

## In situ ozonation of anthracene in unsaturated porous media

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### Abstract

Soil column experiments were conducted to investigate the effect of ozonation duration, contaminant content, particle size, moisture content, OH<sup>•</sup> radical scavenger and soil organic matter on the removal of anthracene by in situ ozonation. In the whole study, the gas flow rate was 100 mL/min and concentration of gaseous ozone was 40 mg/L. The removal efficiency increased with the elapsed time, but the removal rate decreased in the range of 0–90 min. As anthracene content in sand decreased from 50 to 10 mg/kg, the removal efficiency increased from 42.1% to 62.0%, and ozone passed through soil column more rapidly. However, the ozone effectiveness reduced when anthracene content dropped. Small particle size provides a large interfacial area, which led to the high removal efficiency and long ozone breakthrough time in the column. The profile of residual anthracene in soil column varied more greatly at smaller particle size. The removal efficiency reduced when the moisture content rose from 0% to 9.1%. The ozone breakthrough time also decreased with the increasing moisture content. The presence of sodium bicarbonate or humic acid reduced the removal efficiency to some extent. GC–MS was employed in this study to determine 9,10-anthraquinone as the main ozonation product.

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**Keywords:** In situ; Ozonation; Anthracene; Unsaturated porous media

### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an environmental concern because of their biological recalcitrance, common occurrence in contaminated sites, and carcinogenic or potential carcinogenic properties. Conventional methods such as pump and treat, soil vapor extraction, and bioremediation could not remove PAHs from subsurface efficiently. Great effort has been made to find effective methods to remediate PAHs contaminated soils. Recently, in situ chemical oxidation (ISCO) was proposed as an innovative treatment technology to remove PAHs and other organic pollutants in the subsurface [1]. In situ ozonation is such an ISCO that has been employed to clean up soils contaminated by PAHs [2,3], diesel fuel [4], 2-chlorophenol [5], aniline and trifluralin [6]. It was also employed as a pre-oxidation step

for enhancing bioremediation of PAHs contaminated soils [7,8]. However, the efficiency of in situ ozonation may be limited by factors such as ozonation duration, PAHs content, particle size, moisture content, OH<sup>•</sup> radical scavenger and soil organic matter. This study was conducted to determine the effect of these factors on the removal of PAHs in sand by in situ ozonation using anthracene as a model compound.

### 2. Materials and methods

#### 2.1. Soil column preparation

Sands were first passed through one (0.5 mm) or two sieves (0.5–1.0 and 1.0–2.0 mm) to provide a consistent surface area. Then they were suspended in 5% H<sub>2</sub>SO<sub>4</sub> solution. After the acid treated sands were washed thoroughly with distilled water, they were dried overnight at 105 °C in an oven to eliminate the moisture. A given amount of anthracene (MERCK-

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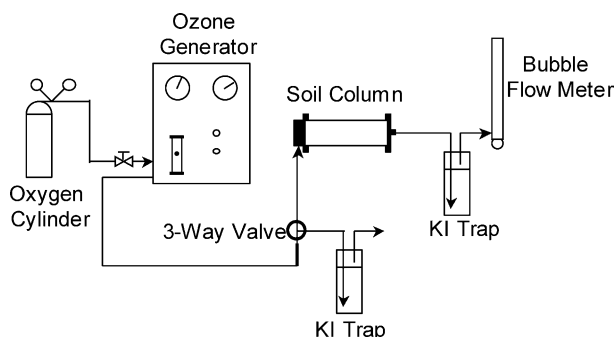


Fig. 1. Experimental setup.

Schuchardt, Germany) was dissolved in acetone and spiked with the sands by hand. The spiked sands were placed under the hood to evaporate the solvent. Then distilled water was added to the spiked sand to achieve the selected moisture content. The sand sample was packed into a 20 cm long column (prexy glass) with an inner diameter of 4 cm.

