Destruction of anthracene and phenanthrene using PDS/UV, one of advanced oxidation processes in terms of degree of destruction and by-products.

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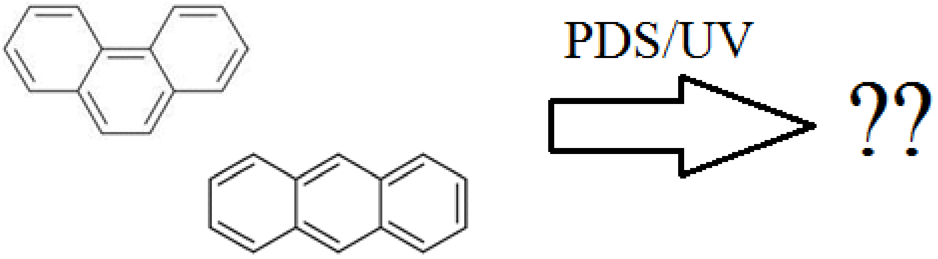
GRAPHICAL ABSTRACT



ABSTRACT

Anthracene and phenanthrene belong to a group of persistent environmental contaminants called PAHs. This study aimed to evaluate the structure of two selected PAHs, i.e., anthracene and phenanthrene, on their resistance to destruction by UV-activated PDS. The authors focused on two aspects of this problem:

- the role of the so-called ‘bay-region’, in the structure of phenanthrene, during PDS/UV oxidation
- formation of substituted forms of these PAHs in the absence and presence of three nitrogen-containing compounds, i.e., ammonia and nitrite or nitrate ions.

Even though phenanthrene and anthracene have the same molecular formula, the difference in their ring assessment influences their degradability. While considering the results, anthracene was degraded faster and/or had a higher degradation rate. That proves phenanthrene to be more stable and resistant for degradation. However, comparison of PDS/UV systems vs. UV– irradiation alone confirms that the addition of PDS accelerates the degradation of anthracene and phenanthrene.

A comparison of PDS/UV with the addition of three different nitrogen-containing compounds showed a significant difference between anthracene and phenanthrene. In the experiments with phenanthrene, additional peaks were observed with an absorption maximum between 230-240 cm^{-1} which is characteristic of the nitro-group. Based on their absorption maximum and the addition of nitrogen-containing compounds, emerging by-products are assumed to be nitro-derivatives of phenanthrene. The GC/MS analysis results suggest the possibility of the formation of many compounds which can be formed from phenanthrene and are embedded in its skeleton. These analyses also suggest the rearrangement of phenanthrene's aromatic rings and the formation of new compounds.

Keywords: Anthracene, Phenanthrene, AOPs, substituted PAHs

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are of high interest among researchers due to their impact on humans as well as the environment. PAHs are organic compounds characterized by at least two fused aromatic rings [1]. They are carcinogenic and mutagenic substances and can undergo many chemical reactions, which lead to the development of compounds that often display higher toxicity than parent PAH [2]. The great concern is directed to Oxygenated and Nitrated Polycyclic Aromatic Hydrocarbons (OPAHs, NPAHs) due to their increased polarity and reactivity [3]. As a result, in comparison to the parent PAHs, their mutagenicity, as well as carcinogenicity, is higher. Oxy- and nitro-PAHS form strong DNA adducts, which could be the start of cancerous cells [3]. As a result of PAHs toxicity and a broad range of sources to appear in the environment, they create great danger for organisms` health and life. PAHs are mainly formed and emitted due to the incomplete combustion of organic energy sources like coal, oil, gas, and wood [4]. Significant PAH emission sources may be highlighted as stationary sources (including domestic and industrial sources), mobile emissions, agriculture activities, and natural sources [2]. The air is of primary concern, as the major sources of PAHs production are their combustion and emission into the atmosphere. However, these pollutants can also enter the water by attaching to the surface of dissolved organic particles or organic fracture of sediments and soils through several means of binding as well as adsorption process, which leads to their presence in the water or deposition in the sediment [5]. Due to the widespread applications of PAHs and their low removal capacities in conventional treatment systems, PAHs are consistently detected in secondary effluent across the globe [6]. That is why there is a continuous need for a better technique to stop the toxic effects of these pollutants on the environment.

