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Ozonation of polycyclic aromatic hydrocarbon in hexane and water: Identification of intermediates and pathway

Young-Ik Choi† and Andrew Hong*

Department of Environmental Engineering, Silla University, Busan 617-736, Korea
*Department of Civil and Environmental Engineering, University of Utah, Salt Lake City, Utah 84112, USA
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Abstract−The recalcitrant nature of pyrene and other polycyclic aromatic hydrocarbons (PAHs) lies in part in their low solubility in water, rendering them less susceptible to chemical and biological degradation. To overcome this remediation obstacle, this work investigates the use of a 2-stage ozonation process, first in nonpolar hexane phase then in polar aqueous phase, for the treatment of hydrophobic contaminants using pyrene as a model compound. The objectives of this research are to break down pyrene by using ozonation, identify the intermediates of pyrene, show a general degradation pathway of pyrene subject to ozonation and test the biodegradability of intermediates and byproducts of pyrene in the aqueous phase. The first stage briefly ozonates the contaminant at high concentration in organic solvent hexane, which facilitates very efficient conversion of the hydrophobic compounds into ring-opened polar intermediates containing alcohol, aldehyde, and acid functional groups.

Key words: Chemical, Degradation, PAHs, Pyrene, Ozone

INTRODUCTION

Many polycyclic aromatic hydrocarbons (PAHs) including pyrene are priority pollutants because of their toxic and mutagenic properties. Methods employing chemical, biological, or a combination of both have been devised for the remediation of PAHs as recently cited [1-3]. The recalcitrant nature of PAHs owes at least in part to their limited solubility in water that is naturally abundant and ubiquitous in the environment; thus it also limits the contaminants exposures to attacks by chemical and biological agents in the aqueous phase. To circumvent this access limitation, an organic cosolvent incorporated either in a single phase or multiple phases have been used in past treatment studies. The main impetus in using cosolvent systems, which typically involve an organic solvent in addition to water, in contaminant treatment studies lies in enhanced solubility of the contaminants afforded by the organic portion. Early studies of pyrene degradation by O_3 were carried out in different organic solvents including methanol [4], and t-alcohol [5]. Kefely et al. [6] studied the kinetics and mechanism of ozone with polystyrene using CCl_4 as a solvent. Lugube et al. [7] identified byproducts from ozonation of a concentrated naphthalene solution using H_2O/CH_3OH (50/50, v/v) as the cosolvent and found a reaction stoichiometric ratio of 2 moles of O_3 per mole of naphthalene removed. Heterogeneous cosolvents involving 2 phases were also used in ozonation of PAHs and other hazardous contaminants. Kornmuller et al. [8] used dodecane as an aliphatic cosolvent to promote an oil/water emulsion that allowed the delineation of relative reaction rates of PAHs with ozone. Two-phase solvent system consisting of a flurocarbon (FC77) and water were used to study the degradation of phenol and naphthol [9] and other chlorinated phenolic compounds [10,11]. Freshour et al. [12] employed a 2-phase system that consisted of a contaminant-laden aqueous solution in contact with a fluorinated hydrocarbon solvent (FC40) saturated with dissolved ozone to study the degradation of contaminants including pentachlorophenols, oxalic acid, chlorendic acid, 1,3-dichlorbenzene, and trichloroethylene. Yao et al. [13,14] mimicked the degradation of pyrene and benz[a]anthracene in ozonated aqueous environment by exposing dissolved pyrene and benz[a]anthracene, respectively, in 90% acetonitrile:water (v/v) homogeneous mixture to varying dissolved ozone concentrations. Hong and Chao [15] recently reported the use of a polar-nonpolar solvent system involving equal portions of acetic acid and heptane as the medium for ozonation of pyrene. They reported an advantage of the medium being able to maintain all parent and daughter compounds in solution throughout the treatment, hence maximizing the compoundsíexposure to ozone through the entire course of treatment.

Ozone is also a strong disinfectant that has been widely used as an alternative to chlorine. Since ozone has high oxidation capacity and electrophilic character, it is a powerful oxidant to degrade PAHs [16]. 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 carbon-oxygen double bond forms. Ozone has an electrophilic character that attaches to an alkene to make an unstable cyclic compound.

