

Two-Phase Chemical Oxidation of Pyrene

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Polycyclic aromatic hydrocarbons (PAHs) are a major concern because of their potential mutagenic and carcinogenic risks to human beings. One of these harmful, yet commonly observed PAHs is pyrene. Pyrene is one of the 16 PAHs listed by the United States Environmental Protection Agency as priority pollutants. The purposes of this research are to develop a method of pretreatment for PAH contaminants prior to a typical biological treatment and to demonstrate the biodegradability of these compounds. Since pyrene is non-polar, hexane was chosen as a solvent to effectively dissolve pyrene. Pyrene solutions were treated with ozone, as it has high oxidation capacity and electrophilic character. The intermediates and byproducts of pyrene were dissolved in alkaline water at pH 11.4 and neutralized to test for BOD₅, COD, and toxicity. These solutions were further ozonated and assessed of biodegradability. The first-order rate constant k_0 was found to be between 0.121day^{-1} and 0.081day^{-1} , depending on the duration of reozonation. The BOD₅/COD ratio was found to 0.66. The toxicity test showed that after 10 min of reozonation time, the byproducts and intermediates of pyrene were within the non-toxic range of $\pm 10\%$ inhibition for *E-Coli* bacteria.

Key Words : Biodegradability, BOD₅, COD, Ozone, PAHs, Pyrene

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) can be formed from both natural and anthropogenic sources. While both sources are contributors of environmentally hazardous compounds, anthropogenic sources are considerably more damaging to the environment. We are exposed every day to an environment containing a myriad of potentially harmful substances, both natural and anthropogenic¹⁾.

The properties of PAHs are unique. PAHs are practically insoluble in water. However, most organic solvents such as benzene, acetone, hexane and tetrahydrofuran readily dissolve PAHs. Carcinogenic PAHs readily vaporize at high temperatures and have high boiling points of over 300 °C. They have a high tendency to adsorb to particulate matter, such as dust particles. These adsorbed particles create respiratory problems as they are easily inhaled in the lungs. Ozone readily reacts with PAHs, yielding oxidized products. PAHs are generally formed during in-

complete combustion or pyrolysis of organic matter. Incomplete combustion of organic matter is a larger concern at concentrated points of emissions, such as an industrial site. PAH-contaminated sites are associated with processing, combustion, and/or disposal of crude oil, coal tar, and fossil fuels²⁾. PAHs are widespread environmental contaminants and one of the most potent classes of carcinogenic chemicals. PAHs have been suspected to play a major role in causing cancer in humans^{2,3)}.

In order to reduce the risk of high PAH levels in drinking water, several methods of water treatment is practiced, such as chlorination and ozonation. Although chlorination may reduce PAH levels, the formation of chlorinated PAH derivatives is a likely result. The possible formations of toxic chlorinated end products are resulting from chlorination of both domestic and industrial waste discharges. Ozone is also strong disinfectant that has being widely used as an alternative to chlorine. Since ozone has high oxidant capacity and electrophilic character, ozone is the most powerful oxidant technique to degrade PAHs⁴⁾. Ozone is formed when an electric discharge is passed through oxygen gas. The reaction of alkene with ozone makes the carbon-carbon double bond break and a carbon-oxygen

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double bond forms. Ozone has an electrophilic character that attaches to an alkene to make an unstable cyclic compound. This is called a monoozonide. Most aromatic and aliphatic unsaturated heterocycles are readily attacked by ozone because it has an electrophilic character. Therefore ozone is known for reacting with PAHs resulting in ring cleavage by bond attack.

A combination of chemical and biological processes is a more effective method for the destruction of many organic contaminants in wastewater. Initial chemical oxidation can destroy compounds that would be not destroyed by the biological process. The intermediates are formed by initial chemical processes that are amenable to further degradation by using the biological process⁵. Although Low-Molecular-Weight PAHs are liable to degradable, High-Molecular-Weight (HMW) PAHs stand against extensive biodegradation in soil and sediment media^{6,7}. Due to the recalcitrant character of HMW PAHs, the PAHs strongly adsorbed onto soil matter⁶.