Advanced oxidation processes (AOPs) are considered to be beneficial techniques concerning water treatment for eliminating organic contaminants categorized as bio-recalcitrant [7] as well as pathogens not touchable via traditional methods [8]. AOPs are described as the oxidation processes linked to the production of reactive oxygen species (ROS) like hydroxyl radicals ($^{\bullet}OH$) in adequate amounts to generate recuperated effluents [8]. Hydroxyl radicals possess high redox potential (2.8 eV), which are considered excellent oxidants and can be applied for oxidation of organic compounds [9], chemical decomposition, and in some situations, mineralization of the target water pollutants [10]. Starting from the 1990s, a new alternative to the use of H_2O_2 as a precursor to generating the reactive oxygen species has gained a lot of interest [11]. This approach utilizes peroxymonosulfate (PMS) or peroxydisulfate (PDS) to generate sulfate radicals ($SO_4^{\bullet-}$). In contrast to the hydroxyl radicals, sulfate radicals display equal or even higher redox potential (2.5-3.1 V), and have higher selectivity and longer half-life, which makes it a very promising technique [12]. The advanced oxidation process proves its effectiveness in the degradation of polycyclic aromatic hydrocarbons. However during this process, many different oxidized derivatives are formed [13,14,15]. For most PAHs, reaction in the gas phase occurs with the addition of OH radical, NO_3 radical or O_3 to the aromatic rings. In this process, energy-rich adducts react with NO_2 or O_2, transforming into nitro-, oxy- derivatives compounds and ring-opened products [16]. Such a process arouses whether PAHs can also react with nitrogen compounds and oxygen in the aqueous phase leading to the creation of nitro- and oxy-PAHs. [17] presents the research regarding the impact of nitrite ion on the formation of nitro-PAHs by photolysis of pyrene. They discovered that the photolysis of pyrene with the addition of the nitrite ion formed a highly mutagenic compound identified as 1-Nitropyrene. At the same time, no mutagenic activity was observed in the photolysis of pyrene without nitrite ion. What is more, the mutagenicity increased with the higher concentration of nitrite ions [17].

This work aimed to investigate the possibility of the formation of nitro-, oxy- and hydroxy-PAHs as by-products of PAHs degradation. For this reason, the oxidation of PAHs, especially anthracene and phenanthrene, was investigated in an aqueous phase by potassium peroxydisulfate activated with the UV light (PDS/UV Advanced Oxidation Process). Moreover, the influence of the addition of nitrogen-containing compounds, especially NH_4OH, NO_2^-, NO_3^-, for the formation of nitro-PAHs was also considered. What is more, to establish the destructibility of PAHs in chosen experimental conditions, the comparison of the following experimental systems: UV, PDS, and PDS/UV with different PDS concentrations was also presented.

This study aimed to evaluate the structural influence of two selected PAHs, i.e., anthracene and phenanthrene, on their resistance to destruction by UV-activated PDS.. The authors focused on two aspects of this problem:

- the role of the so-called ‘bay-region’, in the structure of phenanthrene, during PDS/UV oxidation
- formation of substituted forms of these PAHs in the absence and presence of three nitrogen-containing compounds, i.e., ammonia and nitrite or nitrate ions.

2. Experimental

2.1 Apparatus

Experiments were performed with the following equipment:

- 600 mL aluminum foil-covered reactor,
- UV-C lamp (low pressure, mercury lamp 254 nm, 9 W),
- High-performance Liquid Chromatograph Waters 2690 with dual wavelength UV-Vis detector Waters 2487 and Luna Omega 3 µm PS C18 100Å LC column (100 x 4.6 mm):
  - Mobile phase: acetonitrile:Millipore water (1:1),
  - Flow velocity: 1.20 ml/min,
  - Column temperature: 30°C,
- Detection wavelength: Anthracene 254 nm and 249 nm, Phenanthrene 292 nm and 251 nm,Gas Chromatography - Thermo Scientific Focus gas chromatograph equipped with a mass detector and TG-SQC GC capillary column (30m x 0.25mm x 0.25µm). The measurement was performed with the temperature program: 3 min. at 60ºC, heating 15°C/min. to 280°C, and keeping at this temperature for 10 min. The dispenser temperature was 250°C, detector

temperature was 280°C. The flow of carrier gas (helium) was equal to 1 mL/min. Full scans of mass spectra from 50 to 500 m/z were made.

2.2. Methods

All the experiments were conducted for both anthracene and phenanthrene, where the concentration of each compound was identical and equal to the half of maximum water solubility of less soluble compound (anthracene), i.e., 0.12 μmol/L. The reaction time of 60 min, pH=5.8, and chosen AOP (UV-activated PDS) were the parameters that remained unchanged in all the experiments. The oxidized PAH was taken as a variable.Into the 600 mL aluminum foil-covered reactor, 400 mL of Millipore water was measured. 0,87 mL (0.049 μmol) of 10 mg/L acetonitrile solution of model compound (anthracene or phenanthrene) was added to obtain 0.022 mg/L concentration of model compound for analysis. The analytical solution was placed on the magnetic stirrer, and pH was adjusted to the value of 5.8 (adjusting of pH was made after adding the oxidant). The molar ratio PDS/PAHs was 2500:1, and nitrogen-contained compounds (if used) were added five times as molar excess to PAHs.. The temperature of the experiment was 20-25 °C.

Samples of 4 ml were collected to the analytical flasks in 0 min., 1 min., 3 min., 5 min., 15 min., 40 min., and 60 min. of the analysis. To each sample drop of methanol was added to inhibit the reaction. All the samples were analyzed with an HPLC system.

3. Results and Discussion

Anthracene and phenanthrene have three condensed aromatic rings, the same molecular formulas (i.e., $C_{14}H_{10}$) and molecular weight (i.e., 178.23 Da). Anthracene and phenanthrene differ, for example, in rings arrangement, see Figure 1.

