Application of a Microbial Toxicity Assay for Monitoring Treatment Efficiency of Pentachlorophenol in Water using UV Photolysis and TiO_2 Photocatalysis

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Abstract

Degradation efficiency of pentachlorophenol (PCP) by using direct UV photolysis and TiO_2 photocatalysis was evaluated with both chemical analyses and acute toxicity assessment employing luminescent bacteria *Vibrio fischeri*. PCP was chosen as a target compound in this study because of its wide application as fungicide, bactericide, insecticide and wood preservative in agriculture and many industries, in addition to its well-known environmental consequences.

The acute toxicity to the microbe was reduced by >60% when applying UV alone, and was completely removed when treated with UV-TiO_2 combinations. Toxicity reduction pattern determined with the Microtox Assay generally corresponds with the chemistry data: However, it should be noted that toxicity was greater than expected by the chemistry data. Formation of TCBQ, a toxic byprodut, could not explain observed microbial toxicity. These observations are probably due to the presence of unidentified toxic PCP byproducts, which may include polychlorinated dibenzodioxins and polychlorinated dibenzofurans. When Microtox results were compared between different exposure time, i.e., 5 min and 15 min, an interesting pattern was noted with UVA- TiO_2 treatment. While no microbial toxicity was observed with 5 min exposure, an EC50 value of 45.4% was estimated with 15 min exposure, which was not observed in UVB- TiO_2 exposure. This result may suggest the presence of unidentified toxic degradation products generated in the later stage of treatment. Based on this study, TiO_2 photocatalyst, together with UVB photolysis could improve the removal of both PCP and its toxic derivatives in more efficient way. The Microtox Assay is promising and economical method for monitoring efficiency of wastewater treatment processes.

Introduction

Conventional approaches for monitoring wastewater treatment processes include evaluation of degradation of the target compound and/or generation of its nontoxic byproducts. However, this approach has some limitations: Chemical analyses alone are not always sufficient to assess potential impacts of complex waste mixtures to aquatic biota, because existing analytical techniques are limited while very costly, and complete chemical characterization of wastewater is nearly impossible. In addition, it is hard to grasp the interactions of multiple chemical constituents in wastewater. To resolve these issues, several researchers applied acute toxicity assays for monitoring the treatment efficiencies of wastewater.

Pentachlorophenol (PCP) has been employed in various applications in agriculture and industry. It is highly toxic and persistent in water and soil, and adversely affects aquatic flora and fauna.[2] Even at low levels ranging 0.1-1μg/L, PCP could affect sensitive organisms and potentially lead to damage to the aquatic ecosystems. Several researchers investigated the potential of titanium dioxide (TiO_2) photocatalysis for removing this chemical from water.[2, 3] However, no report has been made as to the removal of this chemical employing UV system. In the present study, we evaluated the efficiency of PCP degradation using both UV photolysis and TiO_2 photocatalysis. In addition to chemical analyses of the target chemical and its degradation byproducts, we conducted aquatic toxicity assays using microbes to compare the treatment efficiency.

Materials and Methods

Vendor certified PCP (99%), and tetrachlorobenzoquinone (TCBQ, 99%) were employed as standards in chromatographic analyses. Titanium dioxide (Degusa P-25), of which average particle size was 30 nm and BET surface was 50± 15 m2/g, was used without any pre-treatment. All the experiments were carried out in a continuous flow photo-reactor containing 10-columns (diameter 12-mm) with recirculation of the suspension. This reactor is equipped with eight UV-A_{365nm} and UV-B_{315nm} lamps (Sankyo Electrics Co., G20T10, 20 W, 580-mm length, 32.5-mm-diameter). UV intensity was measured with a VLX-3W radiometer (Cole Parmer Instrument Co.).

Levels of PCP and TCBQ were analyzed with an HPLC (Dionex) equipped with a diode array detector UVD 340S, and C-18 silica column (25cm×4.6mm i.d., 5μm particles, Supelco Park) at 220 nm. The chloride ion was measured using Ion Chromatography (Dionex) with Ion-Pac AS-14 column. Toxicity assay using a microbe *V. fischeri* was

conducted to evaluate removal of PCP and its toxic derivatives.

