

Photoassisted biodegradation of halogenated breakdown products in nuclear fuel recovery process water-Hybrid reaction process

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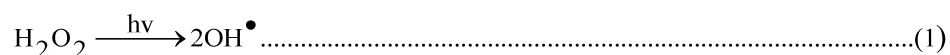
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The composition of the process water from nuclear fuel recovery contains a variety of toxic organic compounds. These compounds originate from the organic materials used in the coater between the inner fuel containing matrix of the pebble and the outer heat resistant protective graphite layer. There are many conventional methods to destroy such hazardous organic compounds but each one has its short comings including generation of secondary waste, environmentally unfriendliness, and cost prohibition. The biological technology is the most cost effective alternative when compared to the other conventional treatment options. The 4-chlorophenol (4-CP) was used as a model compound representing a family of hard-to degrade aromatic compounds such as those generated as low level nuclear waste from pebble processing. Experimental runs were performed by varying the initial 4-CP concentration from 50-1000 mg/L, and adding H₂O₂ at various concentrations in order to determine the influence and optimum dose for degradation without affecting the biological stage. The final effluent concentration for 50 mg 4-CP/L feed was found to be 1.31 mg/L giving an overall process performance of 98%. When 0.1ml H₂O₂/L was added to 50mg 4-CP/L, the overall performance of 63% was achieved

1. Introduction

The composition of the process-water from nuclear fuel recovery contains a variety of toxic organic compounds. These compounds originate from the organic materials used in the coater between the inner fuel containing matrix of the pebble and the outer heat resistant protective graphite layer. There are many conventional methods to destroy such hazardous organic compounds but each one has its short comings including generation of secondary waste, environmentally unfriendliness, and cost prohibition (Androzzi *et al.*, 1999). A promising alternative to the slower biological process is the use of advanced oxidation processes (AOP) as a pre-treatment step to convert initially

biorecalcitrant compounds to more readily biodegradable intermediates followed by biological oxidation of these intermediates to CO₂ and water (Sarria *et al.*, 2002). Generally, the UV/H₂O₂ Process involves generation of OH[•] radical through UV photolysis of H₂O₂. During UV/H₂O₂ process, a molecule absorbs light and result in electronic excitation which increases the molecule's ability to lose or gain electrons. This makes the excited state more suitable as an oxidizing or reducing agent that in turn makes it more likely and a highly reactive species such as the OH[•] radical can be produced from an electron transfer process between the excited state and contacting medium (Antoniadis *et al.*, 2007). Most organics contaminants absorb UV light and decompose due to direct photolysis and become excited as well as more reactive with chemical oxidants. According to Vogelpohl and Kim (2003) UV radiations accelerates the decomposition of O₃ and H₂O₂ molecules. The most accepted mechanism for H₂O₂ is the rapture of the O-O bond by the action of ultraviolet light forming two hydroxyl radicals (Al-Momani, 2003).



Numerous researchers have previously used the UV/H₂O₂ process to oxidize various organic substances in water since the sixties. It was found that H₂O₂ oxidation of organics does not produce complete oxidation to CO₂ and H₂O in many cases. In some cases the intermediates oxidation products remaining in the solution was found to be as toxic as or more toxic than the initial compound in some reactions. In this study, consideration is given to application of AOP/Biological Hybrid systems in treating the halogenated breakdown products from pebble elements. This is simulated at the laboratory scale by two CSTRs connected in series. The first tank acts as chemical reaction chamber where the AOP process takes place, whereas the second reactor containing bacteria acts as the polishing step. This study represents a unique application of the AOP/activated sludge hybrid system for the treatment of a highly toxic waste stream applicable to the nuclear industry.

2. Materials and Methods

2.1 Culture and Media

A mixed culture of activated sludge bacteria was originally collected from sand drying beds at a nearby wastewater treatment plant (Brits, Northwest Province). The culture was aerobically grown in Basal Mineral Medium (BMM) containing 2g/L of D-Glucose. Since the culture was collected from WWTP treating industrial effluent, it was expected to be previously exposed to similar pollutants as those tested in this study (4-CP). The culture was incubated at 30°C in a 1L Erlenmeyer flasks containing 500ml of growth medium on a rotary shaker at 120 rpm for 24 hours. The 4-CP solution was prepared by dissolving the weighed quantity of 4-CP solids. The coculture and consortium cultures used in this study were cultivated in basal mineral medium prepared from (in grams per litre of distilled water): 0.535 NH₄Cl; 10.744 NaH₂PO₄·2H₂O; 2.722 K₂HPO₄; 0.0493 MgSO₄·7H₂O; 0.0114 NaSO₄ ·2H₂O; and 0.0493 MgSO₄·3H₂O.