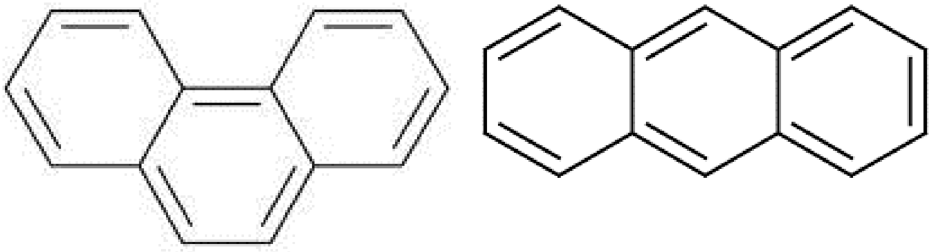
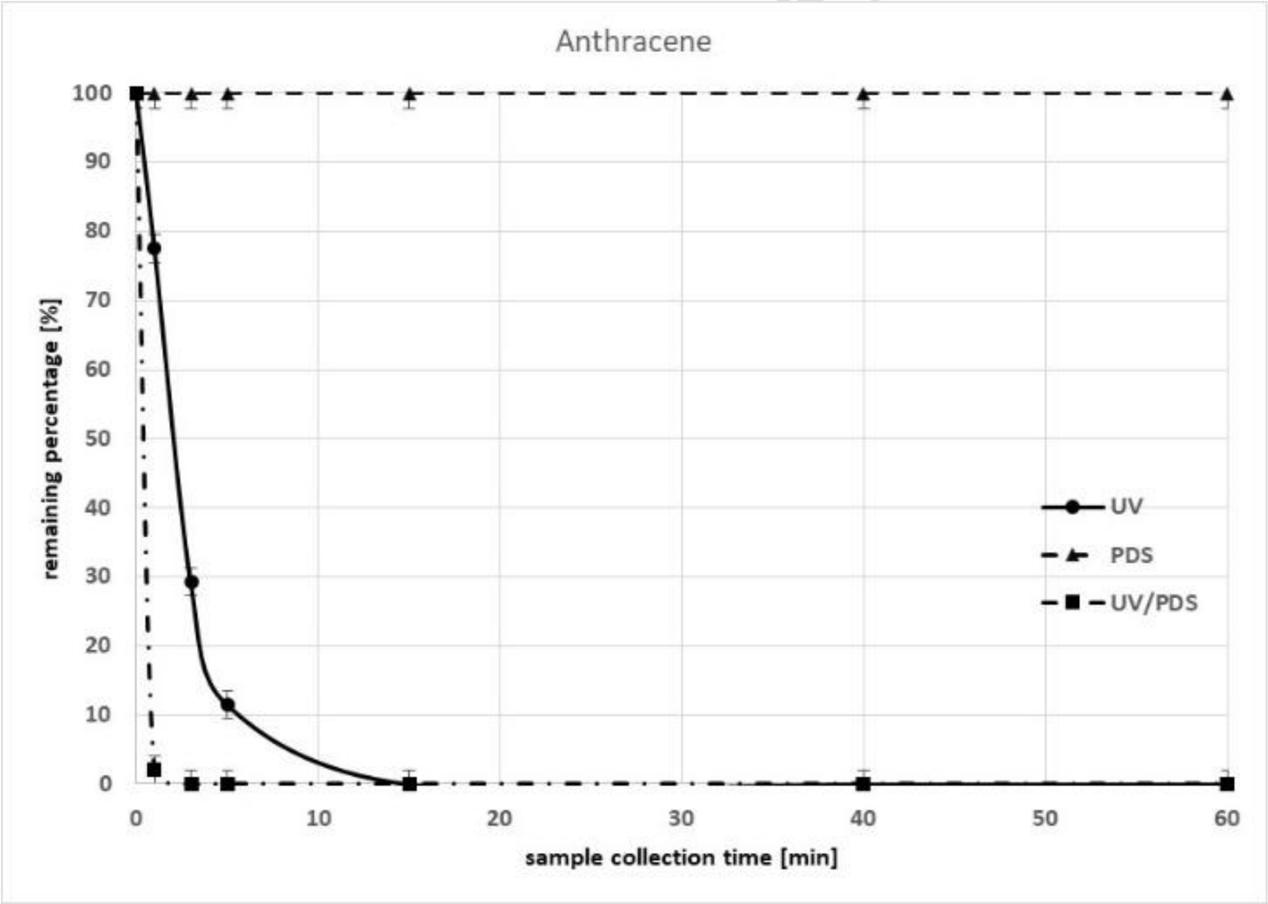


Figure 1. Structures of anthracene (right) and phenanthrene (left)

This difference affects some properties of these compounds, such as differences in water solubility or a specific weight.

The efficacy of these PAHs' destruction during its oxidation by UV beam alone, PDS alone, and PDS/UV system was shown in Figure 2.



