpose: (1) enable the treatment of VOCs present in the gas and aqueous phases simultaneously, and (2) overcome two major difficulties that prevent the use of photocatalytic oxidation (PCO) systems in large scale applications by providing uniform UV distribution and a practical catalyst support.

THEORY

The initial process in heterogeneous photocatalysis, presented in Eq. 1, is the generation of electron-hole pairs in the semiconductor particles by the excitation of an electron with photons of energy, $h\nu$, greater than the bandgap energy ($h\nu > 3.2$ eV or $\lambda < 388$ nm for TiO_2). In this process, an electron from the conduction band (e_{CB}^-) is promoted to the valence band (VB), creating a hole in the VB (h_{VB}^+). The electron in the CB can act as a reductant while the hole in the VB acts as oxidant (Linsebigler et al., 1995). In the presence of water, hydroxyl radicals can be produced through reaction with the holes (Eq. 2). In the presence of air, e_{CB}^- may react with oxygen to produce other reactive species such as superoxide radicals (Eq. 3), among others. The highly reactive radicals can lead to complete degradation of the organic (or inorganic) compounds, by initiating an oxidation (or reduction) pathway (eg. Eq. 4) (Hoffmann et al., 1995).



EXPERIMENTAL METHODS

REACTOR DESIGN

The overall conceptual design of the reactor consists of three sections: a middle section that can treat VOCs simultaneously in the gas and aqueous phases and two end polishing sections to treat the remaining contaminants present in each phase individually. The end sections have been extensively studied by others, and these reviews can be found in the literature (Blake, 1999); and thus, were not a focus in this research; accordingly, the treatment of VOCs in air and water simultaneously, which has not been previously investigated, was the purpose of this work.

The preferred reactor configuration and setup, shown in Figures 1 and 3, comprises a photocatalytic packed tower that operates in a countercurrent flow mode. The tower consists of a clear PVC cylindrical column (20.3

cm in diameter and 1.8 m in length), equipped with a liquid inlet and distributor in the form of a spray nozzle at the top; a gas inlet and distributor in the form of a perforated plate at the bottom; liquid and gas outlets at the bottom and top, respectively; three gas sampling ports vertically aligned 30.5 cm apart on the wall of the column; five non-ozone producing UV lamps emitting UV-C radiation with a peak at 253.7 nm (Phillips, TUV 64T5 4P SE UNP) covered by quartz envelopes; and packing occupying 1.2 m of the total height of the tower. The colored fluid connections illustrated in Figure 1 represent the inlets and outlets for the liquid phase (in blue) and gas phase (in red).

The packing material was supported by the bottom perforated plate. The reactor was packed with composites made of titanium dioxide embedded in a silica matrix. The silica in the composites served as the TiO_2 catalyst support and can be casted in any desired cylindrical pellets size. Figure 2b shows the 9 mm diameter by 8 mm long pellets used in this study. These silica-titania composites (STCs) were commingled with plastic pall rings of 15 mm nominal diameter shown in Figure 2c (Rauschert Industries Inc.) to decrease the pressure drop through the reactor, increase the interfacial area available for mass transfer and increase the penetration of UV intensity. The commingled packing (Figure 2a) consisted of about 16% by bulk volume of STCs. The remaining volume was filled with plastic pall rings, which have a void fraction of 91%. The porosity of the tower, determined by dividing the volume of water required to completely fill the packed section of the tower by the empty volume of the same section was 0.71. The mass percentages were 55% and 45% of the total mass in the reactor for STCs and pall rings, respectively.

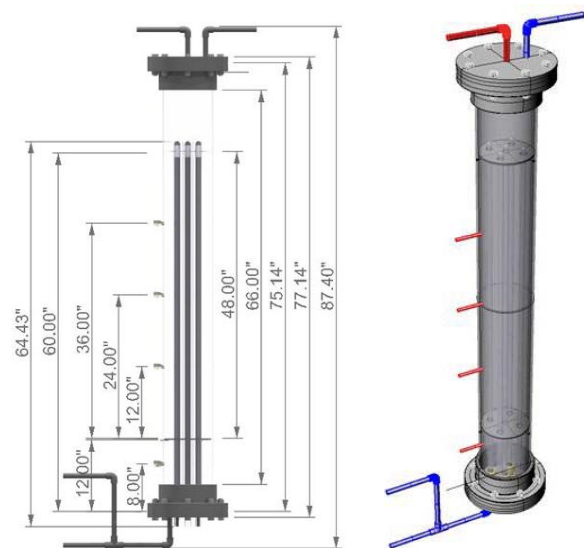


Figure 1. Two – phase photocatalytic countercurrent flow reactor. Dimensions are shown in inches (IPS).