Previous studies using different solutions for pyrene degradation by ozone were accomplished. The different solutions were methanol⁸, t-butyl alcohol⁹, two-phase fluoro-carbon-water¹⁰, two-phase an inert fluoro-iodinated hydrocarbon-water¹¹, oil/water-emulsions¹², and cosolvent system consisting of heptane and acetic acid². By dissolving a highly insoluble a recalcitrant PAH in hexane solvent, a higher solubility and ozone concentration in organic phase will be evident. These mechanisms make an almost limited water-soluble pyrene into a water-soluble compound.

The purposes of this paper are to break down pyrene and to demonstrate the biodegradability of these compounds. This should generate a need to evaluate the potential of a combined chemical-biological treatment process for a highly insoluble, recalcitrant pyrene and other HMW PAHs. This evaluation will provide a greater understanding of environmental hazards and how they can be treated in a more prudent fashion.

2. Materials and Methods

2.1. Chemicals

Pyrene (99%, Aldrich Co) was prepared. Indigo stock solution was prepared by potassium indigo trisulfonate, $C_{16}H_7N_2O_{11}S_3K_3$ (Aldrich Co) per Standard Methods¹³. Polyseed (Hach Co.) was provided in di-

luted water for biochemical oxygen demand (BOD) measurements per Standard Methods¹⁴. COD digestion solutions (0-1,500 mg/L range, Hach Co.) were prepared for chemical oxygen demand (COD) measurement. Inoculum, ToxTrak™ accelerator solution, and ToxTrak™ reagent powder pillows (Hach Co) were prepared for the toxicity test, and used according to the manufactures' instructions. In all procedures requiring water, distilled deionized (DD) water which contains low-organic (<15 ppb as TOC), low-ion (resistivity > 18 M W-cm) and non-pyrogenic (up to 4-log reduction with reverse osmosis pretreatment) was used (4 stage Mill-Q plus system, Millipore Co.). 0.45 μ m of membrane filter papers (Gelman Sciences) were used. Hexane (Fisher Scientific) of HPLC grade was used for dissolving pyrene. Methanol (Fisher Scientific) of HPLC grade was used for dissolving intermediates of pyrene.

2.2. Reactor for hexane and aqueous phases

Ozonation with the hexane solution was done with a batch reactor. The experiments were carried out in 125 mL Erlenmeyer flasks with a magnetic stir bar controlled by a magnetic stirrer. A high-voltage discharge ozonator (Model T-816 polymetrics Corp.) was used to produce ozone from air. The air was supplied to the ozone generator continuously at a flow rate of 2 L/min. The air/ozone mixture was introduced through a glass sparger. The concentration of the pyrene in hexane solution was 2000 mg/L. A total of 0.1 g of pyrene was dissolved in 50 mL of hexane. The ambient temperature was at 21 °C. All experimental conditions were identical.

Ozonation experiments with the aqueous phase were done with a batch reactor. The experiments were carried out in a 500 mL beaker with a magnetic stir bar controlled by a magnetic stirrer. A variable speed pump controlled by a pH meter and controller was used to deliver a 0.1 M NaOH for pH adjustment. A schematic of the reactor configuration is shown in Fig. 1. The ozone was produced from air by a high-voltage discharge ozonator (Model T-816 Polymetrics Corp.). The air was supplied to the ozone generator continuously at a flow rate of 2 L/min. To introduce the air/ozone mixture a glass sparger was used. The volume of test solution was 300 mL. The ambient temperature was at 21°C. All experimental conditions were identical for all procedures.

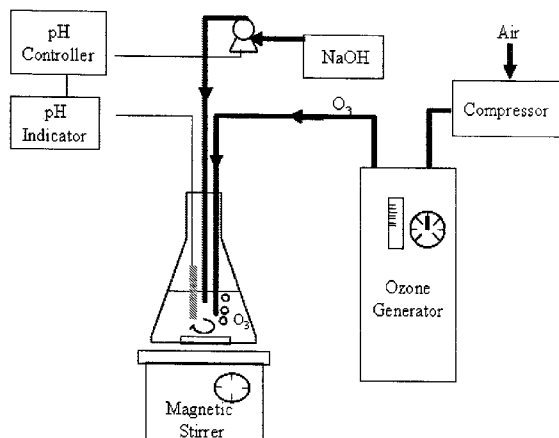


Fig. 1. Reactor configuration for experiments in aqueous phase.