This study examines the breakdown of pyrene by ozone first in hexane, followed by further degradation of the intermediates by ozone in the aqueous phase. The promise of such sequential treatment media is that the nonpolar hexane being a nonpolar solvent is capable of dissolving a large amount of pyrene and exposing it to dissolved ozone, and the intermediates now being more polar with ring-opened, hydroxyl and carboxyl groups in the form of solid precipitates can be readily dissolved once more in water and subject to further ozonation. The 2-stage ozonation process maintains most reactive compounds in solution most of the time, and thus maximizes their exposure to dissolved ozone in the media. The 2-stage

†To whom correspondence should be addressed.
E-mail: coolyoungik@silla.ac.kr

treatment approach would be useful for cleaning up PAHs residues and bottom sludge in old or abandoned storage tanks, and it is most amenable to ex-situ treatment of extracted PAH contaminants, which are common contaminants of soil and sediment.

MATERIALS AND METHODS

Pyrene (99%, Aldrich Co.) was used. Indigo stock solution was prepared by potassium indigo trisulfonate, $C_{16}H_7N_2O_{11}S_3K_3$ (Aldrich Co.) per Standard Methods. In all procedures requiring water, distilled deionized (DD) water that contains low-organic (<15 ppb as TOC), low-ion (resistivity >18 MΩ-cm) and nonpyrogenic (up to 4-log reduction with reverse osmosis pretreatment) was used (4 stage Mill-Q plus system, Millipore Co.). Cellulose nitrate membrane filter papers of 0.45-μm (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.

Each sample containing pyrene, intermediates and byproducts of pyrene were analyzed by using a gas chromatograph (GC) (HP 6890, Hewlett Packard Co.) equipped with a capillary column (DB-1 nonpolar column, 60 m×250 μm×0.25 μm, J & W Co.), and a mass spectrometry detector (MS) (HP6890, Hewlett Packard Co.) interfaced and programmed with HP Chemstation software (Hewlett Packard Co.). The test was set up using a split ratio of 5 : 1, solvent delay at 7 min, and scan range from m/z 15 to m/z 550 at 1.44 scan/sec. The oven temperature was set from 35 ºC (1 min) to 300 ºC (30 min) at 5 ºC/min ramp. Flow rate of He gas in column was 1.7 mL/min. The volume of injecting each sample was 1 μL. To identify the species, the mass spectra were interpreted and the HP Chemstation library (Hewlett Packard Co.) was used. The pyrene and reaction products were analyzed qualitatively and quantitatively with GC/MS. Quantification of pyrene, intermediates and byproducts of pyrene was based on a pyrene calibration curve and peaks integration.

Reozonated compounds in the water solution were analyzed with a Shimadzu Scientific Instruments (Columbia, MD) 10 A vp high performance liquid chromatography (HPLC) system with a 70-vial autosampler. A diode array detector and CLASS-VP v.5 software were also used to analyze the reozonated compounds. Sample injections (12.5 mL) were analyzed using a diode array detector (l= 280 nm). The HPLC was equipped with a YMC HPLC column (300×8.0 mm I. D.). The flow rate was 1.0 mL/min over a period of 25 min.

Ozone was generated by an ozone generator (Model T-816, Polymetrics Corp.) from dry, filtered air at an applied voltage of 65 V and air flow rate of 2 L/min. The concentration of ozone in the organic solvent was determined by absorbance at 270 nm with a spectrophotometer (HP 8452 UV-Vis spectrophotometer, Hewlett Packard Co.) using a predetermined extinction coefficient of 1,955 M^{-1} cm^{-1}. This extinction coefficient was obtained by correlation with actual ozone concentrations in the hexane solvent, which were measured by contacting 10 mL of O_3-saturated hexane solvent with 50 mL of a standard Indigo Blue solution in a separatory funnel, following calibration procedures at 600 nm.

Sample BOD_5 determinations with required controls were made per Standard Methods using an oxygen meter/electrode system (YSI Model 57 oxygen meter with oxygen electrode, YSI Co.) [17]. Chemical oxygen demand (COD) of the sample was measured according to HACHís method (HACH Reactor Digestion Method 467). *E-coli* toxicity of the samples was quantified based on a colormetric method that measured the reduction of the redox-active dye resazurin by bacterial respiration (HACH, Toxicity Method 10017). A spectrophotometer (DR/2000, HACH Co.) was used in CODcr and *E-coli* toxicity measurements.