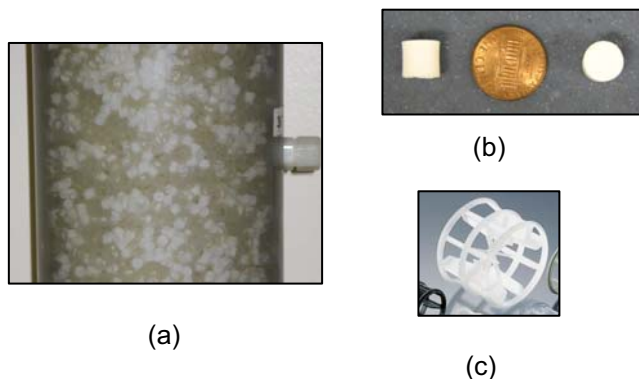


Figure 2. Packing materials used in the photocatalytic reactor. (a) Commingled packing. (b) Silica – titania composites. (c) Plastic pall rings.

During a typical experimental run, aqueous phase toluene (Fisher, Certified ACS grade, >99.5% purity) at concentrations ranging from 150 ppb to 2500 ppb entered the reactor at the top inlet. The water was pumped from a 200 L feed tank to the top of the reactor by a centrifugal pump (AMPCO, Model KC2). Gas phase toluene entered the reactor at the bottom inlet of the tower. Concentrated toluene (100-1000 ppm_v) from a compressed cylinder (Airgas) was diluted to approximately 1 to 10 ppm_v by mixing it with air from an air compressor (Coleparmer, Model 07047) before entering the reactor. Samples were taken from the inlets and outlets for air and water as well as the 3 sampling gas ports on the tower wall. Aqueous phase samples were collected in 40 mL VOA vials while tedlar bags (1L SKC Inc.) were used for gas phase samples.



Figure 3. Picture of the two – phase photocatalytic reactor and experimental setup.

SILICA-TITANIA COMPOSITES (STCs) SYNTHESIS.

The STCs were prepared by a sol-gel method using tetraethyl-orthosilicate (TEOS) as the silica precursor which has been described by others (Byrne et al., 2009; Pintoniak et al., 2003). By this formulation, nanopure water, ethanol (Fisher, 200 proof), TEOS, 1M nitric acid (diluted from Fisher, Certified ACS) and 3%_v hydrofluoric acid (diluted from 49% Fisher Certified ACS) were mixed in volume ratios of 12:6.25:9.25:1:1, respectively. While mixing, 115 mg of TiO₂ (Degussa P25) were added to the mixture per mL of TEOS to obtain STCs containing about 30%_{wt} TiO₂. The suspension was allowed to mix for 20 minutes before being transferred to assay plates for aging and drying. Aging consisted of keeping the assay plates containing STCs at room temperature for 3 days in air tight containers, followed by 3 days at 73°C and another 3 days at the same temperature but without the air tight seal. After aging, the STCs were placed in high temperature resistant trays and exposed to a series of heat treatments using a programmable oven. Initially the temperature was ramped from 25°C to 103°C at a rate of 2°C/min and held constant for 18 h. Next, the temperature was increased to 180°C for 6 h and slowly decreased to room temperature over a period of 90 minutes. The last treatment in the process was heating at 450°C for about 2 h to remove all impurities left in the STCs. The STCs were analyzed using N₂ adsorption – desorption isotherms obtained in a Quantachrome Autosorb 1C-MS gas sorption analyzer (NOVA 2200e) to characterize the composites for their BET surface area, total pore volume, and average pore size. The properties of the STCs used in this study are shown in Table 1.

Table 1. Average Properties of STCs

<i>Property</i>	<i>Average Value</i>
BET surface area (m ² /g)	250 ± 43
Pore diameter (Å)	152 ± 23
Total Pore volume (cc/g)	0.94 ± 0.06
% _{wt} TiO ₂ loading	29.6 ± 1.4
Diameter (mm)	9.1 ± 0.4
Length (mm)	8.1 ± 1.1

ANALYTICAL METHODS – The target VOC in this work, toluene, was analyzed using a GC-MS (ThermoQuest Trace) connected to a Purge and Trap concentrator (Tekmar 3100) following USEPA Method 524.2: “Measurement of purgeable organic compounds in water by capillary column gas chromatography/ mass spectrometry.”