

Photocatalytic Oxidation of Toluene in Water From an Algae Pond With High Dissolved Oxygen Content

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Water in well-mixed ponds containing photosynthetic algae has been observed to have an extremely high Dissolved Oxygen (DO) content. Up to four times saturation levels of DO have been recorded. Since DO is known to have an important role in the photocatalytic oxidation of organic contaminants in water, it was hypothesized that a faster rate of contaminant destruction would be observed in water drawn from algae ponds supersaturated with DO. In order to verify this hypothesis, a bench scale, batch-type photoreactor was constructed. Some baseline tests were performed to investigate the influence of UV intensity, water pH, and DO content on the photocatalytic destruction of toluene in water. An array of ultraviolet blacklight lamps in a lamp box was used to simulate solar ultraviolet radiation. First-order reaction rate constants were calculated from the destruction data, using a kinetic model proposed earlier. The reaction was found to proceed forward equally fast at pH 4 and 10. A power law relation was derived for the reaction rate dependence on UV intensity. Presence of DO in the water was found to be required for the reaction to go forward. Water from an algae pond, supersaturated with dissolved oxygen was spiked with toluene and destruction tests were then conducted in the same reactor. These tests did not show the expected improvement in destruction rates.

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Introduction

The process integration of photocatalytic treatment technologies with other treatment methods might be required to make photocatalysis viable and an economically attractive option. Algae based treatment options result in the removal of phosphates,

which are known to strongly inhibit photocatalytic reactions [1]. Further, water in well-mixed algae ponds is known to have very high dissolved oxygen content. Up to four times saturation levels of DO have been recorded [2]. This high DO content can be expected to speed up destruction rates in photocatalytic reactions.

Industrial wastewater effluents (such as those from paper mills or distilleries) generally have a very low DO content. It has been found that dilution is often necessary in order to photocatalytically treat such wastes. An advantage of dilution is that the dissolved oxygen content of the effluent is raised. On the other hand dilution increases the volume to be treated. Diluting these effluents with high DO water is one way of quickly raising effluent DO levels without increasing the volume to be treated very much. Algae ponds have a very high DO content under good sunlight conditions. Using an algae pond as an initial step in a waste-treatment process might be an effective way to boost the DO content of the treated water, and to eliminate phosphates (if present), which are known to interfere with the photocatalytic process.

Algae are microscopic plants containing photosynthetic pigments such as chlorophyll. They are autotrophic organisms that support themselves by converting inorganic materials using energy from the sun. Therefore, algae are used for biotreatment of wastewaters to remove nutrients such as nitrogen and phosphorous and to provide oxygen for aerobic bacteria [5].

Experimental Procedure

A reaction system was constructed and characterized using toluene as a model contaminant. The influence of pH, UV intensity, and DO content on the destruction rate was studied. A batch type photocatalytic reaction system was constructed for conducting bench scale experiments. The setup consisted of a flow-through reactor placed on a platform under low-pressure mercury vapor lamps housed in an aluminum lamp box (see schematic in Fig. 1). A magnetic stirrer rod was used to keep the tank contents well mixed, so that the TiO_2 stayed suspended and concentration of pollutant within the tank could be assumed constant. The photoreactor is made from an extruded double skinned acrylic panel with built in flow channels of cross-section 30 mm \times 11.5 mm. Figure 2 is a drawing of the reactor with slurry flow path indicated. The measured reactor volume is 93 ml. The total system volume (tank+reactor+ piping) was measured to be 4170 ml.

UV intensity at the reactor window could be adjusted by varying the distance between the reactor and the lamp array. The lamps emitted in the wavelength range of 300–400 nm, with peak intensity around 350 nm. An Eppley model TUVR (Total Ultraviolet Radiometer) which measures radiation in the range of 295–385 nm was used for intensity measurements. Broadband UV intensity measurements using a solar broad band ultraviolet radiometer exposed to a lamp source is discussed in more detail in Vijayaraghavan and Goswami [6].