In a typical run, pyrene was first dissolved in hexane (e.g., 2,000 mg/L) and ozone was then introduced through a gas dispersing tube near the bottom of the reactor to initiate the first-stage ozonation. A fluffy precipitate appeared quickly once ozonation commenced, and was collected by centrifugation and decanting of the excess liquid. The solid and liquid were air-dried at room temperature (21 ºC) for 48 hours. The products contained in both phases were identified by GC/MS. Second-stage ozonation was carried out for the solid that precipitated out of the hexane solvent during the first-stage ozonation. The collected precipitate was introduced into water of pH 11.4, which dissolved most of the precipitates. Any remaining solid was filtered out by a 0.45-μm filter, dried, re-dissolved in methanol, and identified by GC/MS. The aqueous solution containing the intermediates was subject to second-stage ozonation for 10, 30, or 60 min. The pH was maintained around 7 during this stage of ozonation automatic addition of NaOH solution by means of a pH probe/meter/controller system (Cole Parmer Co.). The resulting solution after ozonation was tested for BOD_5, CODcr, and *E-coli* toxicity.

RESULTS AND DISCUSSION

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 a very favorable dilution. Therefore, hexane was chosen as a solvent that dissolves pyrene. Fig. 1 outlines the key experimental steps of this study. In a typical run, pyrene dissolved in hexane (0.1 g pyrene in 50 mL hexane) was first ozonated (i.e., first-stage ozonation) briefly for 2, 3, and 10 min, which resulted in the immediate appearance of a fluffy, yellow precipitate that continued to thicken throughout the duration of ozonation. The precipitate was collected and dried, and it accounted for about 70% of the initial

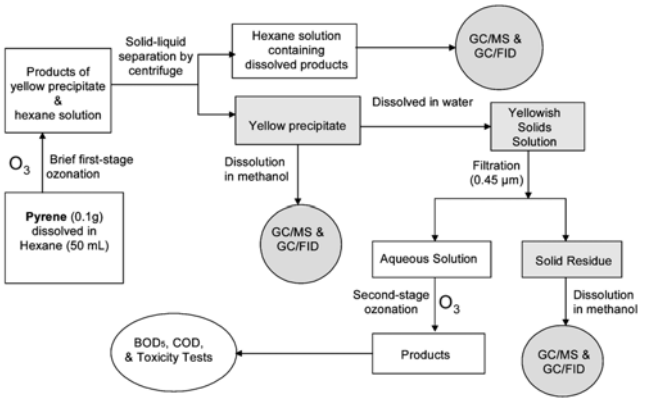

Fig. 1. Sequential ozonation and analyses of pyrene in hexane and aqueous phases.

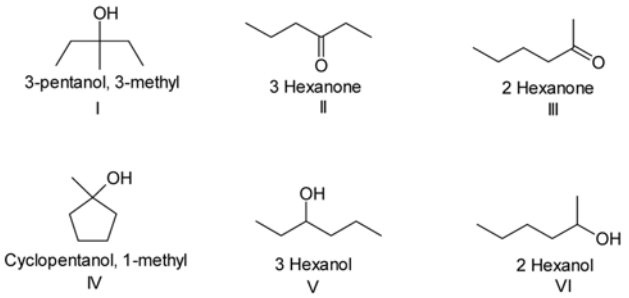

Fig. 2. Byproducts formed during ozonation of hexane itself.

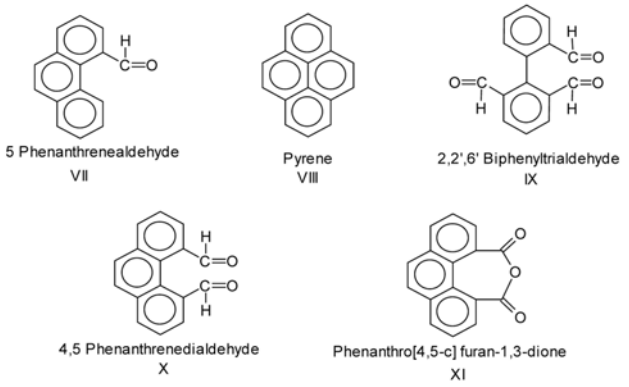

Fig. 3. Compounds that remain dissolved in hexane after the first-stage ozonation in hexane.