2.2 The experimental Setup

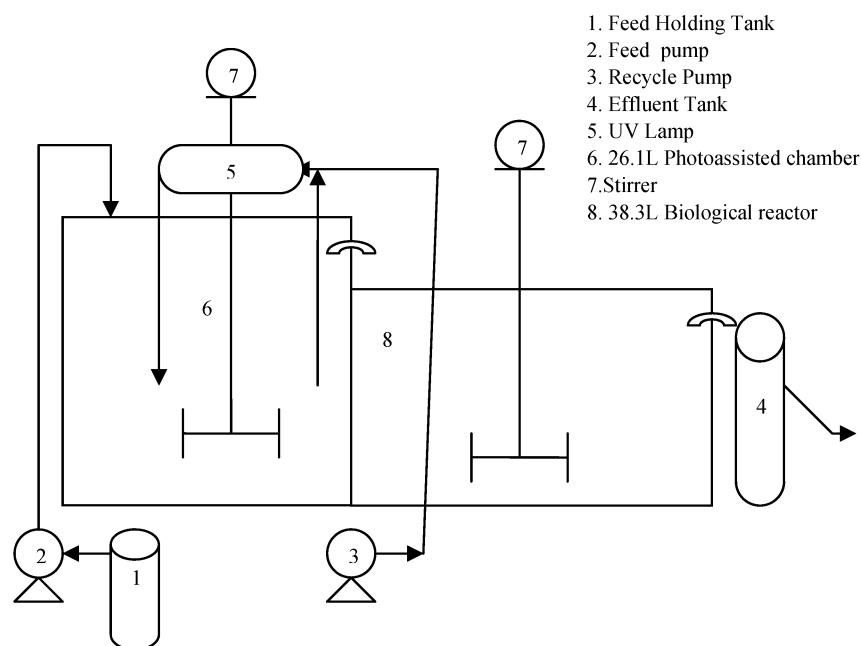


Figure 1: Schematic of the photoassisted bioreactor system.

2.3 Analytical Methods

The HPLC system consisted of the Waters 2695 separation module, 717 plus Autosampler and Waters 2998 photo diode Array detector-Waters 2998 PDA detector) was used equipped with a Synergi Fusion-RP C₁₈ (150 x 4.6mm, 4 μ m) column (Phenomenex) and Empower software for data analysis. A binary gradient mobile phase was applied consisting of 1% acetic acid in water (A) and 1% acetic acid in acetonitrile (B) (gradient: A: B - 30:70 at 0 min, to 0:100 at 20 min) at a flow rate of 1.2mL/min at 25°C, injection volume was 20 μ L. 4-CP concentrations were determined from calibration curves of 4-CP standards. All metabolites were determined by GC-MS (Pelkin-Elmer Clarus 600 System) equipped with a Headspace SPE Autosampler and the MS equipped with the Wiley Science standard spectra database.

3. Results

3.1 Effect of 4-CP initial concentration

Figure 2A shows the time profile for 50 mg 4-CP/L degradation by UV assisted AOP followed by biodegradation in the bioreactor chamber. The culture removed 4-CP up to 1.31 mg 4-CP/L resulting in the overall process efficiency of 98%. The concentration was increased to 100 mg 4-CP/L and the overall process efficiency of 82% was achieved. This was attributed to toxicity effects on the microorganisms due to higher 4-CP concentration coming from the reaction chamber. No steady-state was achieved for

1000 mg 4-CP/L feed. Figures 3 to 5 show the pattern of degradation and the possible degradation intermediates of 4-CP from chemical chamber to the bioreactor system.