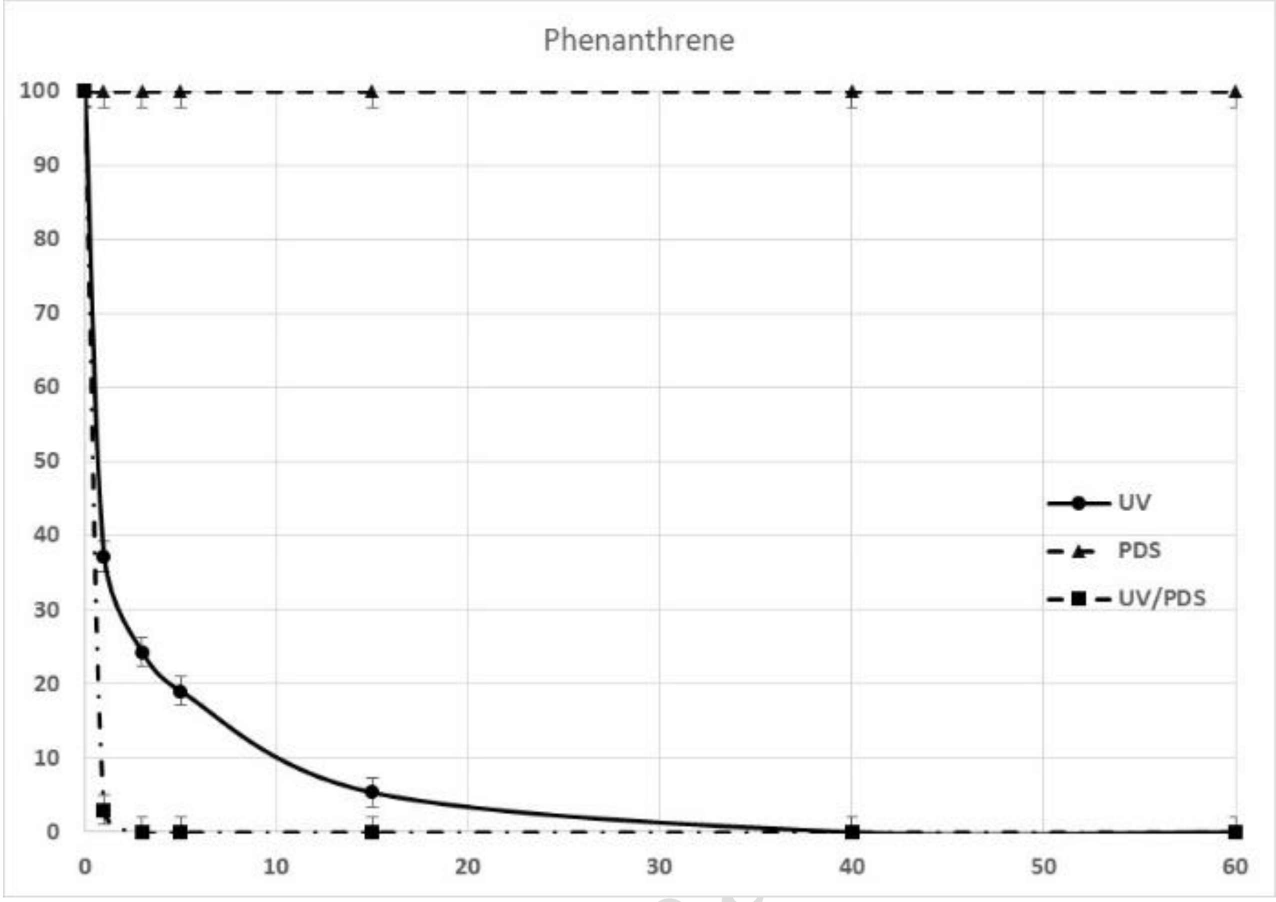
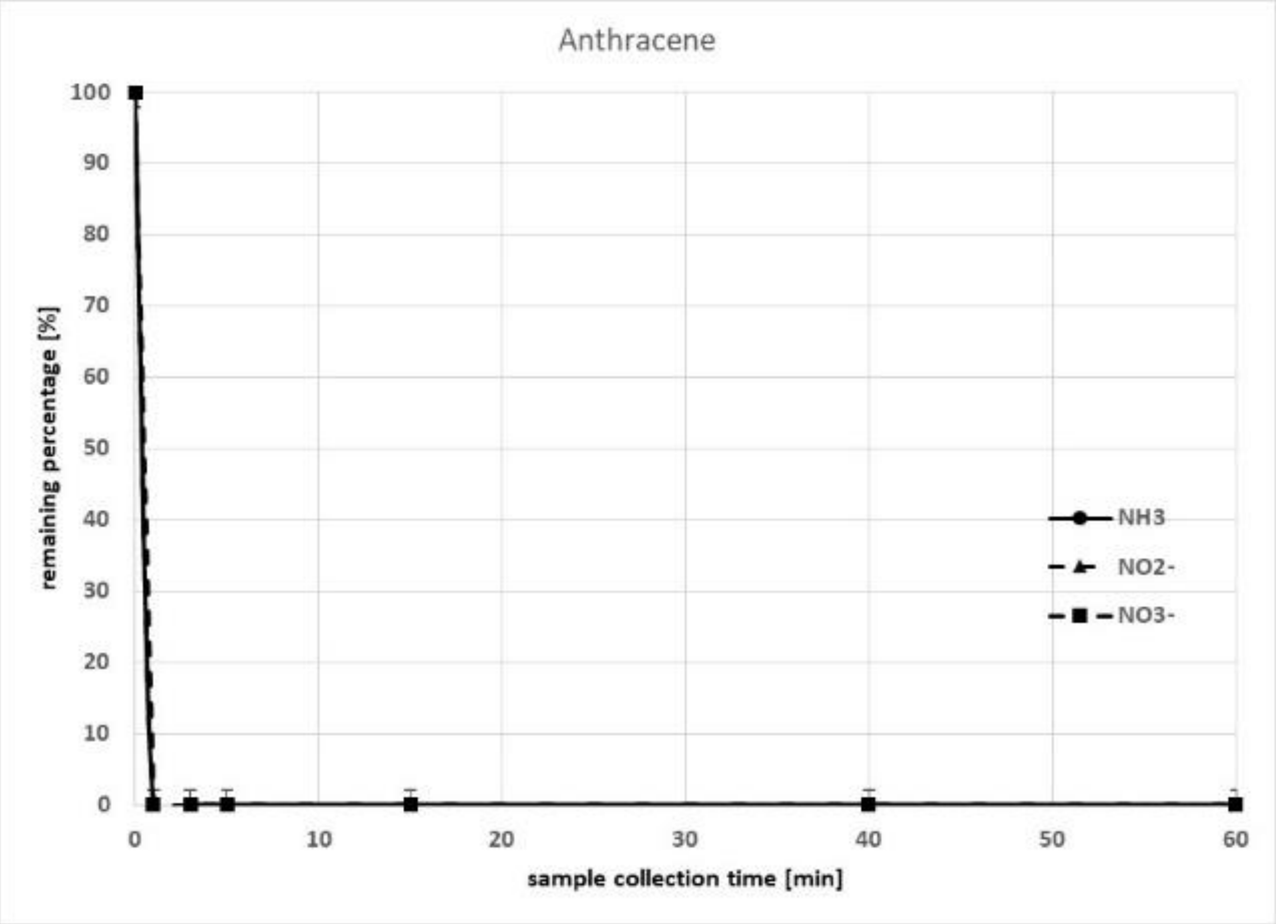