## 2.2. Ozone treatment

Ozone was generated from dried oxygen (99.9%) by electric discharge using an ozone generator (XFZ-5QI, China). The gas flow rate was determined with a bubble flow meter and fixed at 100 mL/min. The gaseous ozone concentration in and out of the column was monitored by the iodometric method with potassium iodide solution [9]. The inlet ozone gas concentration was fixed at 40 mg/L. During soil column experiment, the sand-packed column was first ozonated for a predetermined period of time (see Fig. 1). Samples were taken from the column at six different distances along the axial direction. Then 5 mL acetone was added in 1 g sample and shaken for 15 h. After the sample was centrifuged at 4000 rpm for 15 min, the supernatant was diluted and anthracene dissolved in acetone was analyzed with a fluorescence spectrophotometer (Hitachi F-4500, Japan). In this study the average recovery ratio of anthracene was 80–85% and at least duplicated data was used. The product obtained from the ozone treated samples was identified by GC–MS (Finigen, Trance GC–MS 2000 Series, USA). A DB-WAXETR (30 m length  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m film thickness) fused silica capillary column (J&W Scientific Incorporated, USA) was employed for GC separation, and a 33:1 split injection was used with an oven temperature from 50 °C (1 min) to 260 °C (30 min) at a 7 °C/min ramp.

## 3. Results and discussion

### 3.1. Effect of ozonation time

The removal efficiencies of anthracene at different ozonation times are presented in Fig. 2. Anthracene removal efficiency increased with contact time. However, the rate

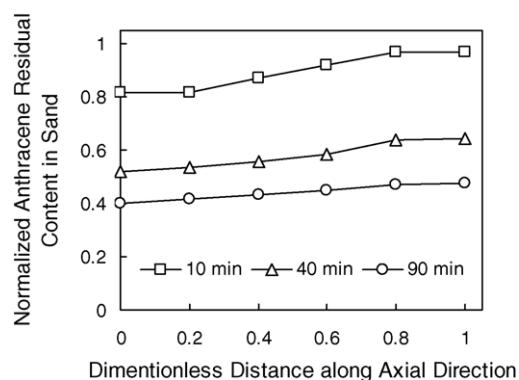


Fig. 2. The effect of ozonation time on anthracene removal ozone gas concentration: 40 mg/L; gas flow rate: 100 mL/min; moisture content: 4.8%; particle size: 1–2 mm; anthracene content: 50 mg/kg.

of anthracene removal slowed down with the elapsed time. During the first 10 min, anthracene removal achieved 10.7%. In the range of 10–40 min, the average removal efficiency increased from 10.7% to 42.1%, but the removal efficiency increased only 13.6% during the following 50 min. The rates of anthracene removal were 1.07, 1.05, and 0.23%/min, respectively during these three time intervals, i.e., 0–10, 10–40, and 40–90 min. This is considered to be due to the sorption effect and the competing reactions between anthracene and its intermediates with ozone. Watts and Dilly [10] stated that chemicals that are sorbed have a reduced reactivity with most species like  $\text{OH}^\bullet$  radical. In the beginning of ozone treatment, the oxidant could easily contact with loosely bound anthracene to initiate a rapid removal rate. However, the anthracene removal rate would reduce when the loosely bound anthracene was being destroyed and the oxidant had to react with anthracene that was firmly bound on the solid surface or sorbed in micropores, as Choi et al. [11] reported when phenanthrene and benzo[a]pyrene were oxidized by ozone in the presence of sand. In addition, it is well known that ozonation of organic compound contains a series of complex reactions, which involve reaction between ozone and parent compound as well as the reactions between ozone and intermediates. With the progress of ozonation, the reactions of ozone and intermediate products become more and more dominant compared with that of ozone and parent compound such as anthracene [12]. This also reduces the efficiency of anthracene removal by ozone.

