CEST 2021
17th International Conference on Environmental Science and Technology

Athens, Greece, 1 to 4 September 2021

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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Abstract

Anthracene and phenanthrene belong to a group of persistent environmental contaminants called PAHs. Evaluation of the structural of two selected PAHs i.e. anthracene and phenanthrene on its resistance to destruction by UV-activated PDS was the aim of this study. Authors focused on two aspects of this problem:

- role of so called ‘bay-region’, in the structure of phenanthrene, during PDS/UV oxidation
- formation of substituted forms of these PAHs in 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 influence their degradability. Considering all the results, in all the cases anthracene was degraded faster and/or had 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 addition of PDS accelerate the degradation of anthracene and phenanthrene.

Comparison of PDS/UV with the addition of three different nitrogen-containing compounds showed significant difference between anthracene and phenanthrene. In the experiments with phenanthrene were observed additional peaks with the absorption maximum between 230-240 cm^{-1} which is characteristic for 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.

Keywords: Anthracene, Phenanthrene, AOPs, substituted PAHs

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are of a 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 development of compounds that often display higher toxicity than parent PAH [2]. High concern is directed to Oxygenated and Nitrated Polycyclic Aromatic Hydrocarbons (OPAHs, NPAHs) due to its 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 cell [3]. As a result of PAHs toxicity and broad range of source to appear in the environment they create a 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]. Major sources of PAHs emission can be highlighted as stationary sources (including domestic and industrial sources), mobile emissions, agriculture activities, and natural sources [2]. Especially endangered is the air as the major sources of PAHs production is their combustion and emission to 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 the reason why there needs to be applied better technique in order to stop the toxic effects of these pollutants on the environment.

Advanced oxidation processes (AOPs) are considered to be a greatly reasonable 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 amount to generate recuperated effluents [8]. Hydroxyl radicals possess elevated redox potential (2.8 eV) for which are considered as great oxidants and can be applied for oxidation of organic compounds [9], to chemical decomposition and in some situations to mineralization of the target water pollutants [10]. Starting from 1990s, new alternative to the use of H_2O_2 as a precursor to generate the reactive oxygen species has gained a lot of interest [11]. This approach utilize 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), has higher selectivity and longer half-life, which makes it a very promising technique [12]. Advanced oxidation Process proves its effectiveness in degradation of polycyclic aromatic hydrocarbons, however during this process are formed many different oxidized derivatives [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 are formed an energy-rich adducts, which further react with NO_2 or O_2 transforming to nitro-, oxy- derivatives compounds and ring-opened products [16]. This arouse the question, whether PAHs can also react with nitrogen compounds and oxygen in the aqueous phase leading to the creation of nitro- and oxy-PAHs. In [17] is presented the research regarding the impact of nitrite ion for the formation of nitro-PAHs by photolysis of pyrene. They discovered that in the photolysis of pyrene with addition of the nitrite ion was formed highly mutagenic compound, that was identified as 1-Nitropyrene. At the same time in the photolysis of pyrene without nitrite ion, no mutagenic activity was observed. What is more, the mutagenicity increased with the higher concentration of nitrite ion [17].

The aim of this work was to investigate the possibility of the formation of nitro-, oxy- and hydroxy-PAHs as by-products of PAHs degradation. For this reason was investigated the oxidation of PAHs, especially anthracene and phenanthrene, in 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, in order to establish the destructibility of PAHs in chosen experimental conditions, was also presented the comparison of following experimental systems: UV, PDS and PDS/UV with different PDS concentrations.

Evaluation of the structural influence of two selected PAHs i.e. anthracene and phenanthrene on its resistance to destruction by UV activated PDS was the aim of this study. Authors focused on two aspects of this problem:

- role of so called ‘bay-region’, in the structure of phenanthrene, during PDS/UV oxidation
- formation of substituted forms of these PAHs in 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 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

2.2. Methods

Reaction time of 60 min, pH=5.8 and chosen AOP (UV-activated PDS) were the parameters that remained unchanged in all the experiments. As a variable was taken the oxidized PAH. All the experiment 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.

