Photocatalytic thin film cascade reactor for treatment of organic compounds in wastewater

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Abstract The photocatalytic oxidation of benzoic acid was investigated in a pilot scale-cascade photoreactor. The photoreactor consists of an array of UV lamps (40 W, 365 nm) illuminating a cascade of three inclined 316 stainless steel plates, on which titanium dioxide (TiO$_2$) was immobilized by electrophoretic deposition. The percentage removal of total organic carbon (TOC) of liquid samples was determined. The photocatalytic process was affected by several operating parameters. Increasing the solution temperature was found to reduce the dissolved oxygen (DO) level and to decrease the rate of the degradation process. The Langmuir–Hinshelwood equation was found to be accurate for modeling the degradation of benzoic acid with initial concentrations of 50 ppm, 75 ppm and 100 ppm. The rate of removal of TOC was positively affected by UV light intensity, but appeared to be independent of solution flowrate in the range examined. Control experiments confirmed that the effects of adsorption of the solute onto the TiO$_2$ catalysts and photolytic degradation were negligible.

Keywords Benzoic acid; cascade photoreactor; immobilized photocatalyst; titanium dioxide (TiO$_2$)

Introduction The photocatalytic oxidation of organic compounds by nanocrystalline titanium dioxide (TiO$_2$) has received increasing attention since it can achieve the mineralization of a wide variety of organic compounds to nontoxic mineral products, including carbon dioxide and water (Matthews, 1986; 1987; 1988). When anatase TiO$_2$ is illuminated with light of wavelength below 400 nm, electrons will be transferred from the valence band to the conduction band, leaving holes in the valence band. If these electron–hole pairs can be separated from each other quickly enough without significant recombination, they will migrate to the catalyst surface. Electron transfer can then take place from the conduction band electrons to an electron acceptor (molecular oxygen) and from an electron donor to the valence band holes. Concurrently, chemical radicals that are strong oxidizing agents are formed and the organic pollutants are oxidized by the radical attack (Goslich et al., 1997).

Matthews (1986) reported the use of suspended TiO$_2$ in a solar illuminated tubular reactor equipped with a parabolic trough concentrator to degrade a collection of organic materials. One typical problem encountered in using suspended photocatalysts is the necessity to separate sub-micrometre TiO$_2$ particles from the reactor effluents. In an attempt to eliminate the need to filter the sub-micrometre catalyst particles, various catalyst supports were tested in a parabolic trough system (Pacheco et al., 1990). However, the problem of the pressure drop caused by the supports has to be taken into account. Apart from the issue of catalyst recovery, the reflectors of high optical accuracy required by the aforementioned light concentrating reactors are expensive and complicated in design, and only the direct component of the UV irradiation is used to drive the degradation process. In contrast, non-concentrating reactors, which utilize both the direct and diffuse components and do not need the expensive reflectors, have greater potential for low-cost process development. Recently, inclined fixed bed reactors, in which organic-containing solution flows across a single flat plate coated with photocatalysts, have been studied (Wyness et al., 1994;
The advantages and disadvantages of this kind of reactor have been summarized by Goslich et al. (1997). For example, these reactors are simple in design (no light reflectors are needed) and easy to operate. Furthermore, the large liquid–air interface over the single flat plate is beneficial to oxygen transfer into the liquid film. However, they require a large area for collecting UV light and the reactions may be constrained by apparent mass transfer limitations resulting from the possibility of laminar flow conditions. In order to promote effective interfacial oxygen transfer, one promising approach is to adopt a cascade design consisting of several flat plates arranged stepwise, instead of employing the single flat plate configuration. The “waterfall” formed when the reaction solution falls from one plate to another potentially promotes a higher degree of aeration in the liquid film. Mass transfer of the organics in the liquid film to the catalyst surface can also be enhanced by the resulting turbulence. A cascade photoreactor has, therefore, been developed to study the process of photocatalytic oxidation of organics under various operating conditions. Benzoic acid was selected as the model compound in this study.

**Methods**

A schematic diagram of the experimental set-up, which is basically a batch recirculating system, is shown in Figure 1. The photoreactor consists of a bank of six fluorescent UV lamps (Philips TLK40W/10R), whose dominant emission was at a wavelength of 365 nm, and a cascade of three flat plates coated with TiO\(_2\) catalysts, 2 cm vertically apart from each other and inclined at an angle of 5° to the horizontal. The flat plates were made of 316 stainless steel. The area of the each plate exposed to UV light was 17.5 cm \(\times\) 28 cm. A solution of benzoic acid (Riedel-de haën, 99.5% purity) was introduced by an overflow to the liquid reservoir and flowed down the cascade in the form of thin film. To avoid the formation of vortices in the reactor tank at higher flowrates, seven litres of solution were treated in all the experiments. A magnetic drive pump was used to recirculate the solution back to the liquid reservoir. The temperature and the flowrate of the solution were monitored by a temperature bath and a flowmeter, respectively.