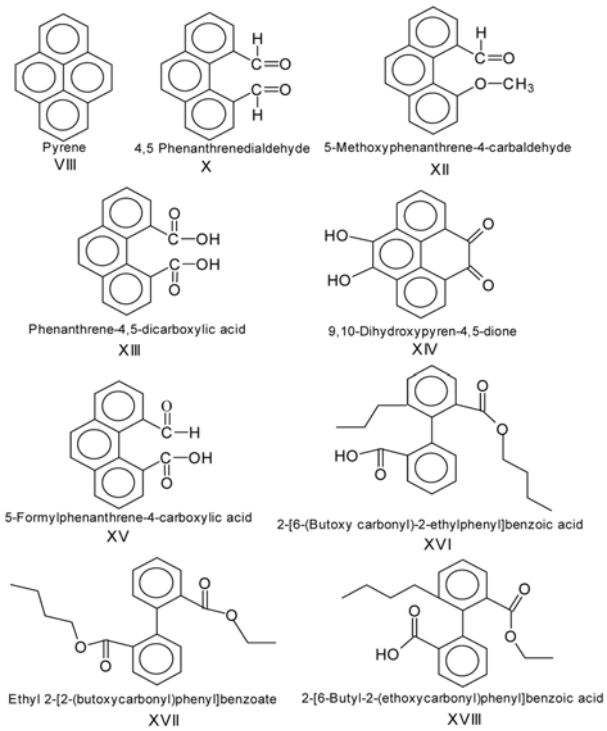

Fig. 4. Intermediate compounds in the yellow precipitate.

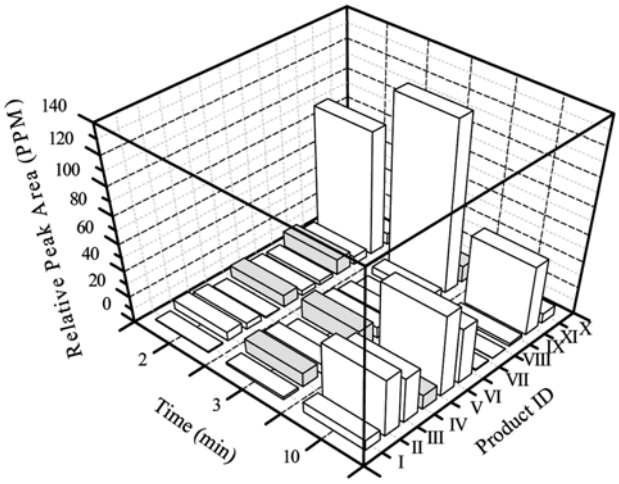

Fig. 5. Concentration profiles of reactants, intermediates and by-products of pyrene after 2, 3 and 10 min ozonation pretreatment in hexane solutions. Concentration estimates were based on the signal response of pyrene.

weight of pyrene. A centrifuge separated the yellowish solids in the methanol solution. The yellowish solids were analyzed by a pyrolysis gas chromatograph at Humble Geochemical Services in the USA. The solids consisted of 66% Carbon, 4% Hydrogen, and 27% Oxygen.

In the hexane phase, two types of ozonation products were formed that ozone reacted with hexane and pyrene. Six compounds which were 3-Pentanol, 3-methyl (I); 3 Hexanone (II); 2 Hexanone (III); Cyclopentanol 1-Methyl (IV); 3 Hexanol (V) and 2 Hexanol (VI) were found in the hexane-type products (refer to Fig. 2). Major product of ozonation of hexane was 3 Hexanol (V). As the concentration of ozone increased, the concentration of hexane-type products also increased. When ozone reacted with pyrene in hexane phase, three phenanthrene-types, which were 5 Phenanthrenealdehyde (VII); 4,5-Phenanthrene (X) and Phenanthro [4,5-c] furan-1,3-dione (XI), and one bipheny-type that was 2,2',6' Biphenyltrialdehyde (IX), were formed (refer to Fig. 3). Fig. 3 shows compounds remaining in the hexane solvent following the first-stage ozonation.

In the yellow solids, nine compounds, which were Pyrene (VIII), 5-Methoxy phenanthrene-4-carbaldehyde (XII), 4,5-Phenanthrene (X), Phenanthrene-4,5-dicarboxylic acid (XIII), 9,10 dihydroxy-pyren-4,5-dione (XIV), 5-Formylphenathrene-4 carboxylic acid (XV), 2-[6-(Butoxycarbonyl)-2-ethyl phenyl] benzoic acid (XVI), Ethyl 2-[2-(butoxycarbonyl)phenyl] bezonate (XVII) and 2-[6-Butyl-2-(ethoxycarbonyl) phenyl] benzoic acid (XVIII), were identified (refer to Fig. 4).

