Oxidation of polycyclic aromatic hydrocarbons by ozone in the presence of sand

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Abstract A series of soil slurry experiments was performed to investigate the characteristics of PAHs removal by ozone in various conditions. Gaseous ozone was bottled into the aqueous phase in the presence of soil contaminated by PAHs. The effects of soil media, OH radical scavengers, ozone dosage, and humic acid were examined at the given experimental conditions. There exists a substantial difference in the removal of PAH according to the types of soil media tested. Baked sand showed the highest removal efficiency compared to the others. The descending order of removal rate was: BS>S>GB. This is considered to be due to the OH radical effect produced by catalytic reactions of ozone with the reactive site on the and. This is qualitatively proved by the experiment of scavenging OH radicals using *tert*-butanol. The comparison of half-lives of ozone in sand and glass bead columns further supports this hypothesis. It was found that about 22% of enhancement of phenanthrene destruction was accomplished by OH radicals produced by the catalytic ozone decomposition. The rate of ozone consumption for the phenanthrene oxidation was obtained as 1.88 mg/mgO$_3$/min.

Keywords Benzo(a)pyrene; catalytic reaction; ozone self-decomposition; ozone; phenanthrene; radical scavenger

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are of environmental concern due to their recalcitrant properties, common occurrence in contaminated sites and carcinogenic potential to human health (Calabresde and Kostecki, 1991). Since most PAHs are semi-or non-volatile, and hardly biodegradable, conventional methods such as soil vapor extraction and bioventing processes are not efficient to remediate those PAH-contaminated sites. Chemical oxidation techniques are receiving increasing attention and the *in situ* introduction of strong oxidants into contaminated soil and groundswater is considered to be an effective method to overcome the limitations of conventional processes imposed by PAH compounds (Lin and Gurol, 1998; Prasad and Watts, 1997; Masten and Davies, 1997). Ozone, hydrogen peroxide, and potassium permanganate are the most commonly used oxidants. Although Fenton-like oxidation involving the decomposition of H$_2$O$_2$ catalyzed by iron(II) leading to OH radical production is a potential process to oxidize a wide range of contaminants, H$_2$O$_2$ is subject to decompose rapidly by iron and iron salts in soil, suggesting difficulties transporting the oxidant to the target area, and has relatively low reactivity (Watts and Dilly, 1996).

On the contrary, ozone, as a powerful oxidant, has several advantages compared to the conventional oxidants. Ozone can be applied as either gas phase or aqueous phase depending on the site conditions, and can be readily decomposed via the catalytic reaction with the reactive site on soil to produce OH radicals, a powerful, effective, and non-specific oxidizing agent (Choi *et al.*, 1998). Several works on the *in situ* ozonation revealed successful remediation on the sites contaminated with PAHs and other chlorinated organic compounds such as

TCE and PCE (Masten, 1991; Masten and Davies, 1997; Choi *et al.*, 1998). However, very few works on the enhanced removal of PAHs by OH radical generated due to the catalytic reaction of ozone, and other factors such as ozone dosage and bicarbonate for PAHs in soil slurry type reactor have been reported. Therefore, it is our objective in the research reported, to evaluate the effectiveness of the PAHs removal by ozone in the presence of soil and investigate the effects of OH radical scavengers like *tert*-butanol and bicarbonate.

Experimentals

Materials
The soil used for the study was Jumunjin sand (Korea). The sand was passed through 355~500 μm sieves to provide a uniform surface area. The physical properties and x-ray fluorescence (XRF) analysis of the Jumunjin sand are summarized in Tables 1 and 2. The size of glass bead purchased ranges from 400 to 600 μm. Prior to use, the sand was washed and baked at 500°C for 24 hrs to remove organic matter and the glass beads were also washed and dried at 105°C for 24 hrs. The TOC of the sand was 0.12%. Unless otherwise specified, all solutions used distilled and deionized water. Ozone was generated from dried oxygen by electric discharge using a PCI Ozone Generator (Model GL-1, USA.). The PAHs used in the experiments were obtained from either Wake Co. or Acros Co. and were at least 95% pure. Humic acid was purchased form Acros Co. as sodium salt. Dimethyl chloride and tert-butyl alcohol were obtained from Fisher Inc. and Junsei Co., respectively. Both chemicals were HPLC grades.