2.3. Concentration of ozone in hexane phase

Ozone (~1% w/w ozone in air) was produced from filtered dry air by an ozonator (Model T-816 polymeric Corp.). To obtain the concentration of ozone in the batch systems, hexane absorbance at 264 nm using a 1-cm quartz cell with a HP-8452 Spectrophotometer was used (HP-8452 UV-V is Spectrophotometer, Hewlett Packard Co.). To determine the ozone concentration the following equation was used to calculating the concentration.

$$O_3 \text{ [mg/L]} = [100 \times A] / [f \times b \times V] \quad (1)$$

Where:

A = difference in absorbance between sample and blank

b = path length of cell, cm

V = volume of sample, ml (20 mL), and

f = 0.42.

Lambert-Beer's law was also used to calculate the ozone concentration in hexane. The following equation 2 is Lambert-Beer's law.

$$A = \log (I_0 / I) = \epsilon bc \quad (2)$$

Where:

A = absorbance, or optical density of solution

I_0 = intensity of light entering solution

I = Intensity of light leaving solution

ϵ = molar absorption coefficient

b = path length of cell, cm, and

c = molar concentration, $L \text{ mol}^{-1} \text{ cm}^{-1}$.

2.4. Concentration of ozone in aqueous phase

The aquatic concentration of ozone in the batch

systems were determined by samples absorbance at 600 nm using a 1-cm quartz cell with a HP-8452 Spectrophotometer (HP-8452 UV-V is Spectrophotometer, Hewlett Packard Co.) according to the Indigo Blue Method¹³. In order to determine the ozone concentration, the following equation 3 was used for our modified procedure based on weighing¹⁵.

$$O_3 \text{ [mg/L]} = \{[(SW + IW)/SW] \times [(DF \times A_{\text{blank}}) - A_s]\} / f \quad (3)$$

Where:

SW [g] = sample weight ($W_{1+S} - W_1$),

W_{1+S} [g] = weight after adding indigo blue solution (7 mL) plus sample (~3 mL),

W_1 [g] = weight after adding indigo blue solution (7 mL),

IW [g] = weight of indigo blue solution ($W_1 - W_{\text{emp}}$),

W_{emp} [g] = weight of the empty test tube,

A_{blank} [#] = absorbance at 600 nm of the indigo blue analytical solution without the sample,

A_s [#] = absorbance at 600 nm of the indigo blue analytical solution plus the sample,

DF [#] = dilution factor, $DF = IW / (SW + IW)$,

f = 0.42.

2.5. Approach

Fig. 2 outlines the key experimental steps of this study. Pyrene was dissolved in hexane because of the nonpolar nature of both substances. Ozone was introduced to the pyrene in hexane solution in order to break down pyrene. Ozone was used because of its high oxidant capacity and electrophilic characteristic. Ozone was introduced to hexane for 2, 3 and 10 min periods. The reaction produced a yellowish solid substance in the solution, which was separated using a centrifuge. The separated yellowish solid was intermediates and byproducts of pyrene.

The biodegradability of intermediates and byproducts was tested in the aqueous phase. Water with a pH of 11.4 was used in order to dissolve a large amount of the yellowish solid. Additional solids were dissolved using ultrasound for agitation for 10 min. A very small amount of solid material remained, which was filtered in order to be separated. The intermediates and byproducts of pyrene solution in aqueous solution were reozonated for 10, 30, and 60 min. This was