Evaluation of GC–MS analysis indicated 9,10-anthraquinone as the main oxidation product from ozone treatment (see Figs. 3 and 4). This is similar to Lee et al.'s work [13]. They reported that about 80% 9,10-anthraquinone was generated during oxidation of 97% anthracene in simulated soil by Fenton's reagents.

### 3.2. Effect of anthracene content in sand

Fig. 5 illustrates the spatial distributions of anthracene after 40 min ozonation at different anthracene content in sand, i.e., 10, 25, and 50 mg/kg. The removal efficiency

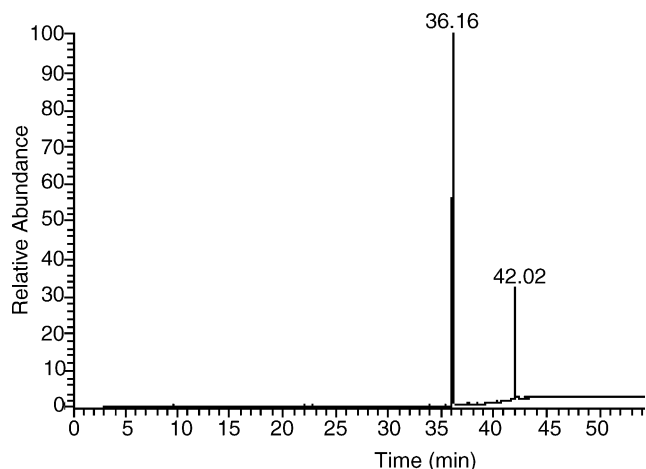


Fig. 3. Gas chromatographs of anthracene and its ozonation product.

decreased with the increasing anthracene content, and the average removal efficiency were 62.0%, 55.2%, and 42.1%, respectively. Defining ozone effectiveness as the ratio of anthracene removal to ozone consumption, we can obtain the ozone effectiveness was 0.217, 0.194, and 0.109 mg anthracene/mg ozone when anthracene contents were 50, 25, and 10 mg/kg, respectively. This indicates that when per unit weight ozone was consumed, less anthracene was destroyed with the decreasing anthracene content, i.e., less dissolved ozone was utilized to oxidize anthracene. As discussed before, ozonation of anthracene includes the reactions of ozone with anthracene as well as ozone with the intermediates produced. When anthracene content was small and anthracene removal was high, the competing reactions of ozone with intermediate products would become dominant. Thus, significant amounts of ozone were consumed by

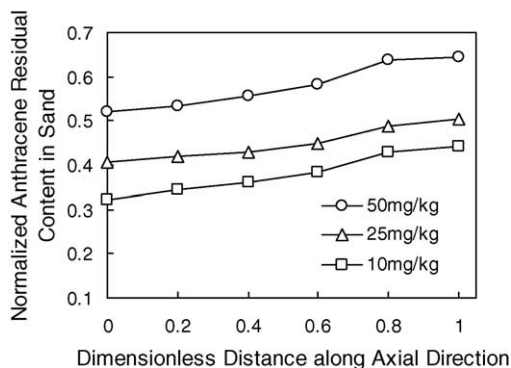


Fig. 5. The effect of anthracene content on removal efficiency. Ozone gas concentration: 40 mg/L; gas flow rate: 100 mL/min; moisture content: 4.8%; particle size: 1–2 mm; ozonation time: 40 min.

the produced intermediates and ozone use was lowered accordingly.