In the baseline experiments a sample of deionized water spiked with approximately 800 ppb of pure toluene was filled in the reaction tank. Titanium dioxide was added to the tank to ensure 0.1% (m/v) loading in the reactor. This catalyst loading was chosen on the basis of previous experimental experience. All the

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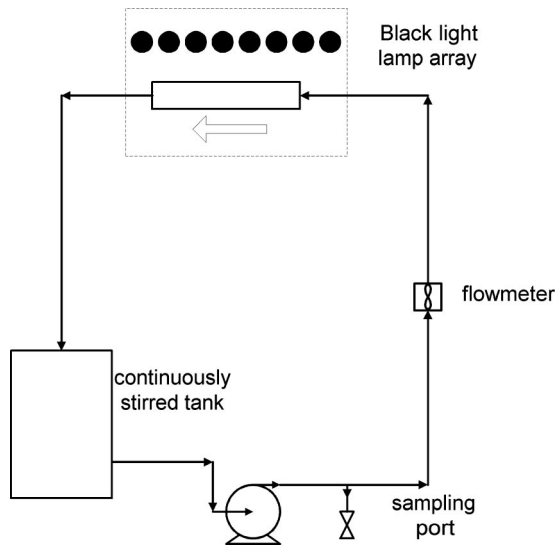


Fig. 1 Schematic showing the flow path in the photoreactor

headspace was filled up at the beginning of the experiment, to minimize the effects of volatilization of toluene. This slurry was circulated with the reactor covered for the first 60 min as a dark control. At the end of 60 min, the covers were removed and the reactor exposed to UV light. Samples were taken at regular intervals and analyzed to record the concentration history of toluene in the tank.

Finally, for tests using water from an algae pond, water was drawn from the pond and the algae filtered out. The algae can interfere with the photocatalytic reaction and block UV radiation from striking the catalyst particles. The pH of this water was adjusted to a value of 10, and the sample was spiked with toluene. The photocatalytic destruction of toluene in this water was studied in the same manner as in the deionized water tests.

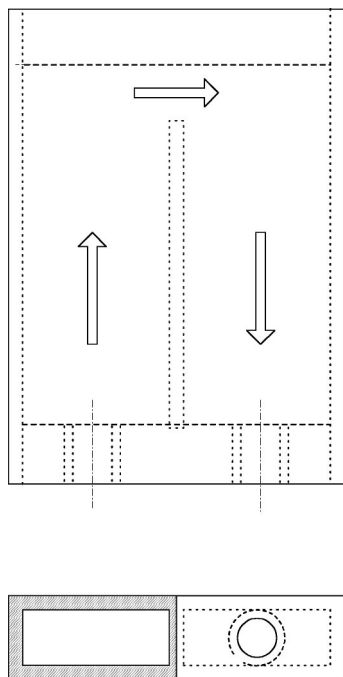


Fig. 2 Drawing of the photoreactor showing the flow path of contaminated water with catalyst in suspension through the reactor

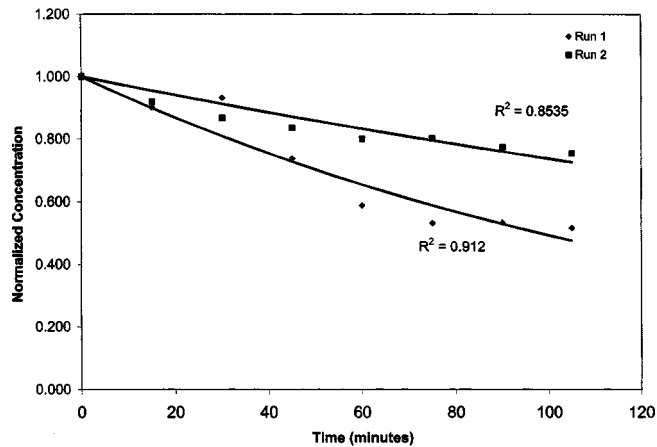


Fig. 3 History of toluene concentration in the tank in algae water tests

Results and Discussion

Baseline Tests With Deionized Water. Toluene destruction was studied at pH values 4, 7, and 10. Reactor distance from the lamp array was adjusted so that UV intensity at the reactor window measured 30, 60 and 90 W/m² for each pH value. Table 1 contains the results from those baseline tests. The apparent and actual reaction rate constants were calculated based on references [3] and [4].

At all three intensity levels, it is observed that the destruction rates at pH 4 and 10 are higher than that at pH 7. The destruction rates at pH 4 and 10 are comparable.

The variation of reaction rate with intensity (in Wm⁻²) was fitted to a power law relation. It was found that for this particular reaction system:

$$\text{at pH 4 } k = 0.08 (I)^{0.63} \quad (1)$$

$$\text{at pH 10 } k = 0.13 (I)^{0.53} \quad (2)$$

For all tests, the initial and final DO content of the water was measured. For tests with the deionized water, initial DO levels were difficult to control, and there was some variation in the initial levels of DO in the water. The average initial DO content was 7.8 ppm with a standard deviation of 0.5 ppm in the data. Interestingly, the final DO content in almost all the experiments was nearly the same at about 7.4 ppm, with a standard deviation of 0.2 ppm in the data. There was no correlation between toluene disappearance and change in DO levels of the contaminated water, probably because the tank was not completely airtight. Destruction was negligible in tests conducted after eliminating DO from the water.