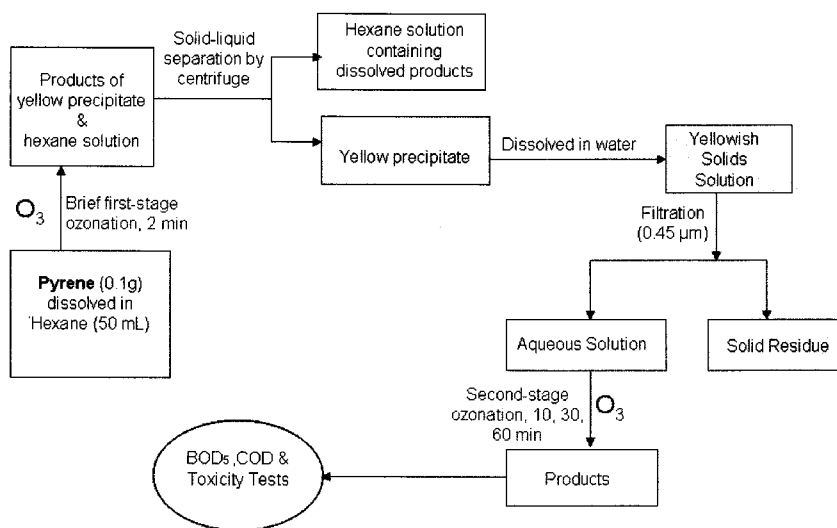


Fig. 2. Sequential ozonation and analyses of pyrene in hexane and aqueous phases.

done in order to prepare the solution for BOD₅, COD and toxicity tests. The BOD₅ and COD tests were performed in order to check the BOD₅/COD ratio. The toxicity test was performed in order to examine whether the compound was toxic to the indicator *E. coil* bacteria.

3. Results and Discussion

The ozonation experiments were conducted in both the hexane and aqueous phases. The aqueous phase displayed a minimal amount of pyrene that dissolved in water (approximately 0.13 mg/L)¹⁵, while the hexane phase dissolved pyrene profusely (approximately 11,600 mg/L). Therefore, hexane was chosen as a solvent for pyrene. Ozonation periods of 2, 3, and 10 min were used, and ozone concentrations in hexane solutions were measured. The data were fitted by regression analysis. The time parameter coefficient was 0.39 and saturated ozone concentration was 0.32 mM in hexane solution. Ozone concentration in the hexane solution was much higher than in the aquatic solution (cf. Fig. 3 and Fig. 4). This clearly indicates that hexane is a much better solvent for pyrene.

Two phases were used to conduct the ozonation experiments: hexane and aqueous. A very small amount of pyrene was dissolved in water during the aqueous phase. However, the hexane phase displayed

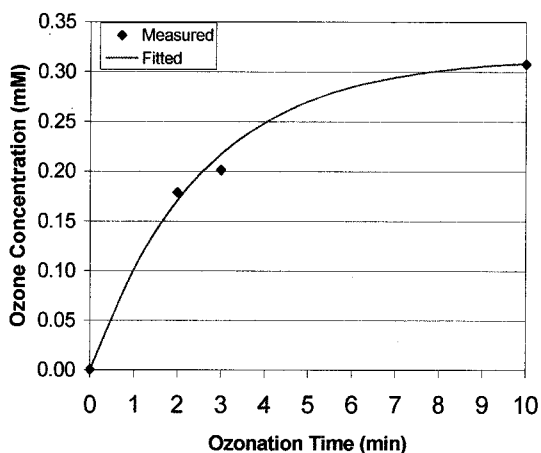


Fig. 3. Concentration of dissolved ozone as ozonation of hexane proceeds.

a very favorable dilution. Therefore, hexane was chosen as a solvent that dissolves pyrene. Fig. 4 shows solubility of ozone in an aqueous solution. The solubility of ozone is much higher in hexane than in water. Since the destruction of hexane by ozone is very slow, hexane is a good solvent for conducting the oxidation of pyrene. Pyrene is a hydrophobic priority pollutant classified by the USEPA that has low water solubility¹⁶.

Ozonation in water at neutral pH was found to be the most effective treatment for three PAH com-

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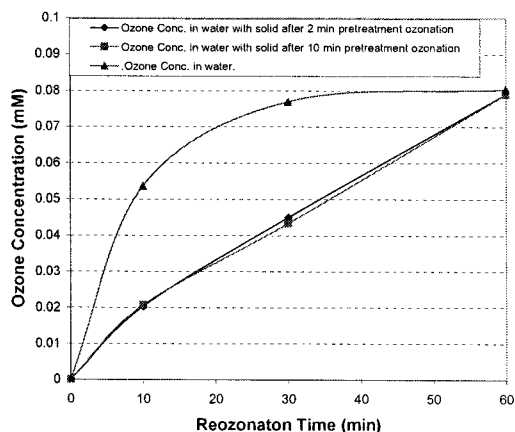


Fig. 4. Concentration of dissolved ozone as ozonation of hexane laden with intermediates and byproducts of pyrene continues.

