Application of KO_2/ClO^- advanced oxidation process to degradation of polycyclic aromatic hydrocarbons on example of phenanthrene

Nowakowski M.[1,*], Andrzejewski P.[1], Wolski R.[2]

[1] Adam Mickiewicz University, Faculty of Chemistry, Department of Trace Analysis, Uniwersytetu Poznańskiego St. No. 8, 61-614 Poznań, Poland

[2] Adam Mickiewicz University, Faculty of Chemistry, Department of Applied Chemistry, Uniwersytetu Poznańskiego St. No. 8, 61-614 Poznań, Poland

*corresponding author
e-mail: micnow2@amu.edu.pl

Abstract Novel advanced oxidation process based on KO_2 and ClO^- was applied to degradation of polycyclic aromatic hydrocarbons. It is a wide group of compounds which are negative impact on human health. Phenanthrene was chosen to represent this group of compounds due to its relatively good solubility in water and relatively low toxicity in comparison to other compounds belonging to this group. Trials of application of this method to degradation PAHs showed that phenanthrene is resistant to oxidation by this method. Only a few percent loss of phenanthrene were observed after one hour of process. Resistant of other compounds belonging to PAHs should be the aim of research in future.

Keywords: PAHs, Advanced oxidation processes, PAHs degradation, wastewater treatment, sewage sludge treatment

1. Introduction

Polycyclic aromatic hydrocarbons are a wide group of compounds which are composed of at least two fused aromatic rings. Many research prove their negative impact of human health. These compounds have not acute toxicity, but are characterized by strong mutagenic and carcinogenic effect (Clerge et al 2019; Lammel et al. 2020). Compounds belonging to this group are present in contaminated air, embedded on suspended particulate matter are a main component of smog. Their solubility in water is poor but these compounds accumulate in sewage sludge or bottom settlement. Removing these compounds from sewage sludge can lead to possibility of using sewage sludge as a fertilizer. In recent years the attention of research has been drown to oxidized forms of polycyclic aromatic hydrocarbons like nitrated and oxygenated polycyclic aromatic hydrocarbons due to their better polarity and water solubility (Nowakowski et al., 2021). It has also be confirmed that oxidized forms of PAHs are more dangerous to health due to better affinity for DNA (Lammel et al. 2020). Formation of nitrated and oxidized derivatives of PAHs in air and water was confirmed already in the 80s (Ohe 1984, Suzuki 1987).

Helpful in the treatment of both wastewater and sewage sludge are adavanced oxidation processes. Advanced oxidarion processes (AOPs) based on combination of classic method of oxidation in order to production strong reactive hydroxyl radicals ($OH^{\cdot}$). High oxidation potential (2.8 eV) of hydroxyl radicals can lead to chemical decomposition of many organic compounds and even mineralization some pollutants (Garrido-Cardenas et al. 2020, Ghernaout and Elbourghdiri, 2020). Also polycyclic aromatic hydrocarbons can be degraded under some advanced oxidation processes. During these reaction an oxidized derivatives of PAHs can be formed (Chua et al., 2020). Also the ring-opened products of PAHs degradation were observed (Clerge et al. 2019).

A novel method of AOP is process based on reaction between potassium superoxide (KO_2) and hypochlorous acid (HClO). During this process a hydroxyl radicals are formed in reaction between superoxide radicals and hypochlorous acid molecule (1):

$$HOCl + O_2\bullet \rightarrow Cl^- + HO\bullet + O_2 \quad (1)$$

There are observed also other radicals, e.g. $ClO\bullet$, $Cl\bullet$ and $HOCl\bullet^-$ (Liou and Dodd, 2021).

The aim of this work is application of these novel KO_2/HClO process to degradation of polycyclic aromatic hydrocarbons on exaple of phenanthrene. Phenanthrene was chosen due to its relatively high water solubility and low toxicity. Structure of phenanthren was shown on Figure 1.