Into the 600 ml aluminum foil-covered reactor was measured 400 ml of Millipore water. 0,87 ml (0,049 µmol) of 10 mg/L acetonitrile solution of model compound (anthracene or phenanthrene) was added, in order to obtain 0,022 mg/L concentration of model compound for analysis. Analytical solution was placed on the magnetic stirrer and pH was adjusted to the value of 5,8 (adjusting of pH was made after addition of the oxidant). The molar ratio PDS/PAHs was 2500:1 and nitrogen-contained compounds (if used) were added in fife times molar excess to PAHs. 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 HPLC system.

2.3. 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, however with rings arrangement, see Figure 1.

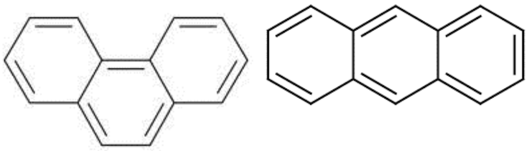


Figure 1. Structures of anthracene (right) and phenanthrene (left)

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

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

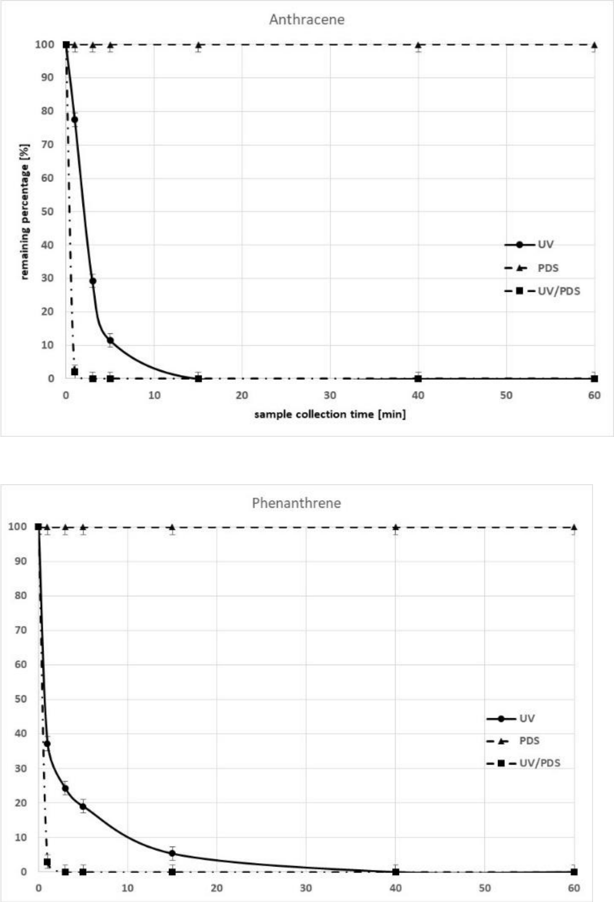
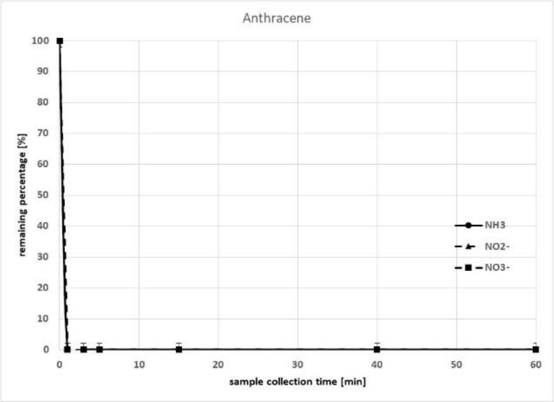


Figure 2. An efficacy of anthracene and phenanthrene destruction during its oxidation by UV beam alone, PDS alone and PDS/UV system.

The removal rate of anthracene was higher than for phenanthrene. Phenanthrene with UV-irradiation alone was fully removed after 40 min of the experiment, while in the same conditions anthracene was removed after 15 min of the experiment. Contrary UV-irradiation alone, neither phenanthrene nor anthracene were degraded during the reaction with PDS alone. PDS/UV process increased the effectiveness both of the anthracene and phenanthrene removal in comparison to UV-irradiation alone. Anthracene was fully removed in the first minute of the experiment, while phenanthrene was almost fully 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 was shown in Figure 3.