Methods
The gaseous ozone was monitored by Anseros® ozone monitor (Ozomat GM series) and measured by trapping in a KI solution (Langlais *et al.*, 1991). Off-gas ozone was also trapped in the KI solution and the mass of ozone consumed was calculated from the mass balance in the system. The residual aqueous ozone was quenched with 1 ml of 2 N $Na_2S_2O_3$. The PAH contaminated soils were prepared in the following manner: 1 mg of target PAHs were dissolved in 20 ml dimethyl chloride, and 1 ml of PAH stock solution was

Table 1 Characteristics of Jumunjin sand

Soil property	Value
Porosity	0.41
Bulk density (g/cm^3)	1.48
Specific weight	2.5
Water content (%)	6.3
Particle size (μm)	355–500
Organic matter content (%)	0.12

Table 2 Results of x-ray fluorescence (XRF) analysis of Jumunjin sand

Contents	Analysis data (%-wt)	Contents	Analysis data (%-wt)
SiO_2	90.41	MgO	<85 ppm
Al_2O_3	5.48	K_2O	3.45
Fe_2O_3*	0.12	Na_2O	0.36
TiO_2	0.02	P_2O5	0.01
MnO	<74 ppm	L.O.I**	0.09
CaO	0.07	Total	100

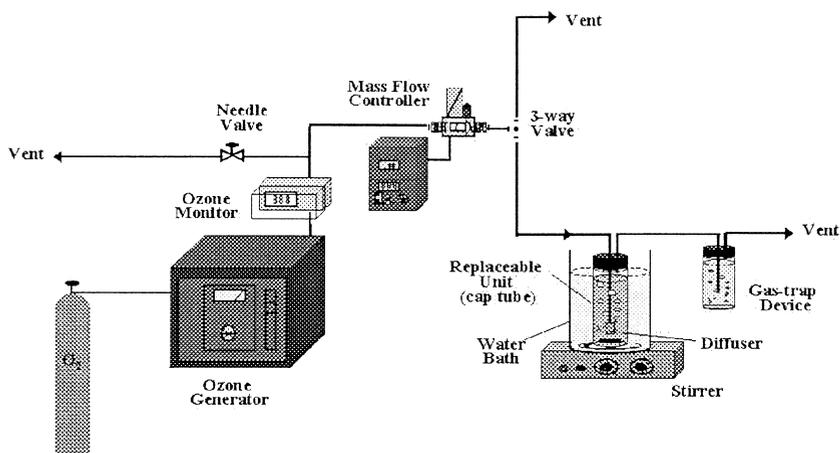Note: *; total Fe, **; Loss on ignition

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Figure 1 Schematic diagram of replaceable soil slurry reactor

added to 5 g of soil. The mixture was well shaken by hand and dimethyl chloride were volatalized. Then 10 mg/kg of PAHs was ready to use. The soil samples were extracted with dimethyl chloride. After adding the dimethyl chloride in the soil sample, it was voltaxed and sonicated for one hour. PAHs dissolved in the solvent were analysed by HPLC. Average recovery ratio of PAH was 70~80% and at least duplicate data was used. Quantification of phenanthrene and benzo(a)pyrene was carried out by Waters™ HPCL system equipped with an autosampler (Waters™ 7170 and UV absorbance detector (Young-in, M720, Korea) at a wavelength of 254 nm. The effluent was 65% acenotrile in water at a flow rate of 1.0 mL/min with a Nova-Pak C_{18} column (3.9×150 mm, Waters). The temperature of the column box was 40°C.