Figure 2. An efficacy of anthracene and phenanthrene destruction during its oxidation by UV beam alone, PDS alone, and PDS/UV system

The removal rate of anthracene was higher than for phenanthrene. Phenanthrene with UV-irradiation alone was entirely removed after 40 min. of the experiment, while in the same conditions, anthracene was removed after 15 min. of the experiment. Contrary to UV-irradiation alone, neither phenanthrene nor anthracene was degraded during the reaction with PDS alone. PDS/UV process increased the effectiveness of both the anthracene and phenanthrene removal compared to UV-irradiation alone. Anthracene was entirely removed in the first minute of the experiment, while phenanthrene was almost entirely removed in the third minute of the experiment.

An influence of nitrogen-contained compounds on two PAHs destruction, during its oxidation by PDS/UV system, is shown in Figure 3.


Anthracene
remaining percentage [%]
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
sample collection time [min]
NH3
NO2-
NO3-

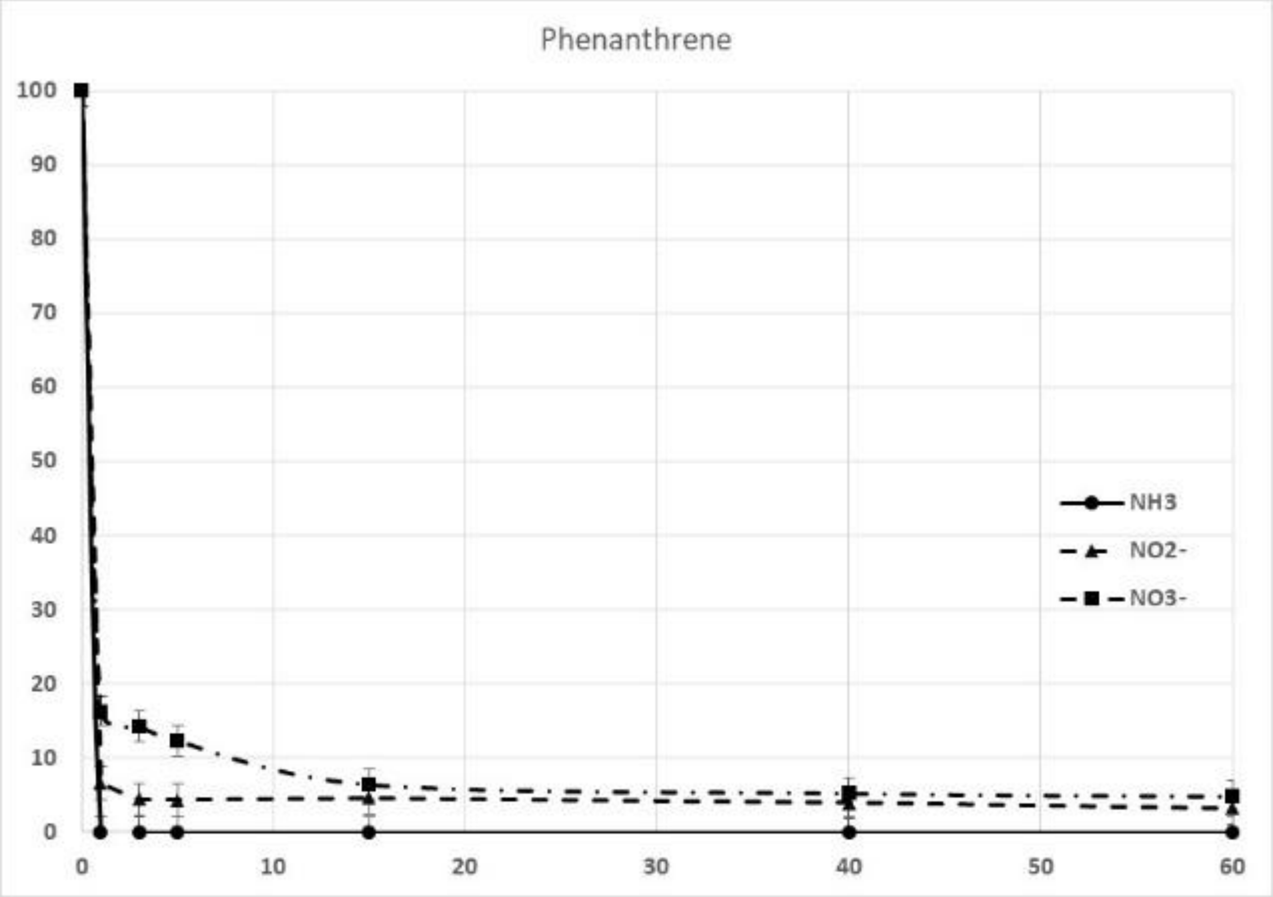

Phenanthrene
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
NH3
NO2-
NO3-

Figure 3. An influence of nitrogen-contained compounds on two PAHs destruction during its oxidation by PDS/UV system