During 2, 3, and 10 min periods of ozonation hexane solutions were also injected in GC/MS directly. Fig. 5 shows a schematic diagram illustrating concentration profiles of reactants, intermediates and byproducts of pyrene after 2, 3, and 10 min of ozonation pretreatment in hexane solution. Fig. 6 indicates a schematic diagram illustrating concentration profiles of reactants, intermediates and by-products of pyrene, which were precipitated (after 2, 3, and 10 min of ozonation pretreatment in hexane solutions) redissolved in methanol (50 ml).

After 2, 3, and 10 min ozonation in 2,000 ppm pyrene hexane solution, the 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

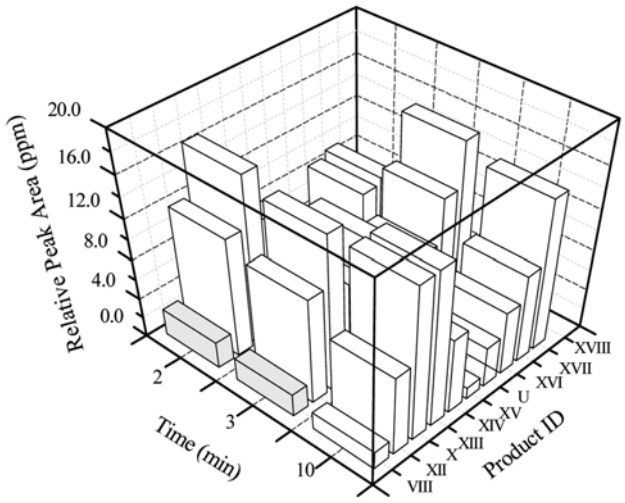

Fig. 6. Concentration profiles of intermediates, and byproducts of pyrene, which were precipitated after 2, 3 and 10 min of ozonation pretreatment in hexane solutions. Concentration estimates were based on signal response of pyrene.

yellowish solid, respectively. For the degradation of pyrene in hexane phase, 3 min of ozonation was an efficient time. The total amount of pyrene degraded was 4.95 mmol or 99.9 mg for 3 min ozonation in hexane phase.

Fig. 7 illustrates a proposed mechanism with identified intermediates and byproducts of pyrene to illustrate the degradation pathway of pyrene in the hexane phase with the sequence of their appearance. The bonds between fused angular rings, as 4,5- and 9,10-bonds, show double-bond character and are more reactive than other bonds. The preferential attack of O_3 on 4,5- and 9,10-bonds of the pyrene molecule could be accounted for in terms of less delocalization energy that makes the site first activated reactive site [18].

During the initial stage of this reaction, the pyrene molecule reacted with ozone to form an aldehyde and/or dialdehyde. 4,5 Phenanthrene dialdehyde (X) was in both the hexane solution and the yellowish solids. In 4,5 Phenanthrene dialdehyde molecular ion peaks, a parent peak is *m/z* 234. According to the loss of aldehydes group (CHO-), other fragments have *m/z* 205 and *m/z* 176. A phenanthrene fragment corresponded to *m/z* 176. In 5-Methoxy phenanthrene-4-carbaldehyde (XII) molecular ion peaks, a parent peak is *m/z* 236.