Ozonation experiments

Soil slurry and column tests were conducted for the removal of PAHs in various conditions and ozone self-decomposition. Figure 1 shows the schematic diagram of the soil slurry reactor. A fifty mL Kimax® tube was used for the reactor. All tubing and fittings were made of Teflon and used stainless steel valves (Swagelok). Test runs were made in the semi-batch mode. Gaseous ozone was bubbled into a series of the slurry reactor containing 25 mL water and 5 go of soil media contaminated by PAHs. The gas flow rate of 50 mL/min was regulated by using a mass flow controller (Rich Field, Inc.). Total volume of 2.5 L column made of pyrex glass was set up to study the self-decomposition rate of ozone. Details of the experimental procedure for the ozone decay test are presented elsewhere (Choi *et al.*, 1998).

Results and discussion

Experimental investigation was conducted to delineate the characteristics of ozone oxidation of PAHs as affected by types of soils, ozone dosage, humic acids, and *tert*-butanol and bicarbonates as OH radical scavengers. All experiments were carried out in isotherm conditions (25°C) and at least duplicate data sets were used to analyze the result. Control tests were paralleled and revealed no loss by oxygen gas.

Effect of media

Three different types of soil media; sand(S), baked sand(BS), and glass bead(GB), were employed to investigate the effect of soil types in the ozone oxidation of phenanthrene and benzo(a)pyrene(PAHs) sorbed on the soil surface. Comparison of the removal of PAHs among those 3 different soils are presented in Figure 2. In all cases, the PAHs removed
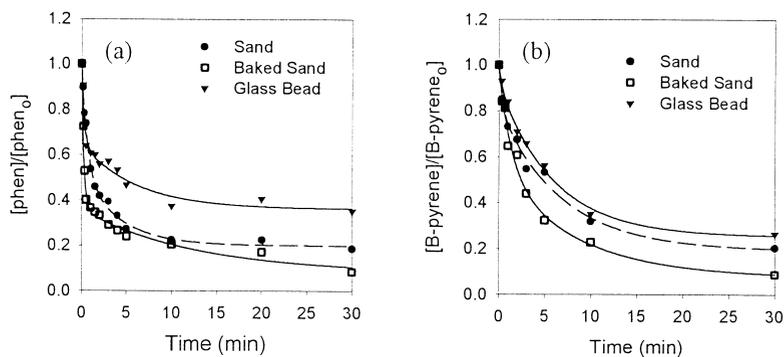
Figure 2 Effect of soil media on (a) Phenanthrene and (b) Benzo(a)pyrene removal by ozone

showed similar trends; a sharp decline within 3 minutes of reaction and then asymptotic decrease was observed. This is considered to be due to the sorption effect. Watts (1996) stated that chemicals that are sorbed have a reduced reactivity with most species used to promote remediation, like OH radicals and aqueous electrons. In the beginning, the oxidant can easily contact with loosely bound phenanthrene to initiate a rapid reaction. However, as the reaction proceeded to some extent, the reaction speed substantially reduced due to the phenanthrene firmly bound on the solid surface or sorbed in micropores.

Close observation of the results reveals that there was a dramatic difference in the removal of PAHs according to the types of soil media. It is obvious that BS has a higher reaction rate with ozone than GB. The descending order of removal efficiency is BS>S>GB. Over 90% removal of phenanthrene on BS was achieved, of which 60% was degraded within 1 minute of the reaction. On the contrary, only 65% of phenanthrene was oxidized in GB with 25% removal in 1 minute. This difference in the removal pattern of phenanthrene can be attributed to the catalytic properties of the sand surface to enhance the self-decomposition rate of ozone (Choi *et al.*, 1998; Limvorapituk, 1991) and to generate more OH radicals in the system. OH radicals are well known to have a strong, nonspecific oxidation power on organic compounds with the reaction rate constant of $10^7 \sim 10^{10} \, \text{M}^{-1} \, \text{s}^{-1}$ (Galze, 1987).

