

# ADVANCED OXIDATION PROCESSES (AOP) FOR THE OXIDATION OF AROMATIC AND POLYAROMATIC HYDROCARBONS: KINETICS AND REACTION PRODUCTS

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**Abstract.** The kinetics and by-products of AOP treatment of substituted phenols and polycyclic aromatic hydrocarbons were studied. Ordinary ozonation was shown to be more effective than other AOPs for the destruction of these hazardous compounds.

**Key words:** ozonation, advanced oxidation processes (AOP), phenols, polyaromatic hydrocarbons (PAH), waste water.

## INTRODUCTION

Among ozone treatments, advanced oxidation processes (AOP) have proved to be very efficient for the destruction of different organic pollutants. AOP use different combinations of oxidants, irradiation, and catalysts to generate free hydroxyl radicals in water, that is highly reactive species that can be of great virtue for complete destruction of organic micropollutants. The AOP combinations include  $\text{H}_2\text{O}_2/\text{O}_3$ ,  $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  (Fenton reaction), photo-Fenton reaction, ozonation in alkaline pH, and  $\text{UV}/\text{TiO}_2$  (semiconductor photocatalysis). The efficiency of these oxidation processes depends on the various parameters, such as oxidant dose, UV-light intensity, pH, etc. They are also compound-specific. AOP have become quite commonly used for drinking and waste water treatment.

Ozonation and AOP have been studied for two groups of aromatic compounds – substituted phenols and polycyclic aromatic hydrocarbons (PAH) in aqueous media. These compounds are wide-spread in waste waters and are also anthropogenic contaminants of surface waters.

## EXPERIMENTAL

Experiments of ozonation and AOP treatment were performed in a semicontinuous bubble column. The apparatus and experimental conditions as well as analytical techniques applied are described in previous papers [1, 2]. The concentration of phenols (analytical grade) was 0.4 mM/L. Concentrations of PAH (obtained from the Aldrich Chemical Company, USA) did not exceed their aqueous solubility [3]. High performance liquid chromatography (HPLC) was used for measuring PAH [1] and phenol [2] concentration. For the analyses of hexane extracts of benzo(*ghi*)perylene and benzo(*a*)pyrene a method based on Shpol'skij effect was applied [4].

All experiments were conducted at 20°C. The processes were studied in acidic, neutral, and basic media.

## RESULTS AND DISCUSSION

The degradation curves of PAH and phenols in different oxidation conditions were registered in a semicontinuous bubble column with a verification of the chemisorption regime [5]. The analyses of kinetic curves show that the reactions are of the first order with respect to both the concentration of ozone and PAH or phenols, and the ozonation is of the second order overall.

The reaction rate constants of PAH ozonation, UV-degradation, and AOP are presented in the Table. The reaction rates for ozonation, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, and O<sub>3</sub>/UV processes for seven PAH studied follow the series benzo(*a*)pyrene > pyrene > anthracene > phenanthrene > fluoranthene > benzo(*ghi*)perylene > fluorene. The combination of ozone with UV-radiation and hydrogen peroxide did not show any advantages over ordinary ozonation of PAH; on the contrary, the second-order rate constants for AOP followed the series O<sub>3</sub> ≥ O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> ≥ O<sub>3</sub>/UV > O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub>.

Second-order rate constants  $k_2$  (M<sup>-1</sup>·s<sup>-1</sup>) and first-order rate constants  $k_1^*$  (s<sup>-1</sup>) for advanced oxidation processes of PAH

Compound	O <sub>3</sub>	O <sub>3</sub> /UV	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> /UV	UV*	UV/H <sub>2</sub> O <sub>2</sub> *
Fluorene	4.2×10 <sup>3</sup>	-	-	-	1.7×10 <sup>-3</sup>	-
Anthracene	2.7×10 <sup>4</sup>	2.15×10 <sup>4</sup>	2.6×10 <sup>4</sup>	1.7×10 <sup>4</sup>	2.8×10 <sup>-3</sup>	2.5×10 <sup>-3</sup>
Phenanthrene	1.0×10 <sup>4</sup>	1.0×10 <sup>4</sup>	0.91×10 <sup>4</sup>	0.44×10 <sup>4</sup>	3.0×10 <sup>-4</sup>	2.5×10 <sup>-4</sup>
Fluoranthene	9.5×10 <sup>3</sup>	9.7×10 <sup>3</sup>	8.3×10 <sup>3</sup>	6.5×10 <sup>3</sup>	2.5×10 <sup>-3</sup>	-
Pyrene	3.6×10 <sup>4</sup>	3.8×10 <sup>4</sup>	3.05×10 <sup>4</sup>	2.7×10 <sup>4</sup>	1.0×10 <sup>-2</sup>	8.1×10 <sup>-3</sup>
Benzo( <i>a</i> )pyrene	5.3×10 <sup>4</sup>	5.4×10 <sup>4</sup>	4.7×10 <sup>4</sup>	4.3×10 <sup>4</sup>	6.3×10 <sup>-3</sup>	-
Benzo( <i>ghi</i> )perylene	8.4×10 <sup>3</sup>	-	-	-	5.5×10 <sup>-3</sup>	-

- not determined.