The addition of all three nitrogen-contained compounds to anthracene-containing reaction mixtures did not affect anthracene destruction by PDS/UV. However, adding these compounds to the phenanthrene-containing mixture resulted in a significant decrease in the efficacy of phenanthrene destruction, especially if nitrite or nitrate ions were added. Moreover, the addition of each of these nitrogen-contained compounds resulted in the formation of a new compound with not much lower than phenanthrene retention time (4.54 min vs. 4.97 min), but the maximum absorption band of it was shifted from 251 nm (typical for phenanthrene) to 235 nm (nitro-groups containing compounds). See Figure 4. The formation of this compound has not been observed during all previous experiments. The below-listed facts:

- presence only when one of each of the listed above nitrogen-contained compounds was added to the reaction mixture
- strong absorption band at 235 nm,
- relatively similar, however lower than phenanthrene, retention time suggests higher polarity of compound compared to phenanthrene strongly confirmed the formation of one of nitro-phenanthrenes. The formation of nitro-PAHs under UV-irradiation of PAHs, in the presence of nitrite only, however other than phenanthrene, was proved by Ohe [18].

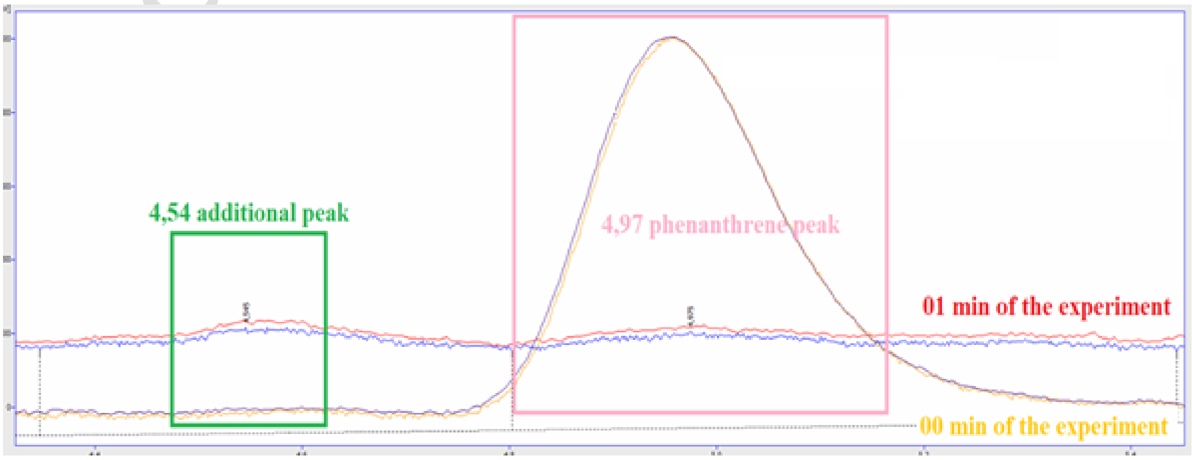


Figure 4. Overlay of extracted parts of two chromatograms for the experiment in PDS/UV system with the addition of ammonia hydroxide in the 0 min. of the experiment and 1 min. of the experiment

The variability of the relative peak areas of suspected nitro-product vs. reaction times, depending on nitrogen-contained compound added was shown in Figure 5.