Silica-alumina (Si-O-Al-Si) on the sand surface is a very reactive site having powerful catalytic function (Ouerderni *et al.*, 1991). According to the x-ray fluorescence analysis of Jumunjin sand (Table 2), SiO_2 occupies 90.4% of the total mass, while Al_2O_3 has the smaller portion of 5.48%. Hence, there are high possibilities for the sand to have sites, to some extent, which have a very strong catalytic reactivity with ozone. This fact provides an appropriate ground to elucidate that BS that contains amorphous SiO_2 has higher PAH removal efficiency than GB of which SiO_2 is crystalline, in other words, nonreactive.

As compared between S and BS, the organic matter in the soil plays some role in the PAH removal. Organic substance consumes ozone and is known to act as a OH radical scavenger (Staehelin and Hoigne, 1985). The organic content of the sand used in this study is about 0.12% by weight. Thus, the phenanthrene removal rate is retarded to some extent due to the scavenging effect of the organic matter on the soil surface.

Ozone self-decomposition in soil

To confirm the enhanced decay of ozone in the presence of sand, column experiments on the ozone self-decomposition test were conducted. Gaseous ozone was injected in the column packed with sand and glass beads for several pore volumes so that the equilibrium ozone concentration is maintained in the column. And then the column is closed on both sides to investigate the effect of the presence of solids on the self-decomposition rate of
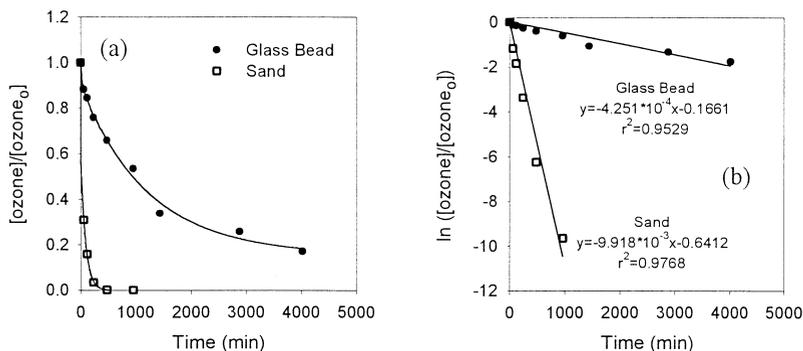
Figure 3 Ozone self-decomposition in sand and glass bead columns. (a) Ozone disappearance (b) Semi-logarithmic plot
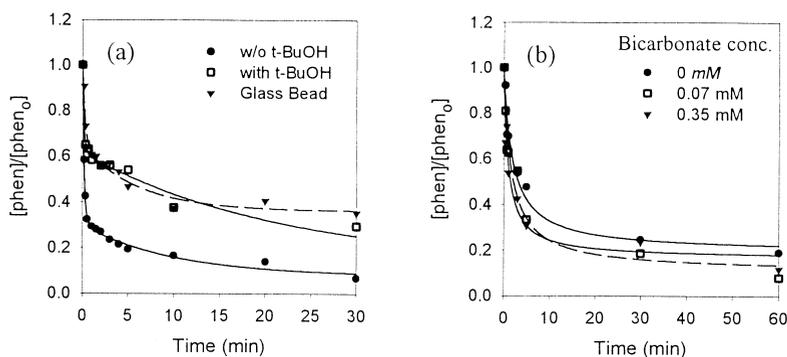
Figure 4 Effect of radical scavenger on the removal of phenanthrene (a) *tert*-Butanol (b) Bicarbonate

ozone. A total of four columns were prepared and each column was sacrificed according to the elapsed time to measure the residual ozone in the column. Figure 3(a) and (b) presents the temporal behavior of the ozone disappearance and the semi-logarithmic plot of the data. It is quite obvious that the ozone decay rate in the sand column is considerably faster than that in the GB column. The half-life of ozone decomposition in the GB column is approximately 1000 minutes while that of the sand column is 40 minutes.