Ozone breakthrough curves (BTCs) under the conditions of three anthracene contents are shown in Fig. 6. The ozone BTCs indicated that ozone transport in gas phase was significantly retarded by ozone consumption due to mass transfer of gaseous ozone into moisture and the following reactions of dissolved ozone with anthracene and its intermediates. The retardation effect was dependent on anthracene content. Ozonation of anthracene in sand can be regarded as a mass transfer process coupled with chemical reactions [5,12]. Ozone is transported by advection and diffusion in the pore gas and also dissolves into moisture covering sand particles. Dissolved ozone reacts with dissolved and sorbed contaminants [14]. The occurrence of chemical reactions will enhance mass transfer of ozone from gas to moisture [5]. The enhancement factor is defined as the ratio of chemical

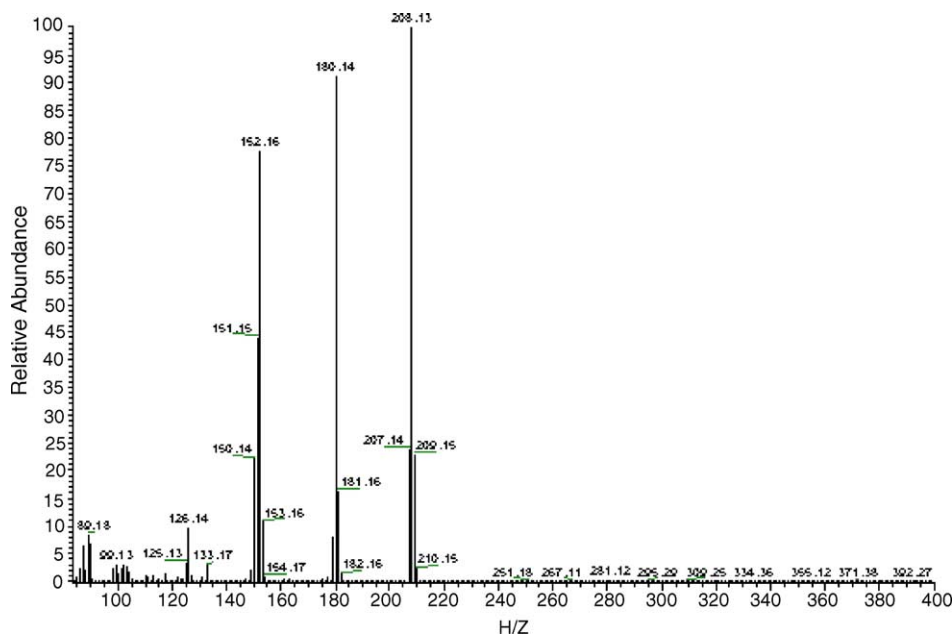


Fig. 4. Mass spectra of 9,10-anthraquinone.

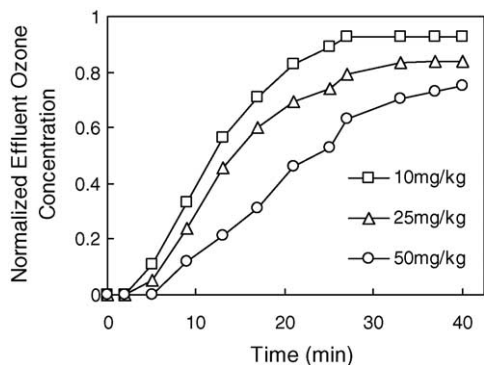


Fig. 6. The effluent ozone concentration at different anthracene content inlet ozone gas concentration: 40 mg/L; gas flow rate: 100 mL/min; moisture content: 4.8%; particle size: 1–2 mm.

mass transfer rate to pure physical mass transfer rate, which is dependent on two quantities, i.e., the enhancement factor for an infinitely fast reaction and Hatta modulus [15]. Both quantities are related to reactant concentration and high reactant concentration leads to high enhancement factor. Thus, as shown in Fig. 6, the increase of anthracene content in sand improved the enhancement of ozone mass transfer, which resulted in the significant consumption of gaseous ozone and long breakthrough time of ozone.