pounds: fluorene, phenanthrene, and acenaphthene. Beltran⁴⁾ researched these three PAH compounds in aqueous conditions subjected to ozonation at three pH levels. The pH levels that Beltran⁴⁾ researched were 2, 7, and 12. When ozone is used to oxidize a solute in water, OH· radical forms from the decomposing ozone. After 2, 3, and 10 min ozonation in 2000 ppm pyrene hexane solution, a concentration of pyrene was 11.6 ppm, 0.2 ppm, and 0.2 ppm in hexane phase and 2.7 ppm, 2.3 ppm, and 1.8 ppm in the yellowish solid, respectively. For the degradation of pyrene in hexane phase, 3 min of ozonation is an efficient time. The total amount of pyrene degraded was 4.95 mmol or 99.9 mg for 3 min ozonation in hexane phase.

Three tests were used in order to determine the biodegradation of intermediates and byproducts during the aquatic phase: the BOD₅, COD, and toxicity. The BOD₅ test has its widest application in measuring waste loading to treatment plants and in evaluating the BOD₅ removal efficiency of such treatment system.

COD could be divided into biodegradable (BDCOD) and nonbiodegradable (NBDCOD). BDCOD is equal to the ultimate BOD. The BOD₅ curve was best fit with first-order kinetics using the least-square method. A first-order rate constant $k_0 = 0.121 \text{ day}^{-1}$ and an ultimate BOD $L_0 = 121.2 \text{ mg/L}$ was used for reozonating up to 60 min of byproducts and intermediates of pyrene

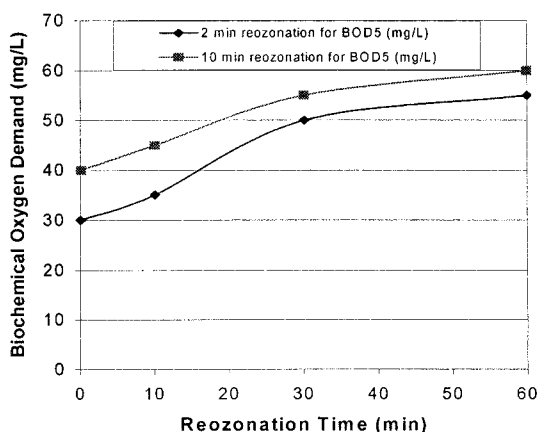


Fig. 5. Change in BOD₅ throughout reozonation of intermediates and byproducts of pyrene (yellowish solids precipitated after 2 min and 10 min in hexane solution) redissolved in 300 mL water.

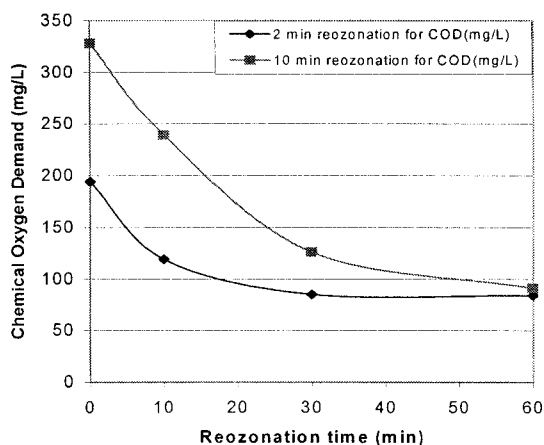


Fig. 6. Change in COD throughout reozonation intermediates and byproducts of pyrene (yellowish solids precipitated after 2 min and 10 min in hexane solution) redissolved in 300 ml water.

water solution (yellowish solids precipitated by 10 min ozonation in 2000 ppm of pyrene hexane solution) in 300 mL water, has a first-order rate constant of $k_0 = 0.081 \text{ day}^{-1}$ and an ultimate BOD $L_0 = 180.2 \text{ mg/L}$.