The behaviour of PAH in ozonation and AOP treatment is compound-specific; however, some general qualities can be noticed. There is no acceleration in PAH destruction when combined oxidation methods are applied, and the reaction rate of ozonation is always higher in acidic and



neutral media than in a basic one. Thus, the main conclusion of this study is that the PAH destruction proceeds mostly by molecular ozone. Therefore, the oxidation system should be designed to guarantee the maximum concentration of dissolved ozone. In general, ozone proved to be very effective for the destruction of PAH.

Substituted phenols (such as methyl-, dimethyl-, and chlorophenols) were investigated to fill the gap in the data on the kinetics of the AOP and to evaluate the efficiency of these methods for the purification of phenolic waste waters containing considerable amounts of substituted phenols (in particular, for industrial waste waters of oil-shale chemical treatment). The efficiency of the ozonation processes of phenols may be remarkably increased if ozonation is conducted in basic media (compare Figs. 1 and 2). The addition of hydrogen peroxide and UV-radiation did not show any acceleration effect on the velocity of the destruction of methyl- and dimethylphenols by ozone. The substituted phenols are commonly destroyed by ozone more easily than ordinary phenol. For the posttreatment of the biologically treated phenolic effluent of the oil-shale chemical industry ordinary ozonation at  $\text{pH} > 9.5$  can be suggested.

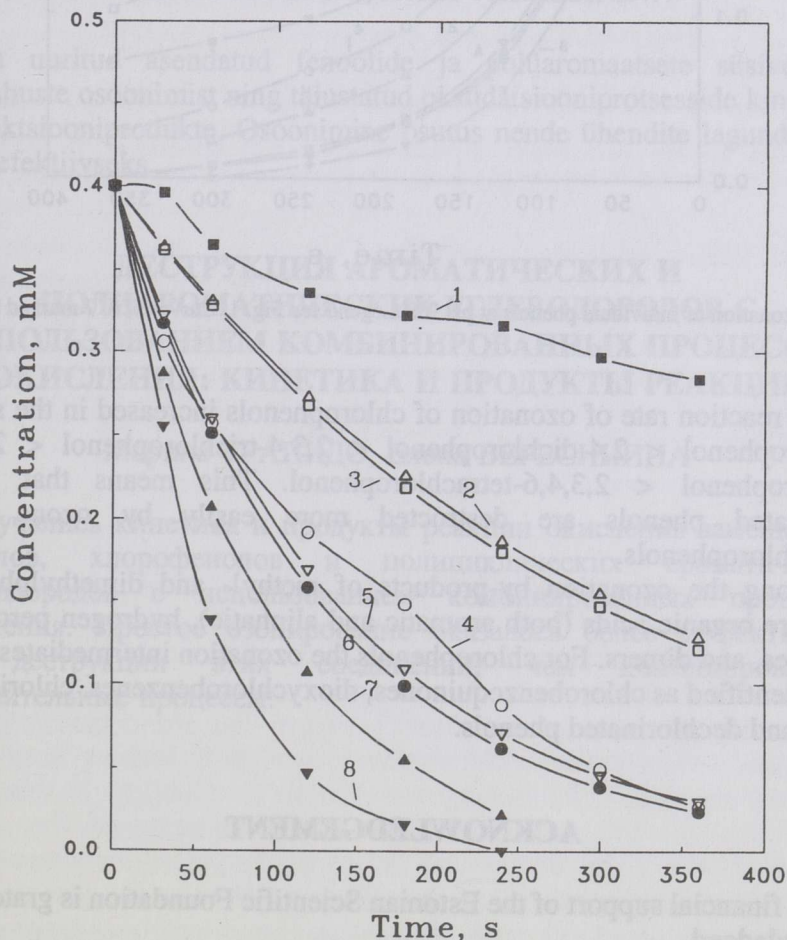


Fig. 1. Ozonation of individual phenols at pH 3.2 (1, phenol; 2, *o*-cresol; 3, thymol; 4, 2,3-xyleneol; 5, 2,6-xyleneol; 6, 2,5-xyleneol; 7, 3,4-xyleneol; 8, 2,3,4-trimethylphenol).