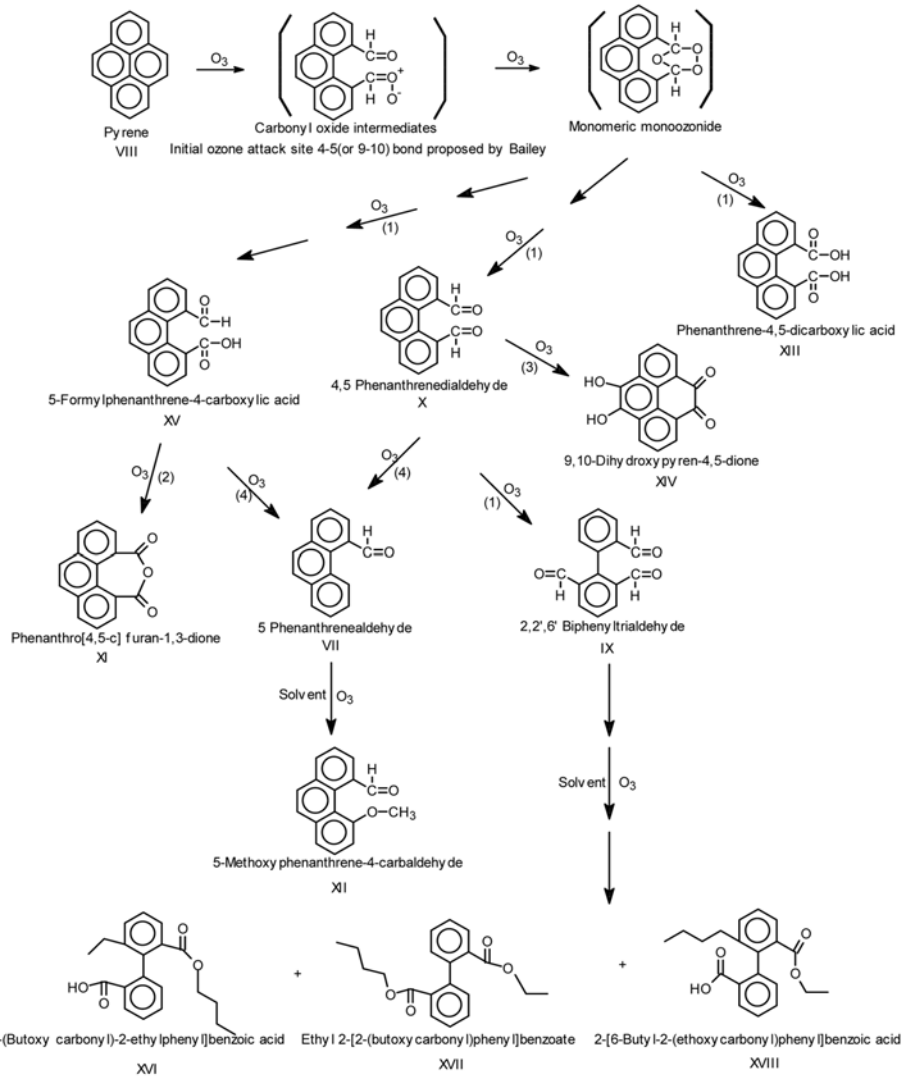

Fig. 7. Proposed pathway for degradation of pyrene during ozonation 1, 2, 3 [18] and 4 [13].

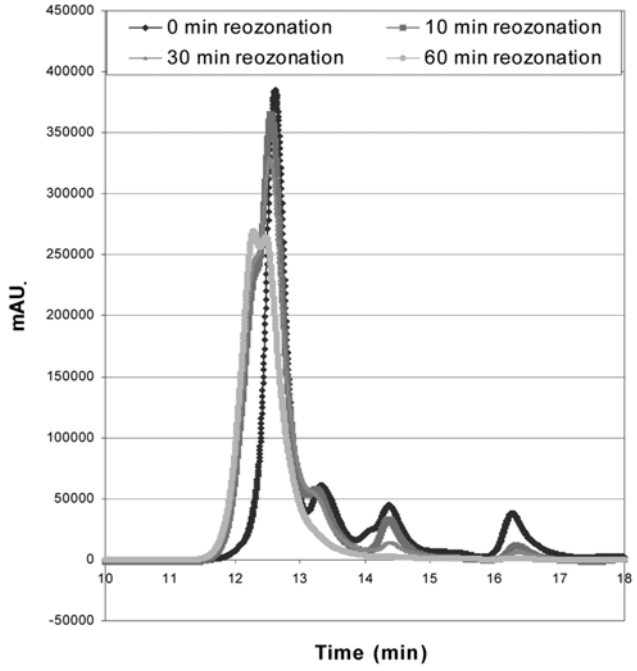

Fig. 8. Liquid chromatograph of intermediates and byproducts of pyrene during reozonation of pyrene (after 2 min ozonation pretreatment in hexane solution).

According to the loss of methyl ether group (CH_3O-) and aldehydes group (CHO-), other fragments have *m/z* 205 and *m/z* 176.