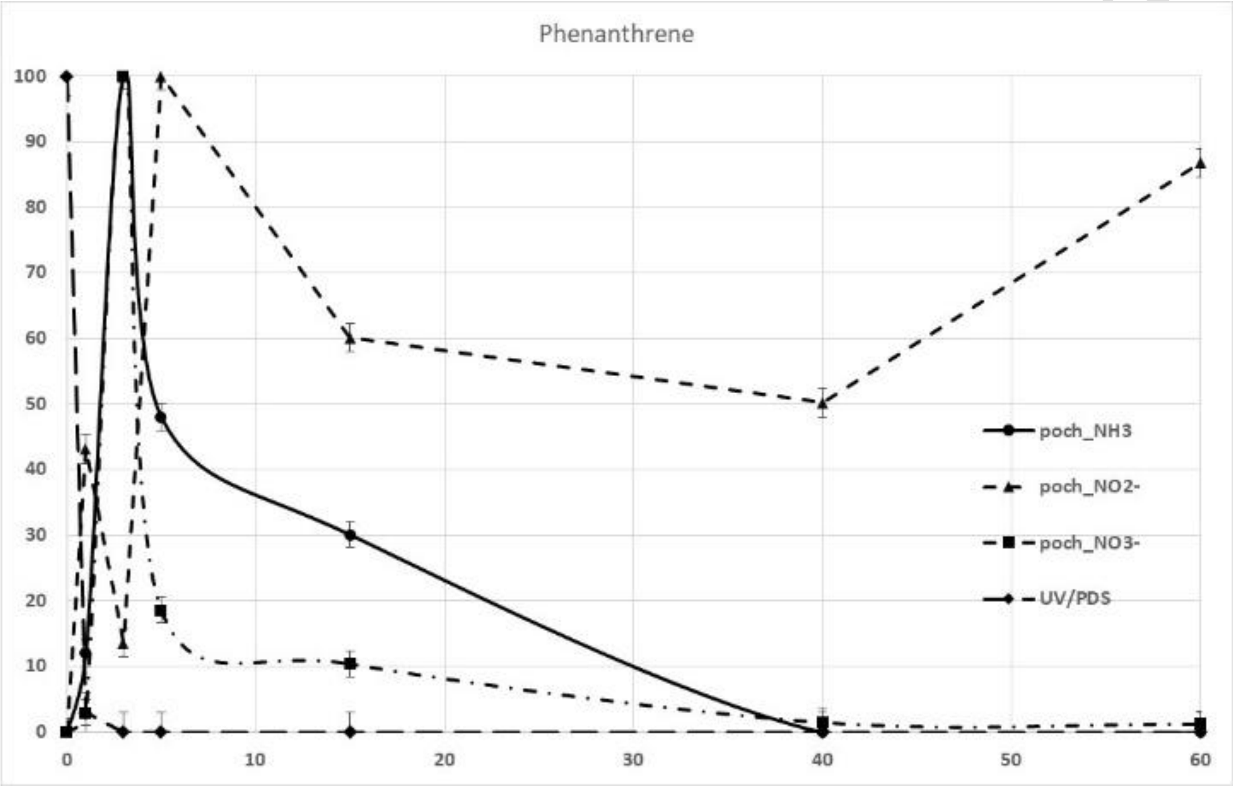
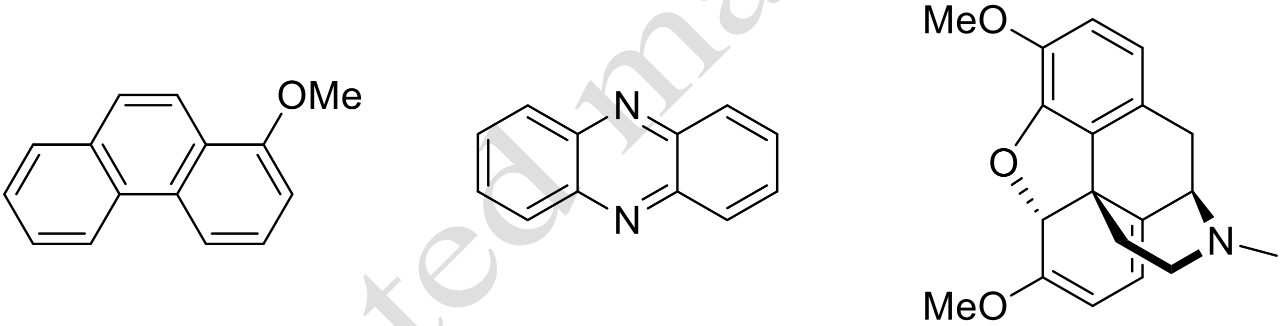