The overall aim of the photocatalytic oxidation process is to completely oxidize the benzoic acid to carbon dioxide, water and/or mineral acids. Therefore the rate of removal of
total organic carbon (TOC) is the key parameter for evaluating the effectiveness of the removal process. A Shimadzu TOC-500 analyser was used to analyze the TOC content of the liquid samples. Evaluation of the photoreactor performance was carried out by varying several operating parameters: the flowrate of benzoic acid solution; the temperature and dissolved oxygen (DO) of the solution; the initial concentration of the solution; and the light intensity of the UV lamps. The experiments used to study these parameters were conducted for steady flow in the dark for 20 minutes. Liquid samples of 25 ml were withdrawn from the reactor effluent at an interval of 30 minutes for a period of three hours. The same set of three coated plates were used for each parameter studied and were washed thoroughly with distilled water after each experiment. In most experiments, no extra aeration was provided, except for the experiment that aimed to determine the effects of DO level on the rate of removal of TOC at higher temperature. In the latter experiment, the solution in the liquid reservoir was aerated by filtered compressed air at 6 l/min via two diffusers. To compare the performance of a single flat plate reactor and a cascade reactor, three special 316 stainless steel plates were made, which could be mounted together to model a single flat plate with an area identical to the total of the cascade plates. The liquid reservoir was lowered to keep the vertical distance from the uppermost plate the same as in the cascade reactor. In the discussions later, we will refer to this experiment as the single plate experiment.

The irradiation intensities at 18 fixed positions over the three stainless steel plates when two lamps and six lamps were switched on were measured at a wavelength of 365 nm by a radiometer (Vilber Lourmat VLX-3W) at the start of the experiments. The average intensities in the two cases were calculated from the irradiation profiles obtained at these locations. The same radiometer was put at a fixed location to monitor the UV intensities of the area illuminated by the lamps at every 30 minutes during the experiments. The DO level and the temperature of the solution in the liquid reservoir were recorded by a DO meter (Cole-Parmer DO 100), while the temperature of the solution at the photoreactor outlet was measured every 20 minutes by a type-K thermometer (Digi-Sense).

Stainless steel plates were used as the supporting substrate for the TiO₂ catalysts. The plates were degreased using a soap solution for 15 minutes and repeatedly rinsed with distilled water. They were then etched by dilute nitric acid (5%) for one hour to provide a better surface for catalyst adhesion, and were washed thoroughly with distilled water again before drying. TiO₂ catalysts were immobilized on the stainless steel plates by electrophoretic deposition (Fernández et al., 1995; Byrne et al., 1998). TiO₂ solution (1% g/ml) prepared by adding 50 g of TiO₂ powders (Degussa P-25) into 5 litres of isopropanol (Lab-Scan, analytical reagent grade) was sonicated for one hour to ensure the homogeneity of the suspension. A magnetic stirrer was also used to continuously agitate the suspension during the coating process. A 316 stainless steel flat plate electrode of the same size as the plate to be coated was used as the anode. A negative potential of 40 V was applied to the cathode (the plate to be coated) for four minutes. During this process, the TiO₂ powders in the suspension moved to the stainless steel anode, followed the parallel electric field between the two electrodes and deposited onto the cathode. After being dried under ambient conditions, the substrate was heated at 473K for 90 minutes in an oven to enhance the stability of the coating to mechanical attrition. A schematic diagram of the deposition process is shown in Figure 2. The problem of catalyst stripping was not found to be significant in the subsequent experiments.

Results and discussion

Photolysis and adsorption

In order to measure the percentage removal of TOC by photolysis and adsorption of the
solute onto the TiO$_2$ catalysts, one control experiment with uncoated plates illuminated by six lamps and another with coated plates without illumination were carried out. These control experiments were carried out at the highest flowrate (5 l/min), the lowest temperature (291K) and the highest initial benzoic acid concentration (100 ppm) – the most favorable conditions for organic adsorption onto catalyst particles. The removal of TOC by photolysis and adsorption was found to be negligible (data not shown).