### 3.3. Effect of particle size

Fig. 7 shows anthracene removal at different particle sizes after 40 min ozone treatment. It can be seen that the removal efficiency increased with the decrease of the particle size. The average removal efficiencies were 62.0%, 71.8%, and 78.1% when the particle sizes were 1.0–2.0, 0.5–1.0, and 0.5 mm, respectively. Ozone venting involves chemical reactions of ozone and contaminants as well as mass transfer of ozone from gas to moisture. According to the two-film theory, the dissolution rate of gaseous ozone into pore moisture can be described as a function of the mass transfer coefficient and the driving force. The mass transfer coefficient is dependent on the interfacial area and the

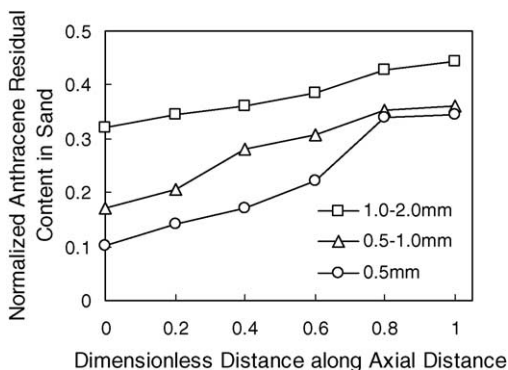


Fig. 7. The effect of particle size on anthracene removal efficiency ozone gas concentration: 40 mg/L; gas flow rate: 100 mL/min; moisture content: 4.8%; anthracene content: 10 mg/kg; ozonation time: 40 min.

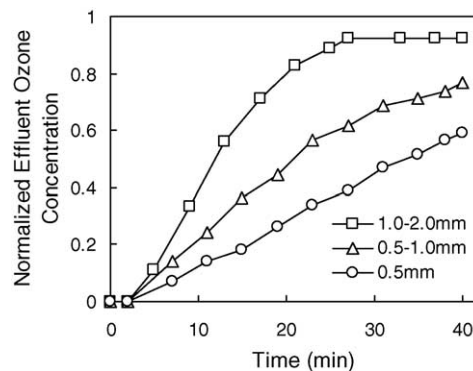


Fig. 8. The effluent ozone concentration at different particle size inlet ozone gas concentration: 40 mg/L; gas flow rate: 100 mL/min; moisture content: 4.8%; anthracene content: 10 mg/kg.

liquid-phase resistance [14]. A finer particle size means a larger specific surface area [6], a higher mass transfer coefficient, and therefore a higher dissolution rate. As more ozone dissolves into an aqueous solution, more anthracene will be destroyed. In the meantime, the higher dissolution rate of ozone leads to more consumption of ozone in the gas phase. Therefore, the ozone transport under the condition of smaller particle size will be more retarded, as shown in Fig. 8.

Fig. 7 also indicates that the spatial distribution of anthracene under the conditions of different particle sizes is different. The residual concentrations at different positions were close under the condition of 1.0–2.0 mm particle size (see Figs. 2, 5 and 7), but they varied more and more greatly when the particle size dropped (see Fig. 7). The differences of normalized anthracene residual content between the top and bottom of the column were 0.12, 0.19, and 0.24 when the particle sizes were 1.0–2.0, 0.5–1.0, and 0.5 mm, respectively. When packed with sands of small particle size, the column provides large contact area [6]. Therefore, more ozone dissolves into the water and less gaseous ozone remains in the pore gas accordingly, which results in the ozone profile in the gas of the column varying greatly. Therefore along the column, less and less ozone in the pore gas is available to diffuse into pore moisture and oxidize contaminants, and accordingly the distribution of anthracene residual content changes significantly.