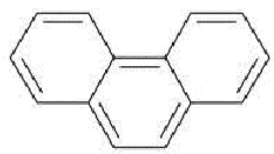

Figure 1. Structure of phenanthrene

2. Material and method

250 mL of water were measured into 600 mL reactor which was shielded from light. Then 0.54 mL of 10 mM acetonitrile solution of phenanthrene was added to reactor to obtain 0.022 mg/L concentration of phenanthrene. The next step was addition 195 mg of dry NaH_2PO_4 as a buffer. The mixture was mixed by magnetic stirrer. A control sample was taken before addition of oxidizing agent. Two solutions of KO_2 were also prepared:

- 500 mg of KO2 were dissolved in 250 ml of 0,1M solution of NaOH (I)
- 500 mg of KO2 were dissolved in 250 ml of 1M solution of NaOH (II)

Then oxidizing agents were added to reactor. The addition of oxidizing agent was done in several ways:

a) 0.36 mL of solution (I) and solution of NaClO (10% mol/mol)
b) 7.1 mL of solution (I) and solution of NaClO (10% mol/mol)
c) 0.36 mL of solution (II) and solution of NaClO (10% mol/mol)
d) 7.1 mL of solution (II) and solution of NaClO (10% mol/mol)
e) The last experiment was a repeating of experiment d) without addition a buffer.

The samples were taken after 1, 3, 5, 15, 40 and 60 minutes of each experiments, collected in 1.8 mL vials and 100 µL of methanol was added to every sample. Then the samples were analyzed by 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/acetonitrile (1:1); Flow velocity: 1.20 ml/min, Column temperature: 30°C, detection wavelength 249 nm.

3. Results and discussion

Figures 2-6 show graphs of percentage of phenanthrene left in reaction mixture, the result of zero sample test adopted as a 100%. A slighty loss of phenanthrene can be observed in all experiments, reaching a maximum of 10% in the last experiment.

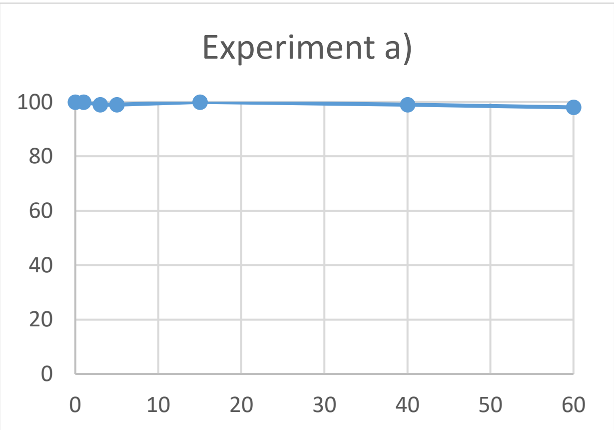

Figure 2. Decrease in the phenanthrene content in the reaction mixture a)

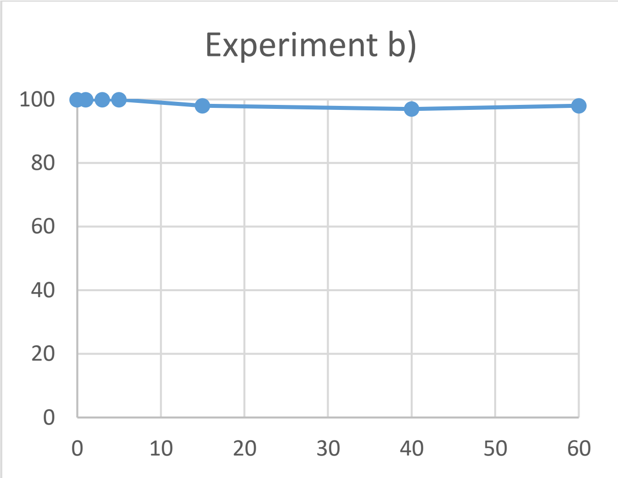

Figure 3. Decrease in the phenanthrene content in the reaction mixture b)