Figure 5. The variability of the relative peak areas of suspected nitro- product vs. reaction times, depending on nitrogen-contained compound added

The addition of each of nitrogen-contained compound resulted in the rapid formation of these by-products during one to five minutes of reactions. For ammonia or nitrate ions addition, however, the abundance of this peak dramatically decreased, and the peak almost vanished after 40 minutes of the process. The addition of nitrite ions resulted in a slight decrease in its abundance. However, after the 40th minute of reaction, an abundance of the peak started to rise again..

Obtaining an additional peak in the HPLC analysis with a retention time lower than phenanthrene's retention time necessitated further research. For this purpose, the experiments analogous to the previous ones were prepared, but these experiments were completed after five minutes. Next, the reaction mixture was concentrated using an SPE system with HLB columns. Compounds were eluted from the SPE column with 5 ml of hexane. The next step was analyzing the extracts using gas chromatography with a coupled mass spectrometer. The obtained results indicate the formation of various compounds deposited on the phenanthrene skeleton or very similar to it. GC/MS analysis indicated the presence of, among others, methoxyphenanthrene and many nitrogen-containing derivative forms (e.g., derivatives of phenazine or thebaine). Rearrangements of the aromatic rings of phenanthrene are also clearly visible. Figure 6. shows structures whose presence in the post-reaction mixture is indicated by GC/MS analysis.



1 **2** **3**

Figure 6. Structures detected in the post-reaction mixture in the GC/MS analysis – 1-methoxyphenanthrene (1), phenazine (2), thebaine (3)

4. Conclusions

1. Even though phenanthrene and anthracene have the same molecular formula, the difference in their ring assessment influences their degradability. While considering all the results, anthracene

was degraded faster and/or had a higher degradation rate. That proves phenanthrene to be more stable and resistant to degradation.

2. Comparison of PDS/UV systems vs. UV – irradiation alone confirms that the addition of PDS accelerates the degradation of anthracene and phenanthrene. The PDS/UV method also compares favorably with other advanced oxidation methods. Table 1 compares the degradation efficiency of anthracene and phenanthrene using different oxidation methods; based on various literature data.

<table>
<tr><td colspan="3">Phenanthrene</td></tr>
<tr><td>Method used</td><td>Degradation range</td><td>Ref.</td></tr>
<tr><td>PDS/UV</td><td>100% after 3 min.</td><td>This work</td></tr>
<tr><td>O_3</td><td>75% after 2 min.</td><td rowspan="3">[20]
[21]</td></tr>
<tr><td>$O_3/H_2O_2/UV$</td><td>55% after 4 min.</td></tr>
<tr><td>O3/UV</td><td>80% after 2 min.</td></tr>
<tr><td>Ultrasonication</td><td>40% after 30 min.</td><td>[22], [23]</td></tr>
<tr><td colspan="3">Anthracene</td></tr>
<tr><td>PDS/UV</td><td>100% after 1 min.</td><td>This work</td></tr>
<tr><td>O_3</td><td>80% after 2 min.</td><td rowspan="3">[21]</td></tr>
<tr><td>$O_3/H_2O_2/UV$</td><td>65% after 2 min.</td></tr>
<tr><td>O_3/UV</td><td>85% after 2 min.</td></tr>
<tr><td>Ultrasonication</td><td>78% after 30 min.</td><td>[24]</td></tr>
</table>

Table 1. Comparison of degradation efficiency of various methods

3. Comparison of PDS/UV with the addition of three different nitrogen-containing compounds showed a significant difference between anthracene and phenanthrene. In the experiments with phenanthrene, additional peaks were observed with an absorption maximum between230-240 cm^{-1} which is characteristic of the nitro-group. Those peaks were not present in experiments without nitrogen-containing compounds. This fact suggests that in those experiments were formed other compounds with different retention times. Moreover, based on their absorption maximum and the addition of nitrogen-containing compounds, emerging by-products are assumed to be nitro-derivatives of phenanthrene.

4. GC/MS analysis of the post-reaction mixtures suggests the formation of many compounds that are direct derivatives of PAHs or loosely associated with them. The detection of methoxyphenanthrene deserves special attention due to its similarity to hydroxyphenanthrene, which cannot be detected by GC/MS technique. The compounds detected in the GC/MS analysis also suggest the possibility of reorganization of the phenanthrene rings during the reaction, emphasizing the middle ring as being the most vulnerable to attack. Attacking the middle ring first in tricyclic PAHs (phenanthrene, anthracene) is consistent with the textbook data on the behavior of PAHs [19].

5. The repeated GC/MS analyzes did not provide an in-depth answer on the structure of the reaction products. In order to unambiguously identify the resulting products, more advanced analytical methods should be used.

Aknowledgments

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