A bench scale reactor was constructed with a flow rate of 1 L/min and UV intensity of 12 mW/cm^2. For photocatalytic reaction, 0.1% TiO_2 (W/V) was applied. A test concentration of 10 mg/L PCP was prepared, and treated under several experimental conditions. PCP was completely degraded when both direct UV and TiO_2 were applied for 120 min as evidenced by almost complete mineralization of the parent compound (>98% of initial PCP) and significant reductions in acute toxicity to *V. fischeri*. However, degradation of PCP was not observed in the TiO_2 only treatment condition. Tetrachloro-p-benzoquinone (TCBQ), a major intermediate degradation product was detected during the first 40 min of both oxidation reactions, after which completely degraded.

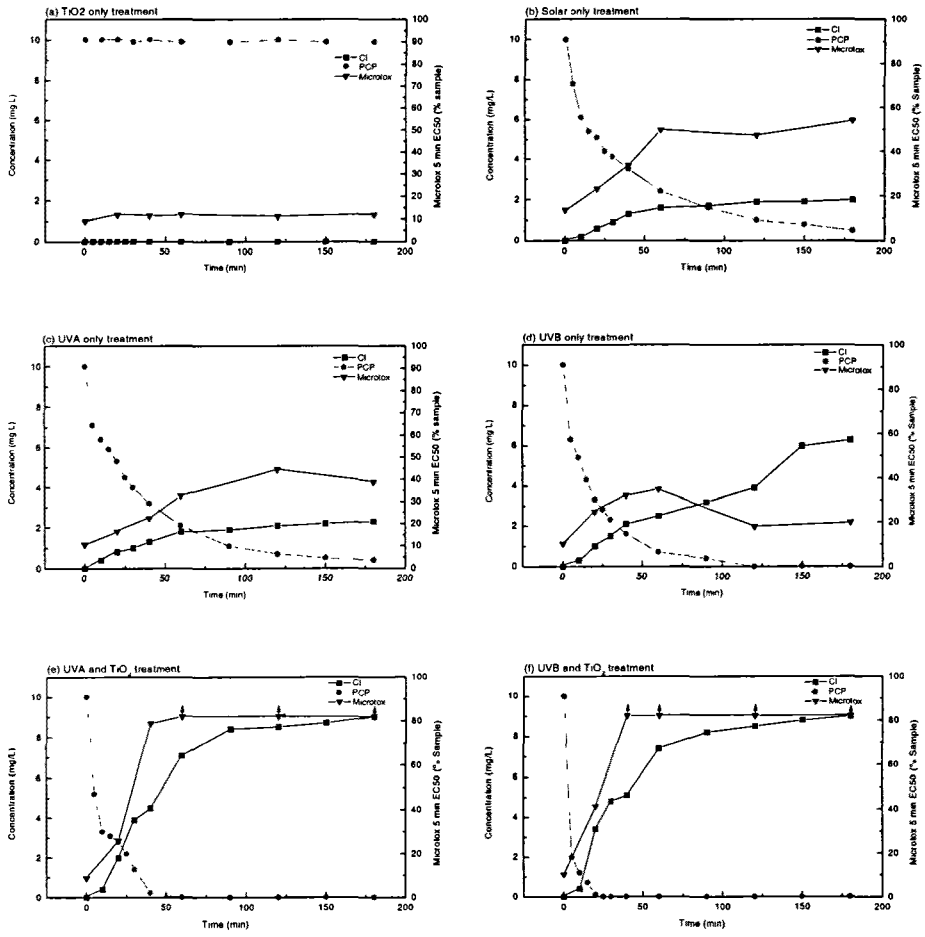

Fig 1 Degradation of PCP, formation of chlorine ion and toxicity reduction by TiO_2 treatment,

direct UV and solar photolysis, and UV+ TiO_2 photocatalysis. (Experimental condition: Initial concentration of PCP=40μM, pH=4.5, UV intensity=12mW/cm^2 , TiO_2=0.1wt %, Flow rate=1L/min)

Results and Discussion

Fig. 1 shows degradation of PCB, formation of chlorine ion, and reduction of microbial toxicity by various treatments employing TiO_2 and UV radiation. TiO_2 only treatment could not remove PCP to any appreciable extent, and microbial toxicity was not reduced virtually at all even after the 180 min of treatment. (Fig 1 (a)) Solar radiation only treatment, and UVA and UVB only treatments resulted in near complete removal of parent PCP, but certain level of microbial toxicity was observed in the treated samples. (Fig 1 (b-d)) When UVA and UVB radiations were applied with TiO_2, treatment of PCP was best achieved: After 20 to 60 min of treatment, complete removal of PCP was noted in UVB-TiO_2 and UVA- TiO_2 treatment, respectively. Five min Microtox EC50 values obtained from each samples indicated complete disappearance of the microbial toxicity after 60 min of treatment. (Fig 1 (e-f))