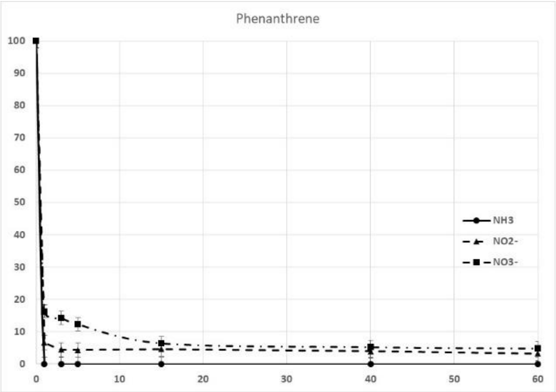


Figure 3. An influence of nitrogen-contained compounds on two PAHs destruction during its oxidation by PDS/UV system.

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

- presence only when one of each of listed above nitrogen- contained compounds was added to reaction mixture
- strong adsorption band at 235 nm,
- relatively similar, however lower than phenanthrene, retention time which suggests higher polarity of compound compare to phenanthrene

strongly confirmed formation of one of nitro-phenanthrenes. Formation of nitro-PAHs under UV-irradiation of PAHs, in presence of nitrite only, however other than phenanthrene was proved by Ohe [18].

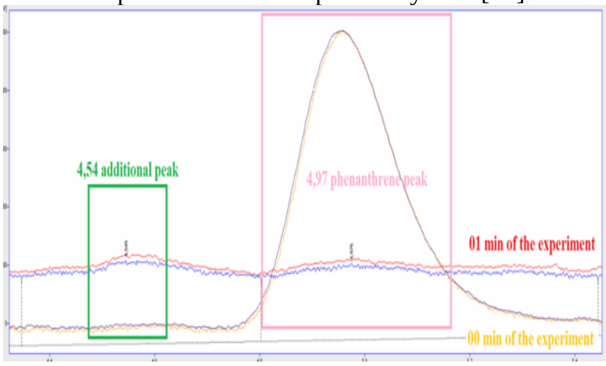


Figure 4. Overlay of extracted parts of two chromatograms for the experiment in PDS/UV system with the addition of ammonia hydroxide in the 0 min of the experiment and 1 min of the experiment.

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.

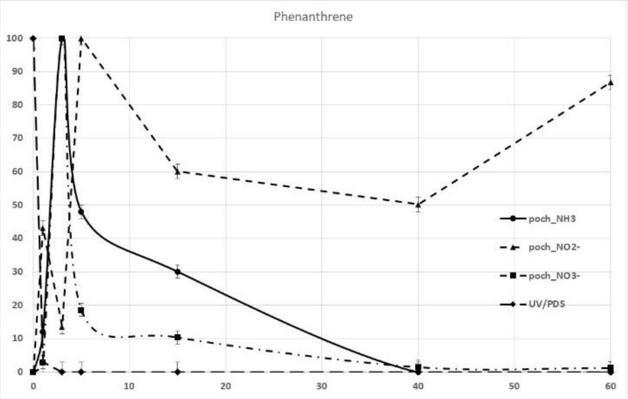


Figure 5. The variability of the relative peak areas of suspected nitro- product vs. reaction times, depending on nitrogen-contained compound added.

An addition of each of nitrogen-contained compounds resulted with fast formation of this by-products, during one to five minutes of reactions. For ammonia or nitrate ions addition however abundance of this peak dramatically decreased and the peak almost vanished after 40 minute of processes. Addition of nitrite ion although resulted in slow decreasing of its abundance but after 40th minute of reaction an abundance of the peak it started to rise again.

3. Conclusions

1. Even though phenanthrene and anthracene have the same molecular formula, the difference in their ring assessment influence their degradability. Considering all the results, in all the cases anthracene was degraded faster and/or had higher degradation rate. That proves phenanthrene to be more stable and resistant for degradation.
2. Comparison of PDS/UV systems vs. UV– irradiation alone confirms that addition of PDS accelerate the degradation of anthracene and phenanthrene.
3. Comparison of PDS/UV with the addition of three different nitrogen-containing compounds showed significant difference between anthracene and phenanthrene. In the experiments with phenanthrene were observed additional peaks with the absorption maximum between 230-240 cm^{-1} which is characteristic for nitro-group. Those peaks were not present in experiments without nitrogen-containing compounds. This suggests that in those experiments were formed another compounds with different retention times. And based on their absorption maximum and the addition of nitrogen-containing compounds, emerging by-products are assumed to be nitro-derivatives of phenanthrene.

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