**Effect of flowrate**

The flowrate of the benzoic acid solution was adjusted from 2 l/min to 5 l/min to investigate the apparent mass transfer limitations of benzoic acid to the TiO$_2$ catalysts. The volume of the irradiated solution was between 121 ml and 205 ml for the corresponding flowrates resulting in a mean film thickness of 0.8–1.4 mm, based on the area of each plate (17.5 cm $\times$ 28 cm). The percentage removal of TOC from 2 l/min to 5 l/min was 7.34, 8.15, 7.14 and 7.95, respectively, which seemed to show no dependence of the removal of TOC on the flowrate, as shown in Figure 3. It is, therefore, anticipated that the role of mass transfer phenomena in the photocatalytic process is unlikely to be important for the range studied. This may be partly attributable to the possibility that the flowrates employed in the experiments were relatively high and may also be the result of the turbulence created by the cascade design, promoting effective mass transfer during the photocatalytic process.

![Figure 2 Schematic diagram of electrophoretic deposition](image)

![Figure 3 Removal of TOC as a function of time at different flowrates. Initial benzoic acid concentration = 100 ppm, temperature = 219K, six lamps on](image)
Effect of temperature and DO

The temperature of the benzoic acid solution was fixed at 291K, 296K and 301K. The temperature deviation of the solution from the desired values at the inlet and outlet of the photoreactor in this series of experiments was ±0.5K, depending on the ambient conditions. This indicates that the temperature variations of the solution caused by continuous UV irradiation were not important. Surprisingly, it is found that an increase in the temperature of the solution without aeration resulted in a reduction in the percentage removal of TOC, as shown in Figure 4. Matthews (1987) reported that the destruction rate of salicylic acid, which is similar to benzoic acid in chemical structure, in a spiral reactor coated with TiO₂ illuminated by a 20 W blacklight fluorescent lamp followed the Arrhenius equation for the temperature range studied. The reduction in the removal of TOC in this study is probably related to the decreased solubility of oxygen in the solution at elevated temperatures, as shown in Figure 5. DO plays an important role in the photocatalytic process for the proposed photoreactor, as evidenced by the observed increase in the percentage removal of TOC at 296K from 3.81 to 5.98, when the solution in the liquid reservoir was aerated by filtered compressed air at 6 l/min. Gupta and Tanaka (1995) also reported that the rate of carbon dioxide formed by the photocatalytic oxidation of perchloroethylene in an enclosed system containing slurry TiO₂ illuminated by a 75 W mercury lamp was increased by three times when the DO level was increased from 0 mg/l to 8 mg/l at a constant temperature of around 308K.

Figure 5 illustrates that the DO decreased quickly at the onset of the photocatalytic process (when the UV lamps were switched on), but then subsequently became quite steady, instead of decreasing gradually. This may be associated with the enhanced uptake of oxygen due to the large liquid–air interface over the plates and the replenishment of oxygen when the solution flowed down the cascade.

Effect of initial solute concentration

The Langmuir–Hinshelwood equation has previously been observed to provide an appropriate model for the rate of destruction of various organics by TiO₂ (Matthews, 1987; 1988; Fernández et al., 1995). In this study, we also adopt the Langmuir–Hinshelwood equation to represent the rate of the degradation of TOC:

\[ r = \frac{k[S]}{1 + K[S]} \]  

(1)

**Figure 4** Removal of TOC as a function of time at different temperatures. Initial benzoic acid concentration = 100 ppm, flowrate = 3 l/min, six lamps on
where \([S]\) is the solute concentration and \(k\) and \(K\) are the reaction and adsorption constants associated with the solute, respectively.

The integrated form of Equation 1 is

\[
t = \frac{1}{Kk} \ln \left( \frac{[S_o]}{[S]} \right) + \frac{1}{k} ([S_o] - [S])
\]

(2)

where \(t\) is the time in minutes for the initial solute concentration \([S_o]\) to decrease to the solute concentration \([S]\) at time \(t\).

When the initial solute concentration is low, Equation 2 becomes Equation 3, which is basically an apparent pseudo-first order equation.

\[
\ln \left( \frac{[S_o]}{[S]} \right) = K_k t_k
\]

(3)

where \(k_a\) (min\(^{-1}\)) is the pseudo-first order apparent rate order apparent constant.