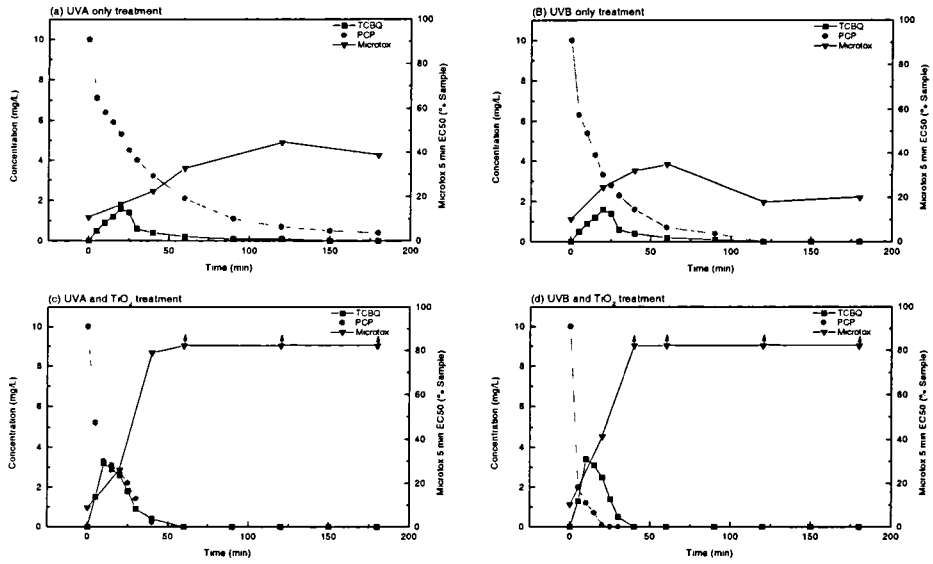

Fig. 2 Degradation of PCP, formation of TCBQ (p-chloranil) and toxicity reduction by direct UV photolysis (a, b) and TiO_2 photocatalysis (c, d). (Experimental condition: Initial concentration of PCP=40μM, pH=4.5, UV intensity=12mW/cm^2, TiO_2=0 1wt %, Flow rate=1L/min)

As shown in Fig 2, formation of a toxic degradation product, TCBQ, could not explain the

microbial toxicity observed with the Microtox assay. When Microtox results were compared between different exposure time, i.e., 5 min and 15 min, an interesting pattern was noted with UVA- TiO_2 treatment. (Fig 3 (a)) While no microbial toxicity was observed with 5 min exposure, an EC50 value of 45.4% was estimated with 15 min exposure. This pattern was not observed in UVB- TiO_2 exposure. This result may suggest the presence of unidentified toxic degradation products generated in the later stage of treatment. The reason we found this unexpected toxicity only with UVA- TiO_2 treatment may be due to the fact that UVA has relatively less potent photolytic capacity comparing to UVB. This finding suggests that UVB- TiO_2 combination is the best treatment system for PCP containing wastewater among tested in this study.

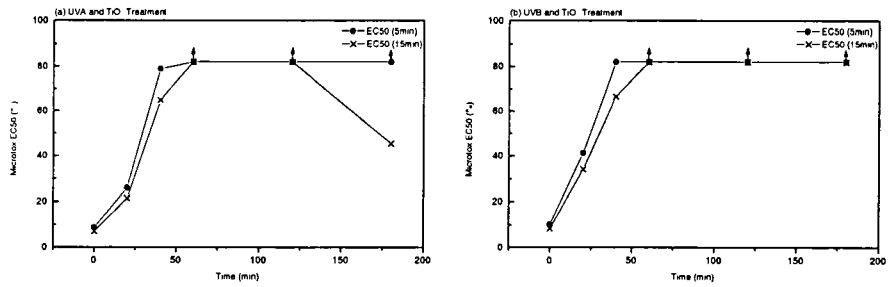

Fig 3 Comparison of the Microtox EC50 values obtained from samples of UVA- TiO_2 and UVB- TiO_2 treatments, after 5 and 15 min of exposure

The results of this study clearly shows the utility of a biologically based toxicological assay in monitoring efficiencies of wastewater treatment systems: The analyses of parent target compound and a limited array of its degradation products in the samples could not accurately show the removal of potential environmental harm. The Microtox assay provides a promising measure to evaluate efficiencies of wastewater treatment systems.

References

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