### 3.4. Effect of moisture content

Fig. 9 illustrates anthracene removal at different moisture contents after 90 min ozone treatment. Less moisture content led to more anthracene removal, i.e., 51.8%, 55.8%, and 59.3% average removal efficiencies when moisture contents were 9.1%, 4.8%, and 0%, respectively. At the same particle size, interfacial area decreases with the increase of moisture content [16]. Therefore, less ozone dissolves into soil moisture and oxidizes contaminants. In addition, ozone oxidizes organic pollutants via two pathways: by direct oxidation with ozone molecules and by the generation of free-radical inter-

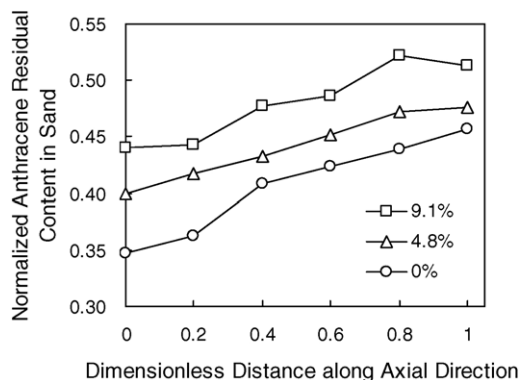


Fig. 9. The effect of moisture content on anthracene removal efficiency ozone gas concentration: 40 mg/L; gas flow rate: 100 mL/min; particle size: 1–2 mm; anthracene content: 50 mg/kg; ozonation time: 90 min.

mediates, such as  $\text{OH}^\bullet$  radical, a powerful, effective, non-selective oxidizing agent [17]. It has been reported that in the absence of moisture,  $\text{OH}^\bullet$  radical would be produced by catalytic reaction of ozone with the reactive site on the sand [11,18,19]. When the oxidation is carried out via  $\text{OH}^\bullet$  radical reactions, the destruction of PAHs will be enhanced. In the presence of moisture, the moisture layer covers the sand surface even at lower moisture content. The pore water blocks the reactive sites of the sand, thus reducing catalytic reactions with ozone [18]. Although dissolved ozone in pore water may undergo similar reactions, the reaction rate is much faster in the gas phase than in the aqueous phase [11,18]. Therefore, the oxidation efficiency drops to some extent.

Fig. 10 indicates the ozone BTCs during the first 60 min treatment. It can be seen that rising moisture content decreased ozone breakthrough time. When moisture content increases, the interfacial area drops [16]. Therefore, the rate of ozone dissolution decreases and less ozone is consumed in the pore gas. In addition, the average liner gas velocity increases as a result of reduced gas pore volume in the column [18]. This leads to the shorter ozone breakthrough time at a higher moisture content.

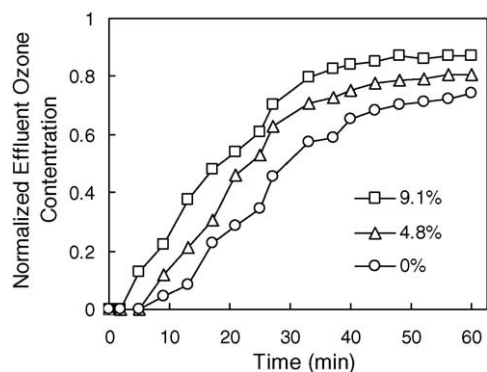


Fig. 10. The effluent ozone concentration at different moisture content ozone gas concentration: 40 mg/L; gas flow rate: 100 mL/min; particle size: 1–2 mm; anthracene content: 50 mg/kg.

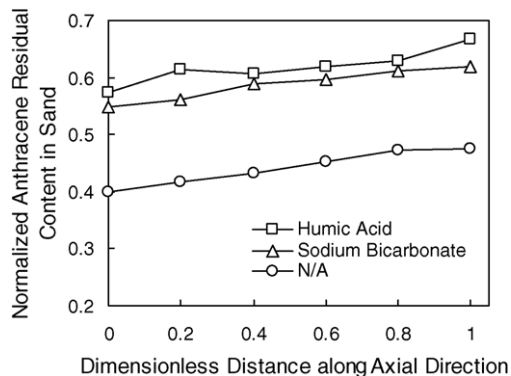


Fig. 11. The effect of  $\text{OH}^\bullet$  radical scavenger and soil organic matter on anthracene removal efficiency ozone gas concentration: 40 mg/L; gas flow rate: 100 mL/min; moisture content: 4.8%; particle size: 1–2 mm; anthracene content: 50 mg/kg; ozonation time: 90 min.