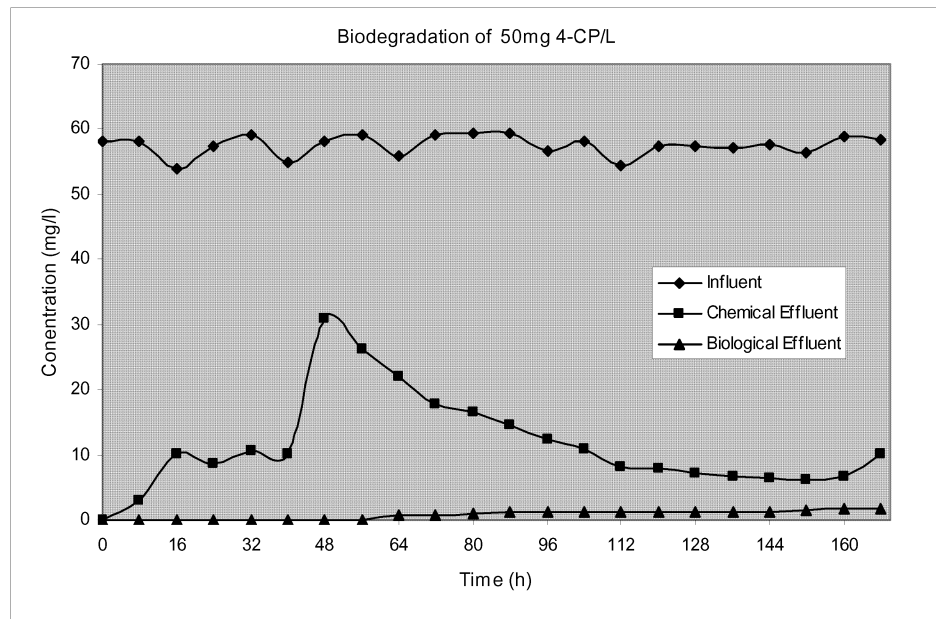


Figure 2A: Biodegradation of 50 mg 4-P/L in a photoassisted AOP process

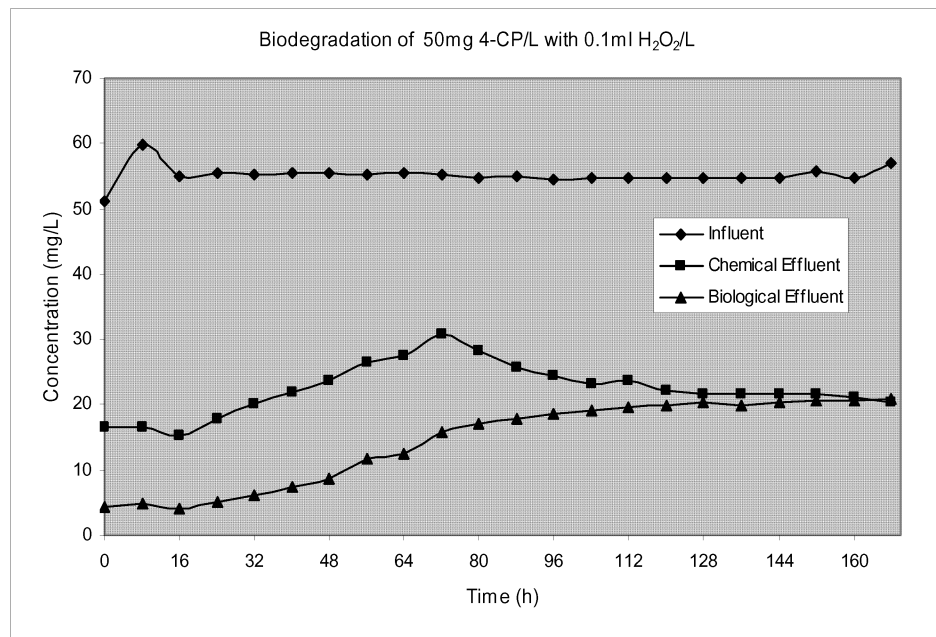


Figure 2B: Biodegradation of 50 mg 4-P/L with 0.1 ml H₂O₂/L in a photoassisted AOP process