Fig. 5 and Fig. 6 show the changes in BOD₅ and COD contents in the samples after first- and second-stage ozonation in hexane and aqueous phases. In the first-stage ozonation, there is a general increase of COD but little change in BOD₅ corresponding to the increase of ozonation periods from 2 to 10 min. In the second-stage ozonation, there is a decrease in

COD contents, but slightly increasing BOD₅, corresponding to the increasing duration of in the aqueous phase. These changes have resulted in an increasing BOD₅/COD ratio according to the increasing second-stage ozonation. Such increasing ratios generally reflect the increasing biodegradability in the samples. At the end of 60 min of ozonation, the ratio has approached 70%, which approximates those of typical domestic wastewaters (e.g., 68% of ultimate BOD as BOD₅) that are routinely treated by the activated sludge process.

Fig. 7 corroborates the reduced E-coli toxicity after second-stage ozonation in the aqueous phase. This method of toxicity test is based on the reduction of resazurin, a redox-active dye, by bacterial respiration. When it is reduced, resazurin changes color from blue to pink. Toxic substances can inhibit the rate of resazurin reduction. A chemical accelerant was added to shorten the reaction time. An inhibition values within $\pm 10\%$ would indicate relative non-toxicity in the sample, while any values outside the range would signify toxicity. The results suggest that toxicity is apparent in the samples having been subjected to first-stage ozonation but not the second-stage ozonation. The results also show that a second-stage ozonation of 10 min would be sufficient to render the samples non-toxic, and that the duration of first-stage ozonation (2 or 10 min) exhibits little effect in the reduction of toxicity.

The results of this work suggest the possibility of

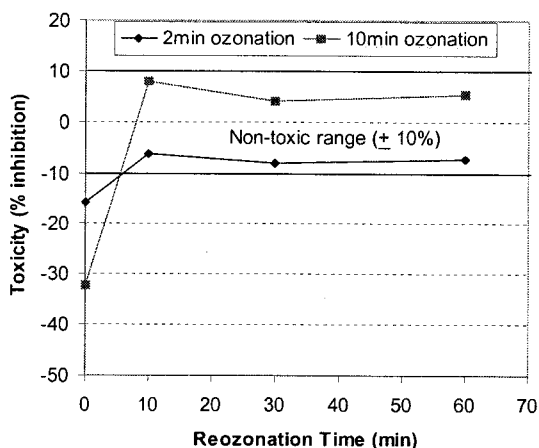


Fig. 7. E-Coli toxicity changes after subjecting pyrene to sequential first- and second-stage ozonation durations in hexane and aqueous phases.

treating highly recalcitrant, hydrophobic contaminants via a 2-stage ozonation in organic and aqueous phases. The process provides the benefits of increasing exposure of the contaminants to chemical treatment agent such as O₃ in this case. The process can be useful targeting clean-up of PAHs residues and bottom sludge in old and abandoned storage tanks especially in developing countries. The process is particularly useful for highly concentrated hydrophobic chemical wastes, which dissolve readily in hydrophobic solvents, and therefore will provide effective first-stage ozonation treatment, to be followed by second-stage treatment in the aqueous phase to the extent of rendering the wastes nontoxic, biodegradable by microorganisms common in activated sludge. The process is therefore more amenable to *ex situ* treatment of extracted hydrophobic contaminants such as PAHs commonly present in contaminated soils. It should be noted that the nonpolar solvent is often capable of dissolving a very high loading of hydrophobic compounds (e.g., >11,600 mg/L of pyrene in hexane) and is reusable once the polar intermediates are removed by means of separation.

4. Conclusions

Previous studies have shown that it is possible to break down pyrene in water, however it was accomplished with a very small quantity and was very ineffective. A solvent must be used in order to dissolve pyrene in order to prepare it to be dissolved in water. Selecting the type of solvent is the most important requirement for an efficient ozonation. This research proved that it is possible to dissolve more than a thousand times more pyrene than those in previous studies. This paper discussed the advantage of a higher solubility of PAH and ozone concentration in hexane in comparison to water. Pyrene can be brought to a state where it can be tested for BOD₅, COD and toxicity tests in an aqueous phase.

Ozone plays an essential role in breaking down pyrene. Ozone is the most powerful oxidant technique used to degrade PAHs because of its high oxidant capacity and electrophilic character. A higher ozone solubility was achieved by ozonating in hexane solvent, which lowered the ozone generation requirements. By taking advantage of the higher ozone solubility, the insoluble recalcitrant pyrene as HMW PAHs could be

easily attacked by biological processes.