Compounds of the yellowish precipitate were redissolved with high pH water, which were XIII, XIV, XV, XVI, XVII, and XVIII. Fig. 8 shows how the compounds appeared or disappeared in water as they were subjected to reozonation for different duration times (0, 10, 30 and 60 min) as indicated by the HPLC chromatograph. The peaks around 13.3 min, 14.4 min, and 16.3 min were lowered with ozonation. After 60 min of reozonation in aqueous phase, all peaks disappeared completely. A huge peak around 12.6 min could be related to XVI, XVII, and XVIII compounds that were constituted isomers. Other destroyed compounds formed a peak around

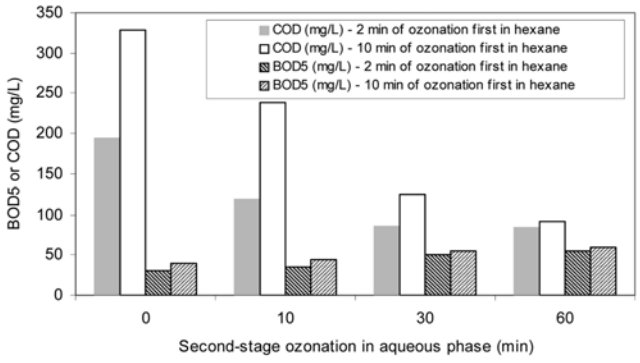

Fig. 9. BOD_5 and CODcr contents of samples after subjecting pyrene to 2 or 10 min of first-stage ozonation in hexane; following by recovery of the yellow precipitates, redissolution of the precipitate in aqueous solution (300 mg/L), and various durations of second-phase ozonation in the aqueous phase.

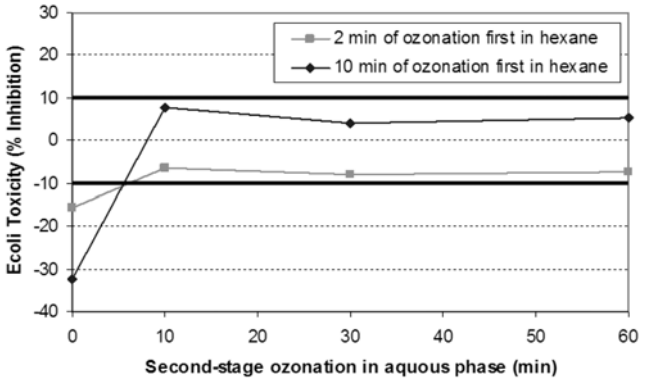

Fig. 10. *E-coli* toxicity changes after subjecting pyrene to sequential first- and second-stage ozonation durations in hexane and aqueous phases.

12.3 min.

Compounds dissolved in high pH water were XIII, XIV, XV, XVI, XVII, and XVIII. Fig. 9 shows the changes in BOD_5 and CODcr 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 CODcr but little change in BOD_5 corresponding to the increase of ozonation periods from 2 to 10 min. In the second-stage ozonation, there is a decrease in CODcr contents, but slightly increasing BOD_5, corresponding to the increasing duration of the aqueous phase. These changes have resulted in an increasing BOD_5/CODcr 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 approached 70%, which approximates those of typical domestic wastewater (e.g., 68% of ultimate BOD as BOD_5) that are routinely treated by the activated sludge process.

Fig. 10 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 value within ±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 nontoxic, and that the duration of first-stage ozonation (2 or 10 min) exhibits little effect in the reduction of toxicity.

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 was 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 pre-

vious studies. Pyrene can be brought to a state where it can be tested for BOD_5, CODcr and toxicity tests in an aqueous phase. The biodegradability could be tested on the intermediates and byproducts of pyrene using the CODcr and BOD_5 tests. The toxicity test showed that the byproducts and intermediates were non-toxic. Biodegradability was performed using both chemical and biological treatments. Chemical and biological treatments of the intermediates and byproducts of pyrene were susceptible to rapid degradation by each process. The design of integrated chemical and biological systems was more effective and efficient than an individual system. The objectives of this research were to break down pyrene by using ozonation, identify the intermediates and byproducts of pyrene, show a general degradation pathway of pyrene subject to ozonation and test the biodegradability of intermediates and byproducts of pyrene in the aqueous phase.

This work illustrated a more effective way to dissolve pyrene. Ozone was the means of accomplishing this great task. The oxidation of PAHs in two-phase was more powerful and effective than any single-phase to be accessible to biodegradability. Reozonated intermediates and by-products of pyrene in aqueous solution were rendered completely non-toxic. This was verified by the acute aqueous toxicity tests. By using this technology to reduce the amount of PAHs that was being emitted into the environment, the air, water, and soil can be cleaner and human life will be healthier. The yellowish solids that were not dissolved in high pH water are subjects of continuing study for toxicological effects.

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