A linear relationship between \(\ln (\text{TOC}_o/\text{TOC})\) and time can be obtained for initial concentrations of 50 ppm, 75 ppm and 100 ppm, as illustrated in Figure 6 when the solute concentrations in Equation 3 are tentatively substituted by the available TOC data in this study.

Figure 7 illustrates that the apparent rate constant decreases with increasing initial benzoic acid concentration. A similar trend for pseudo first-order apparent rate constants, calculated from the Langmuir–Hinshelwood equation for phenol degradation in a fixed bed photoreactor (Degussa P-25 on glass), has also been reported by Sclafani et al. (1999). The
decreasing trend is possibly associated with intermediate and/or product inhibition to catalyst active sites as quoted by Gupta and Tanaka (1995). Examples of the possible intermediates formed by the photocatalytic oxidation of benzoic acid include salicylic acid as well as m-hydroxyl and p-hydroxyl isomers of salicylic acid (Matthews, 1986; 1987).

**Effect of light intensity**

When the number of lamps decreases from six to two, the average UV intensities calculated based on the measurements at the 18 fixed positions over the three plates decreases from 1.39 mW/cm² to 0.56 mW/cm² and the removal of TOC also decreases from 19.43% to 11%.

Obviously, the removal of TOC increases with the UV photon flux, which is the driving force for the catalysts to form electron–hole pairs. Previous work by Wyness et al. (1994) showed that the relationship for normalized first-order rate constant versus UV irradiation and liquid film thickness in a flat plate reactor was linear for the operating conditions tested. The UV intensities only varied slightly during each experiment in this study.

**Comparison between single flat plate and cascade photoreactors**

The flowrate, temperature and initial concentration of the benzoic acid solution employed in these experiments were 3 l/min, 291K and 50 ppm, respectively. The DO profiles for the single plate and cascade reactors are shown in Figure 8. Both profiles decreased initially and then approached a steady value. Initial inspection suggests that the final DO concentration for the single plate reactor was slightly lower than that of the cascade reactor, both with nearly the same initial DO value. As mentioned earlier, the large interface for fixed bed is beneficial for oxygen transfer to the liquid film from the ambient air. The cascade design, however, is very likely able to add more oxygen. The removal of TOC slightly decreased from 19.43% for the cascade reactor to 17.10% for the single plate reactor, as shown in

![Figure 7](image-url)  
*Figure 7* Pseudo first-order apparent rate constant against initial benzoic Concentration (ppm) acid concentrations. Flowrate = 3 l/min, temperature = 291K, six lamps on

**Table 1** Comparisons between mean intensity and percentage removal of TOC with two and six lamps on. Initial benzoic acid concentration = 50 ppm, temperature = 291K, flowrate = 3 l/min

<table>
<thead>
<tr>
<th>No. of lamps on</th>
<th>Mean intensity mW/cm²</th>
<th>% removal of TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.56</td>
<td>11.00</td>
</tr>
<tr>
<td>6</td>
<td>1.39</td>
<td>19.43</td>
</tr>
</tbody>
</table>
Figure 9. It is believed that the differences in the final DO concentration and the percentage removal of TOC will be more pronounced when using stainless steel plates with a longer length, or an extended cascade with an increased number of steps against a single flat plate.

Conclusions

The performance of a cascade photoreactor for the photocatalytic oxidation of benzoic acid was investigated by varying several operating parameters: solution flowrate; solution temperature and DO content; initial solute concentration; and UV light intensity. Photolysis and adsorption were found to be negligible in the overall degradation process. The percentage removal of TOC appeared to be independent of the solution flowrate from 2 l/min to 5 l/min – mass transfer limitations were unlikely to be significant for the range studied. Increasing temperature from 291K to 301K was found to decrease the DO level in the solution, hence reducing the percentage removal of TOC. Aeration should be important for operations at elevated temperatures. The Langmuir–Hinshelwood equation was found to be appropriate for modeling the degradation process of benzoic acid with initial concentrations of 50 ppm, 75 ppm and 100 ppm. An increase in UV light intensity resulted in a higher removal rate of TOC. Comparative studies demonstrated that the cascade reactor performed better than the single plate reactor by enhancing the DO level in the liquid solution.

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Figure 8 DO profiles for the single plate and cascade reactors. Initial benzoic acid concentration = 50 ppm, flowrate = 3 l/min, temperature = 291K, six lamps on.

Figure 9 Removal of TOC as a function of time for the single plate and cascade reactors. Initial benzoic acid concentration = 50 ppm, flowrate = 3 l/min, temperature = 291K, six lamps on.
References