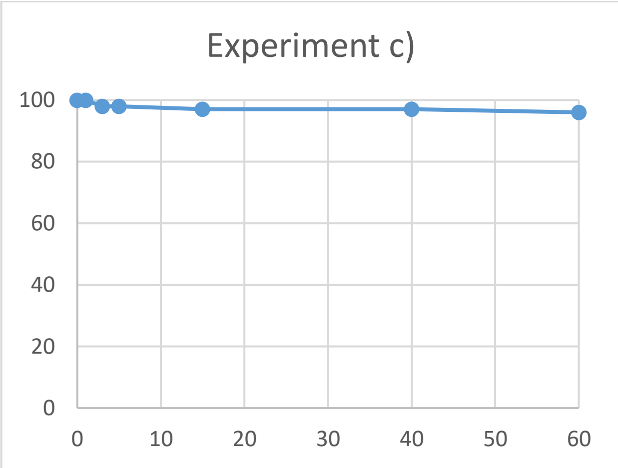

Figure 4. Decrease in the phenanthrene content in the reaction mixture c)

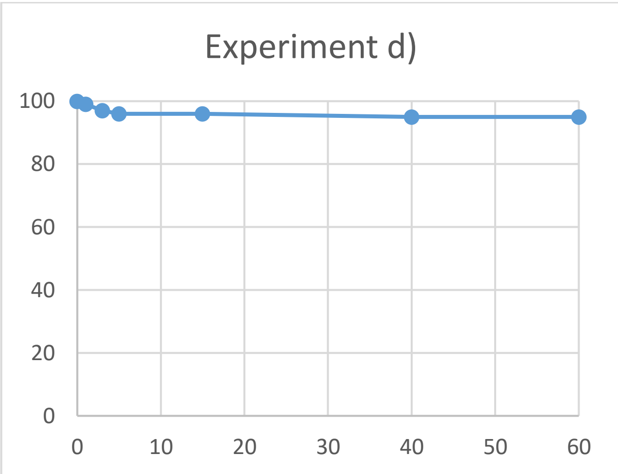

Figure 5 Decrease in the phenanthrene content in the reaction mixture d)

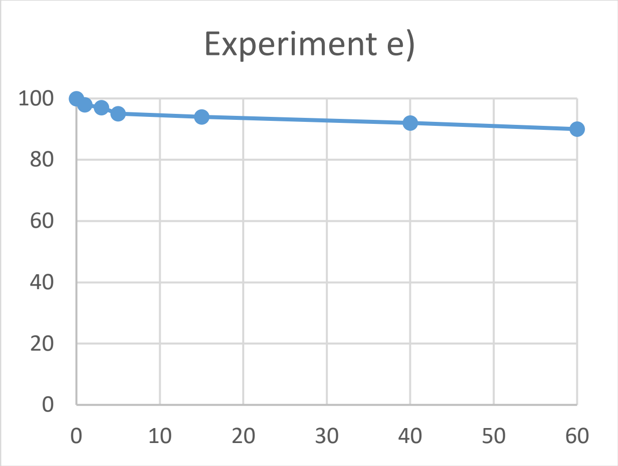

Figure 6. Decrease in the phenanthrene content in the reaction mixture e)

The poor degradation levels of phenanthrene are suprising especially that the susceptibility of this compound to oxidation was proven in previous work (Nowakowski et al, 2022). In the situation of such a low level of phenanthrene degradation, the study of possible by-products of this degradation becomes meaningless.

4. Conclusions

The proposed new oxidation method based on the reaction between potassium superoxide and hypochlorite anion is not a good choice for the destruction of phenanthrene. After an hour of reaction, only a maximum 10% loss of the original amount of this compound was achieved. The impact of this method on other representatives of polycyclic aromatic hydrocarbons requires further research. Due to the sensitivity of PAHs to ultraviolet radiation, a comparison of the effectiveness of other method not based on UV light may also be the basis for further research.

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