Tests With High DO Water From Algae Pond. For experiments with the water from the algae pond, the DO within the pond was measured to be above saturation, around 11 ppm (at 26°C). The algae were filtered out of the water. The filtered water was spiked with toluene and run through the photoreactor. The water pH was adjusted to 10 and UV intensity at the reactor window was 60 W/m². Tank concentration histories for both tests are plotted in Fig. 3. The initial and final DO levels in both tests are tabulated in Table 2.

The initial DO content was slightly above saturation in both cases, while the final DO levels were slightly below the saturation values with air. The destruction rates under these conditions were well below that observed with deionized water, under the same conditions. This could be because of the presence of organic compounds other than toluene in the water. The presence of other organics in water can cause competition for reaction sites on the

Table 1 Apparent and actual reaction rate constants from the experimental data

Intensity (W/m ²)	pH 4		pH 7		pH 10	
	k _{app} min ⁻¹	k min ⁻¹	k _{app} min ⁻¹	k min ⁻¹	k _{app} min ⁻¹	k min ⁻¹
30	0.014	0.59	0.010	0.44	0.017	0.75
60	0.027	1.19	0.009	0.39	0.027	1.19
90	0.029	1.27	0.023	1.02	0.032	1.37

Table 2 Initial and final values of TOC, DO, and Temperature of the water in algae water test runs

	Initial			Final		
	TOC (ppm)	DO (ppm)	T (°C)	TOC (ppm)	DO (ppm)	T (°C)
Run 1	43.82	9.6	24	26.04	8.0	28
Run 2	24.58	9.2	24	24.23	7.8	27

illuminated catalyst surface. The first and the last samples from both experimental runs were analyzed for TOC (Total Organic Carbon) using a TOC analyzer. TOC is a measure of total organic content of the water. Before TOC analysis, the water was purged with nitrogen to eliminate all volatiles. The results are shown in Table 2. There appears to be a considerable drop in TOC in run 1, whereas in run 2, the drop in TOC is very small. Toluene destruction rates in the two experimental runs also show a much slower rate of destruction in run 2 as compared to experimental run 1. Although there is a substantial amount of other organic compounds in the water, as seen from the TOC analysis, it appears as if some other factor is causing the variation in observed reaction rates. One other possible reason could be the presence of microorganisms such as bacteria in the water. UV illuminated TiO₂ is known to destroy microorganisms in water [7], hence a higher biological concentration in the second sample could have competed with the organic compounds present for destruction.

Another issue of importance is the mechanism by which DO levels are maintained in water. The DO content of any body of water exposed to the atmosphere is the result of a variety of processes which include mass (oxygen) transfer at the water-air interface and dissolved oxygen consumption by the various living organisms in the water and also by any other process occurring inside the water body that generates (for example, photosynthesis) or consumes oxygen. The high DO content observed in algae ponds is because of the rapid generation of oxygen by the thriving algae and slow rate of mass transfer at the surface with the air. If the pond is well mixed and if there is sufficient growth of algae, the high oxygen concentration can extend to considerable depth within the pond. The process of filtering the algae out appears to result in a decrease in DO content of the water. In measurements carried out with water from an algae pond used to treat pig farm waste, a very rapid drop in DO from (> 15 ppm—out of scale on the DO meter) to values around 11 ppm (at 27°C) was observed on filtering out the algae. The algae have to be filtered out because their presence in the water could interfere with the photocatalytic reaction. Even this relatively high DO filtered water, supersaturated with oxygen, will start losing oxygen to the atmosphere with time. Mixing or agitation of the water will speed up this process substantially.

Conclusions

The presence of dissolved oxygen appears to be essential for the forward progress of photocatalytic oxidation reaction of toluene. However, using high DO water from an algae pond did not increase the reaction rate, in fact, the *k* value actually decreased. Further, it was observed that although the conditions for both reaction runs were identical, the observed destruction rates were very different, contrary to what was expected. A TOC analysis showed the presence of other organic compounds in the water, which probably competed for reaction sites on the illuminated catalyst surface.

In general, one big disadvantage of using water from a high DO water pond containing algae is that the algae has to be filtered out of the water before using it in a photocatalytic oxidation process. The process of filtration appears to result in the immediate lowering of the very high DO content of water. The expense of adding a filtration stage in a wastewater treatment facility, which removes all the algae from the water, can be substantial. Water from algae ponds can also contain bacteria.

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