In other words, the half-life of ozone in the sand column is almost 25 times shorter than that in the GB column. The ozone decay follows first order kinetics and the rate constants are $4.3 \times 10^{-4}\,\text{s}^{-1}$ and $9.9 \times 1010^{-3}\,\text{s}^{-1}$ for GB and S columns, respectively. Although the gas phase reaction is much faster than the aqueous phase reaction, the basic mechanisms can be considered to be the same. Therefore, one can conclude that the presence of sand in the ozonation of PAHs enhances the remediation efficiency.

Effects of t-butanol and bicarbonate as radical scavengers

Further investigation to qualitatively verify the enhanced remediation of phenanthrene by OH radicals generated by the catalytic reaction of ozone on the sand surface is necessary and worthwhile. *tert*-Butanol and bicarbonate are well known as OH radical scavengers (Staehelin and Hoigne, 1985; Galze *et al.*, 1987). Hence, these two compounds were selected to study the effects of OH radical scavengers. Twenty microlitres of *tert*-butanol (0.112 mmol) was added to 2.87×10^{-4} mmol of phenanthrene on BS and ozone (0.106 mmol) was injected at a rate of 0.17 mg/min. The removal of phenanthrene was compared with and without the scavenger. Figure 4(a) shows the test results. It is easily noticed that there exists a considerable difference in the removal rate of phenanthrene between BS
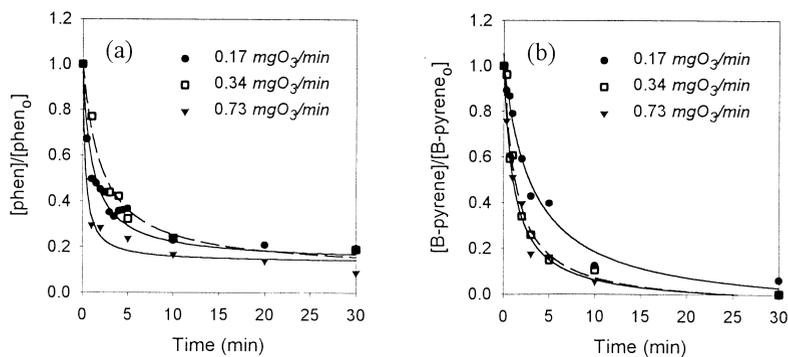
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Figure 5 Effect of ozone dosage on the removal of (a) Phenanthrene and (b) Benzo(a)pyrene

with and without *tert*-butanol. BS without *tert*-butanol has more than 20% higher removal rate than with *tert*-butanol. Therefore, it is clear that the reactive surface, which is mainly the silica-alumina site, can generate OH radicals via the catalytic reaction with ozone molecule and enhance the phenanthrene removal. It is interesting to note that the comparison between BS with *tert*-butanol and GB reveals similar trends. This is considered to be due to the fact that most of the OH radicals generated are scavenged by *tert*-butanol and only the direct reaction with ozone proceeded. Hence, the removal pattern looks similar to that of GB. Based on the integration of the total area of the removal curve, the enhancement of the removal by OH radical during the reaction was found to be approximately 22%.

Figure 4(b) presents the effect of bicarbonate on the phenanthrene destruction. The concentrations of sodium bicarbonate used in this experiment were 0.07 and 0.35 mM. The pH ranges of all experiments were 6.8~7.2. The presence of bicarbonate does not have much influence on the phenanthrene removal. On the contrary, as the bicarbonate concentration increases, a slight increase in the removal is observed. It is hypothesized that bicarbonate may act as a promoter rather than a scavenger of OH radicals (Kang, 1999). However, this is the area of further research recommended.

Effect of ozone dosage

It is usual that the degradation of organic compounds is proportional to the mass of ozone input. A set of experiments was carried out to investigate the effect of ozone dosage on the destruction of phenanthrene and benzo(a)pyrene. The test results are shown in Figure 5. In both cases, the higher removal was achieved as more ozone dosage was applied. In Figure 5(a), the ozone input rates of 0.17 and 0.34 mg/min resulted in almost the same removal rate, although the rate curves looked slightly reversed in order. For benzo(a)pyrene, further ozone input over 0.34 mg/min does not make any difference to removal efficiency. Also the complete destruction of benzo(a)pyrene was achieved at the output input rate of over 0.34 mg/min.