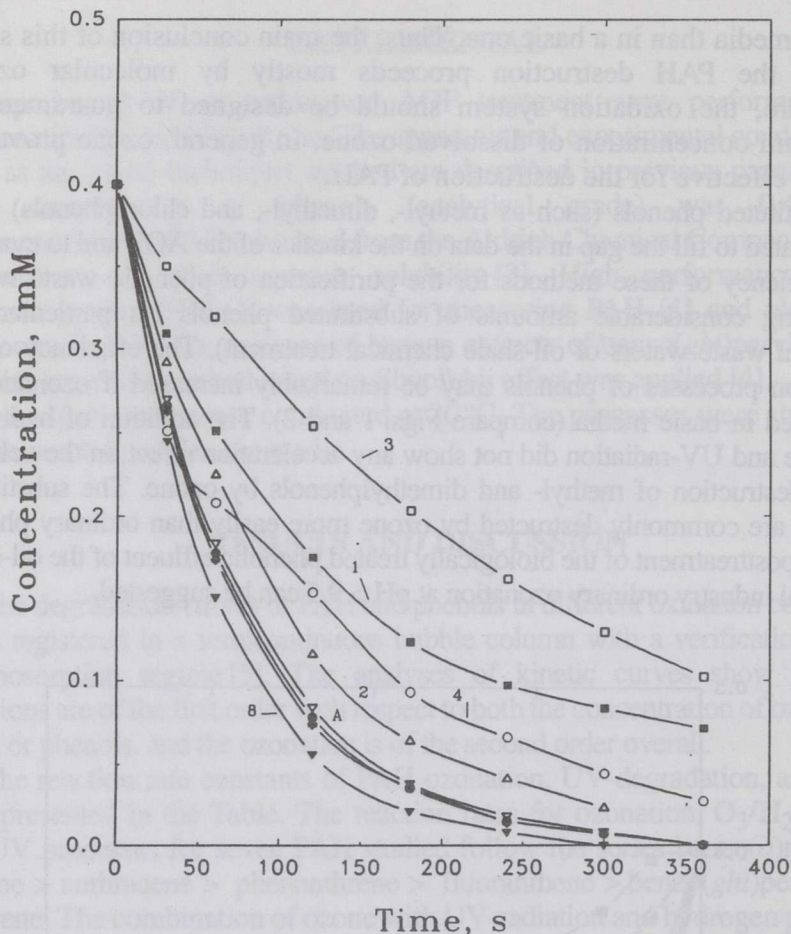


Fig. 2. Ozonation of individual phenols at pH 9.5. Legend see Fig. 1. Curves 5, 6, 7 marked by A.

The reaction rate of ozonation of chlorophenols increased in the series 4-chlorophenol < 2,4-dichlorophenol < 2,3,4-trichlorophenol < 2,4,6-trichlorophenol < 2,3,4,6-tetrachlorophenol. This means that more chlorinated phenols are destroyed more easily by ozone than monochlorophenols.

Among the ozonation by-products of methyl- and dimethylphenols there are organic acids (both aromatic and aliphatic), hydrogen peroxide, quinones, and dimers. For chlorophenols the ozonation intermediates have been identified as chlorobenzoquinones, dioxychlorobenzenes, chlorinated acids, and dechlorinated phenols.

### ACKNOWLEDGEMENT

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## **TÄIUSTATUD OKSÜDATSIIOONIPROTSESSID AROMAATSETE JA POLÜAROMAATSETE SÜSIVESINIKE LAGUNDAMISEKS: KINEETIKA JA REAKTSIOONIPRODUKTID**

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On uuritud asendatud fenoolide ja polüaromaatsete süsivesinike vesilahuste osoonimist ning täiustatud oksüdatsiooniprotsesside kineetikat ja reaktsiooniprodukte. Osoonimine osutus nende ühendite lagundamisel väga efektiivseks.

## **ДЕСТРУКЦИЯ АРОМАТИЧЕСКИХ И ПОЛИАРОМАТИЧЕСКИХ УГЛЕВОДОРОДОВ С ИСПОЛЬЗОВАНИЕМ КОМБИНИРОВАННЫХ ПРОЦЕССОВ ОКИСЛЕНИЯ: КИНЕТИКА И ПРОДУКТЫ РЕАКЦИИ**

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Изучались кинетика и продукты реакции окисления замещенных фенолов, хлорофенолов и полициклических ароматических углеводородов с использованием комбинированных процессов окисления. Простое озонирование оказалось более эффективным для деструкции этих соединений, чем комбинированные окислительные процессы.