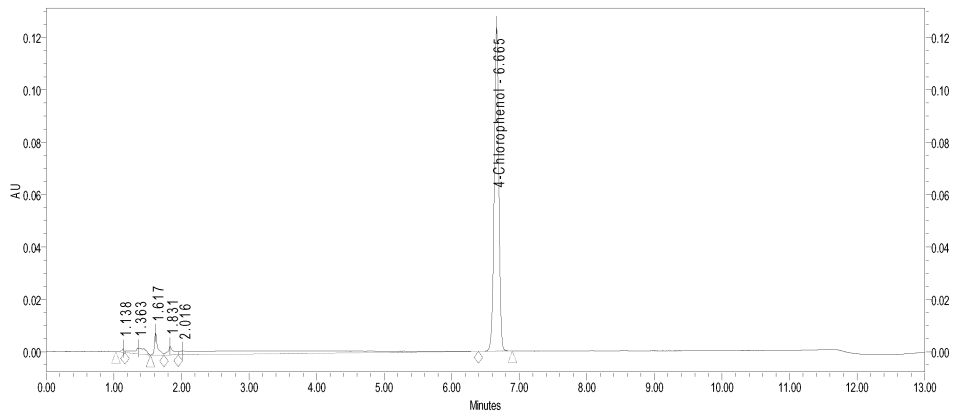


Figure 3: Chromatographic showing residual 4-chlorophenol in the Feed

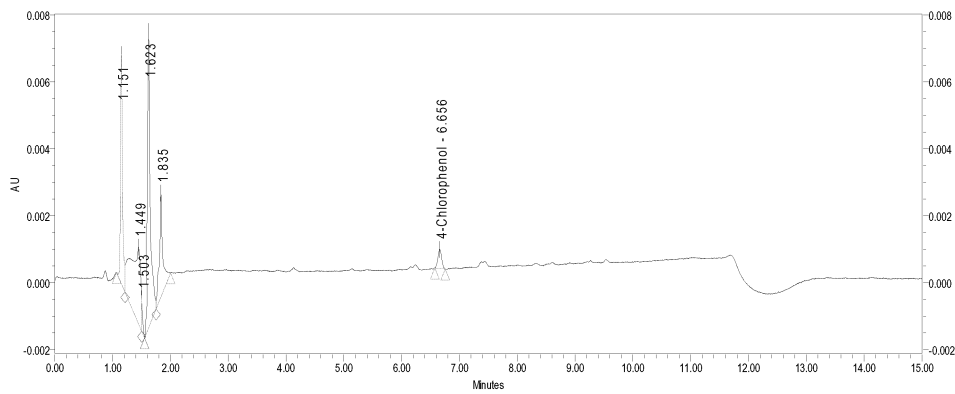


Figure 4: Chromatographic showing residual 4-chlorophenol in the chemical chamber

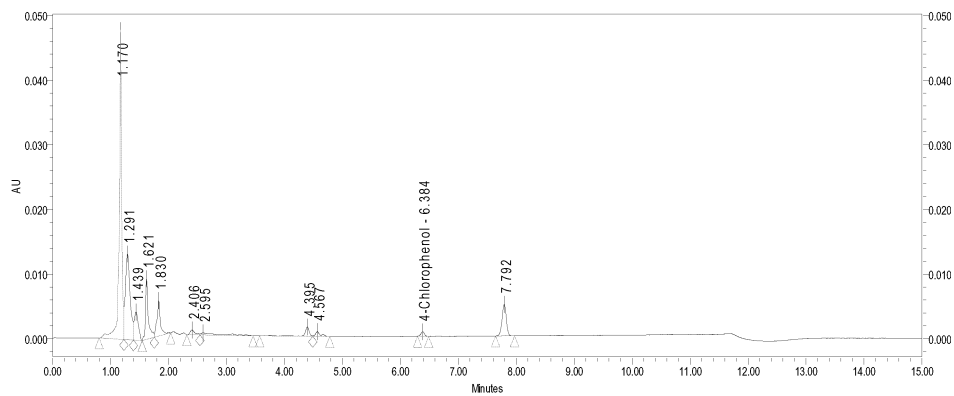


Figure 5: Chromatographic showing residual 4-chlorophenol in the biological reactor

3.2 The effect of adding Hydrogen Peroxide in the feed

Figure 2B shows the time profile for 50 mg 4-CP/L with 0.1 ml H₂O₂/L degradation by UV assisted AOP. When 0.1 ml H₂O₂/L was also added to 100 mg 4-CP/L and 200 mg 4-CP/L, it was observed that overall performance 85% for 100 mg/L and 96% for 200 mg/L respectively compared to overall performance of 63% achieved for 50 mg 4-CP/L. The chromatographic showing residual 4-CP in the feed, chemical chamber and biological reactor for 50mg/L 4-CP concentration are shown in Figure 3, Figure 4, and Figure 5 respectively. It could be seen from the graph in Figure 4 that at a retention time of 4-CP is 6.6. The metabolites formed from the photochemistry of 4-CP are shown on the chromatographic figures.

4. Summary and Conclusion

The results indicated that lowering the H₂O₂ dose in the 4-CP concentration enhances the 4-CP biodegradation in the chemical-reaction stage. However, this phenomenon increases to an optimum after which the degradation rate may decrease due to OH[•] radical scavenging by H₂O₂. H₂O₂ may be used to enhance degradation in the initial stage at lower 4-CP doses. The results show that H₂O₂ dose should be controlled to achieve the optimum efficiency. The intermediates oxidation products remaining in the solution from the biodegradation of 4-CP was found to be less toxic than the initial compound. The study shows the promise of the UV assisted AOP as a pre-treatment stage to increase biodegradability and reduce toxicity of wastewater prior to biological process.

5. References

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