The mass balance of ozone was checked in the system to better understand the characteristics of PAHs removal in the presence of soil. The input mass of ozone were monitored by the ozone analyzer and cross-checked by KI trap method and off-gas ozone was directly trapped by KI solution to measure the cumulated ozone concentration during the experiment. For the case of $0.17 \ MgO_3/min$, the rate of ozone consumption for the phenanthrene oxidation was $4.8 \ mgO_3/kg/min$ and the unit phenanthrene removal was obtained as 1.88 mg phenanthrene/mgO_3/min.

Effect of humic acid

As mentioned earlier, organic matter such as humic substances reacts with ozone, suggesting that the ozone demand is required in employing *in situ* ozone remediation process. The
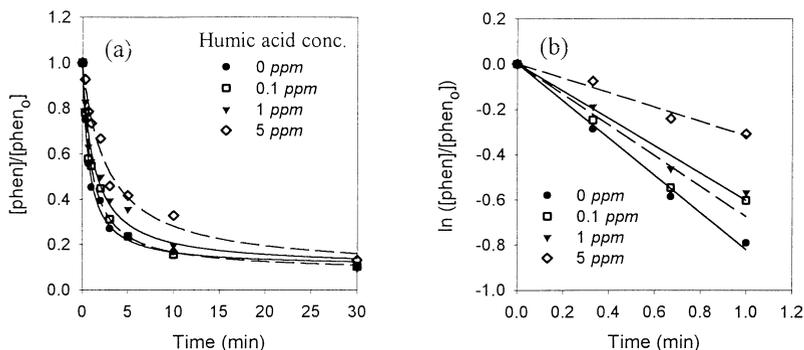
Figure 6 Effect of humic acid on the removal of phenanthrene. (a) Concentration profile
(b) Semi-logarithmic plot

effect of humic acid on the phenanthrene removal by ozone is investigated. Three different concentrations of humic acid ranging from 0 to 5 mg/L were applied. BS spiked with 10 mg phenanthrene/kg soil was used in the experiment. Figure 6 illustrates the temporal removal pattern and the semi-log plot. It is noticed that the removal rate decreases as the level of humic acid rises. A retarded destruction rate due to the presence of humic acid was observed within 10 min of reaction after which the rates of all cases converge to 90% removal after 30 minutes. This trend implies that in the beginning of the reaction, say up to 15 minutes, a portion of ozone injected was consumed to oxidize humic acid, since then on all were utilized to remove phenanthrene. The physical observation of the aqueous phase verified this hypothesis; the dark brown color of humic acid gradually disappeared as the ozonation proceeded. The semi-log plot of the phenanthrene removal at the beginning of the reaction reveals the pseudo-first order kinetics.

Conclusion

A number of slurry-type experiments were conducted to investigate the effects of soil media, ozone dosage, humic acid and OH radical scavengers on the removal of PAHs in the presence of soil. The baked sand has the highest capability for phenanthrene removal by ozone due to the catalytic ozone decomposition on the silica-alumina surface. The descending order of removal efficiency is BS>S>GB. From the self-decomposition test of ozone, the half-line of ozone in the sand column was 25 times shorter than in the glass bead column. The removal rate of PAHs was proportional to the ozone dosage. The unit phenanthrene removal was observed to b 1.88 mg phenanthrene/mgO$_3$/min. From the Oh radical scavenger test, it was found that 22% of enhancement of the phenanthrene removal was achieved by OH radicals generated by the catalytic reaction of ozone with the reactive site of the soil. Based on the findings in this study, one can conclude that *in situ* ozone remediation is a potential process in sites contaminated by PAHs.

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