### 3.5. Effect of $\text{OH}^\bullet$ radical scavenger and soil organic matter

To investigate the effect of  $\text{OH}^\bullet$  radical scavenger on the removal of anthracene by ozone, 2 g/kg sodium bicarbonate, a kind of  $\text{OH}^\bullet$  radical scavenger [17], was spiked with anthracene contaminated sand. As shown in Fig. 11, the presence of sodium bicarbonate reduced the extent to which anthracene was degraded. The average removal efficiency reduced to 41.1% compared with 55.8% removal efficiency in the absence of sodium bicarbonate. This means that indirect reactions involving  $\text{OH}^\bullet$  radical occur in ozone remediation. It was reported that the direct reaction rate constant between ozone and PAHs such as anthracene was close to  $1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  in aqueous phase, and  $\text{OH}^\bullet$  radical reaction was one or two orders of magnitude higher [20]. The rate constant between  $\text{OH}^\bullet$  radical and bicarbonate ion is  $2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [21] and is close to  $\text{OH}^\bullet$  radical reaction of anthracene. Therefore we cannot say 41.1% removal efficiency is merely the contribution of ozone direct reaction with anthracene, as sodium bicarbonate may not scavenge  $\text{OH}^\bullet$  radical completely.

Soil organic matter such as humic substances reacts with ozone, suggesting that the ozone demand is required in employing in situ remediation process [11]. The effect of humic acid (Aldrich humic acid as sodium salt used in this study) on the anthracene removal by ozone was investigated. Fig. 11 showed that the removal efficiency dropped in the presence of 2 g/kg humic acid. And the degree of inhibition was greater than with sodium bicarbonate. Humic acid consumes ozone and is known to act as a scavenger of  $\text{OH}^\bullet$  radical like sodium bicarbonate [21]. The rate constant between  $\text{OH}^\bullet$  radical and humic acid is  $3 \times 10^4 (\text{mg/L of DOC})^{-1} \text{ s}^{-1}$  [22]. In addition, the presence of soil organic matter leads to the fact that anthracene was strongly sorbed into soil matrix through the partitioning into soil organic matter. The partitioning of the contaminant into soil organic matter may reduce the reactivity of the compound [2]. Thus, the presence of humic acid inhibits anthracene removal efficiency.



#### 4. Conclusions

The results of this study show that ozone can effectively remove anthracene in sand. 9,10-Anthraquinone was identified as the main oxidation product by GC–MS. The removal efficiency depends on treatment duration, anthracene content, particle size, moisture content, OH• radical scavenger and soil organic matter. With the elapsed time, the removal efficiency increased but the removal rate lowered due to the sorption effect and the competing reactions between anthracene and its intermediates with ozone. As anthracene content in sand decreased from 50 to 10 mg/kg, the removal efficiency increased from 42.1% to 62.0%, and ozone passed through soil column more rapidly. However, the ozone effectiveness reduced as ozone was significantly consumed by the intermediates formed during ozonation process. Small particle provides large interfacial area, which led to the high removal efficiency and retarded ozone transport in the column. Additionally, the profile of residual anthracene varied greatly at smaller particle size since more ozone was consumed and less ozone was available to dissolve into pore moisture and oxidize contaminants along the column. The removal efficiency reduced when the moisture content rose from 0% to 9.1%, which resulted from the decreased contact area and the inhibition of indirect reaction involving OH• radical produced by the reaction of ozone with the reactive site on the sand. The ozone breakthrough time also decreased with the increasing moisture content due to the reduced surface area and pore gas volume. The presence of sodium bicarbonate or humic acid reduced the removal efficiency, indicating in situ ozonation occurs via both direct ozone molecule reaction and indirect OH• radical reaction.

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