This reaction requires additional ozonation, which can be subsequently biodegradable in the aqueous solution. Once these byproducts and intermediates are reozonated, ozone is able to reduce toxicity and improve biodegradability. The biodegradability can be tested on the byproducts and intermediates using the COD and BOD₅ tests. The toxicity test shows that the byproducts and intermediates are non-toxic. Biodegradability is performed using both chemical and biological treatments. Chemical and biological treatments of the byproducts and intermediates of pyrene were susceptible to rapid degradation by each process. The design of integrated chemical and biological systems are more effective and efficient than an individual system. The design of integrated chemical and biological systems are more effective and efficient than an individual system.

References

- 1) Zeng, Y., Hong, A., Wavrek, D. A., 2000, Integrated chemical - biological treatment of benzo[a]pyrene, *Environ. Sci. Technol.*, 34, 854- 862.
- 2) Hong, A., Chao, J. C., 2004, A polar-nonpolar, acetic acid/heptane, solvent medium for degradation of pyrene by ozone, *Ind. Eng. Chem. Res.*, 4, 7710-7715.
- 3) Haapea, P., Tuhkanen, T., 2006, Integrated treatment of PAH contaminated soil by soil washing, ozonation and biological treatment, *Journal of Hazardous Materials*, 136(2), 244-250.
- 4) Beltran, F. J., Ovejero, G., Encinar, J. M., Rivas, J., 1995, Oxidation of polynuclear aromatic hydrocarbons in water. I. Ozonation. *Ind. Eng. Chem. Res.*, 34, 1595-1606.
- 5) Scott, J. P., Ollis, D. F., 1995, Integration of chemical and biological oxidation processes for water treatment: review and recommendations, *Environ. Prog.*, 14(2), 88-103.
- 6) Field, J. A., de Jong, E., Costa, G. F., de Bont, J. A. M., 1992, Biodegradation of polycyclic aromatic hydrocarbons by new isolates of white rot fungi, *Appl. Environ. Microbiol.*, 58(7), 2219-2226.
- 7) Heitkamp, M. A., Cerniglia, C. E., 1989, Polycyclic aromatic hydrocarbon degradation by a *Mycobacterium sp.* in microcosms containing sediment and water from pristine ecosystems, *Appl. Environ. Microbiol.*, 55(8), 1968-1973.
- 8) Danheux, C., Hanoteau, L., Martin, R. H., Van Binst, G., 1963, Beitrage zur kenntnis des pyrens und seiner derivate, *Bull. Soc. Chim. Belg.*, 72, 289-290.
- 9) Sturrock, M. G., Duncan, R. A., 1968, The ozonation of pyrene: A monomeric monoozonide formed in polar solvents, *J. Org. Chem.*, 33, 2149-2152.
- 10) Stich, F. A., Bhattacharyya, D., 1987, Ozonolysis of organic compounds in a two-phase fluorocarbon-water system, *Environmental Progress*, 6(4), 224-229.
- 11) Freshour, A. R., Mawhinney, S., Bhattacharyya, D., 1996, Two-phase ozonation of hazardous organics in single and multicomponent systems, *Wat. Res.*, 30(9), 1949-1958.
- 12) Kornmuller, A., Cuno, M., Wiesmann, U., 1991, Selective ozonation of polycyclic aromatic hydrocarbons in oil/water-emulsions, *Wat. Sci. Tech.*, 35(4), 57-64.
- 13) APHA, AWWA, WPCF (WEF), 1992a, Standard methods for the examination of water and wastewater: Part 4500, ozone (residual), proposed, *Indigo Colormetric Method*, 18th ed.; American Public Health Association: Washington.
- 14) APHA, AWWA, WPCF (WEF), 1992b, Standard methods for the examination of water and wastewater: Part 5210, Biochemical Oxygen Demand (BOD), 18th ed.; American Publish Health Association: Washington.
- 15) Zeng, Y., Hong, A., Wavrek, D. A., 1999, Chemical-biological treatment of pyrene, *Wat. Res.*, 34(4), 1157-1172.
- 16) Upham, B. L., Yao, J. J., Trosko, J. E., Masten, S. J., 1995, Determination of the efficacy of ozone treatment systems using a gap junction intercellular communication bioassay, *Environ. Sci. Technol.* 29, 2923-2928.

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