

UTILIZATION OF OZONIZATION FOR THE POLYCYCLIC AROMATIC HYDROCARBONS ELIMINATION

Ivana KOPÁČIKOVÁ, Maroš SOLDÁN

Authors: Ivana Kopáčiková, MSc. Eng., Maroš Soldán, Assoc. Professor, PhD.
Workplace: Slovak University of Technology Bratislava
Faculty of Materials Science and Technology
Institute of Safety and Environmental Engineering
Department of Environmental Engineering
Address: Botanická 49, 917 24 Trnava, Slovak Republic
Phone: +421 (33) 5522 244 kl. 505
Email: ivana.kopacikova@stuba.sk

Abstract

Oxidation methods have good assertion at the disposal of organic and also anorganic pollution from contaminated waters. Article describes in detail possibilities of the organic pollution elimination which are also polycyclic aromatic hydrocarbons using ozone.

Key words

polycyclic aromatic hydrocarbons, ozonization, advanced oxidation processes

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of several hundred individual compounds defined to be composed of two or more fused aromatic rings. PAHs are of concern because certain of them are classified as probable human carcinogens and show tumorigenic activity and endocrine disrupting activity in mammals [1].

Environmental Protection Agency included 16 of them in the list of priority pollutants (naphthalene, acenaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(1,2,3-*cd*)pyrene, dibenzo(*a,h*)anthracene, benzo(*g,h,i*)perylene [2]. Some representative structures of PAH compounds are visible on Fig 1 [3].

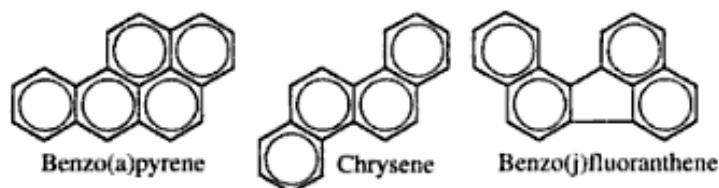


Fig. 1. Some representative structures of PAH compounds

PAHs are important environmental pollutants originating from a wide variety of natural (volcanic eruptions as well as forest and prairie fires) and anthropogenic sources (combustion of fossil materials, motor vehicle, industrial combustion, smoke of cigarettes, etc.) [4, 5].

PAHs are a group of environmental carcinogens widely distributed in the ambient air, in food, in soil, and in many occupational environments. Because PAHs form during incomplete combustion of organic materials, they are found in vehicle exhaust, in wood smoke, in cigarette smoke, and are also found at high concentrations in grilled and flame-broiled [6].

Analysis of PAH

The widespread interest in the analysis of PAH stems from the known and suspected carcinogenicity of many of these compounds present in the environment.

Various analytical approaches have been used for the analysis of PAH in environmental samples. Analytical methods have included column, paper and thin layer chromatography, and more recently capillary gas chromatography (GC) – mass spectrometry (MS) and high performance liquid chromatography (HPLC) using selective ultraviolet (UV) absorption or fluorescence emission.

The bulk of the numerous publications over the last decade relate to the application of HPLC in PAH analysis. HPLC has many distinct advantages over other forms of chromatography and is ideally suited for the study of nonvolatile thermolabile PAH. Recent advances in microparticulate column technology have produced highly efficient analytical HPLC columns with stationary phases capable of providing unique selectivity for the separation of PAH isomers that are often difficult to separate by other forms of chromatography. HPLC also provides a useful fractionation technique for the isolation of PAH from complex environmental samples for subsequent analysis by other chromatographic and spectroscopic methods. In addition, fluorescence spectroscopic detection provides high sensitivity and selectivity of PAH in HPLC analysis [7].

Advanced oxidation processes

The elimination of PAHs from water is undoubtedly necessary. Although various treatment methods have been applied for this purpose, only oxidation technologies, however, seem to be advisable. Advanced oxidation processes (AOPs), are considered to be promising methods for the treatment of hazardous toxic organic pollutants in aqueous solutions.

Advanced oxidation processes although making use of different reacting systems, are all characterized by the same chemical feature: production of OH radicals. OH radicals are extraordinarily reactive species, they attack the most part of organic molecules with rate constants usually in the order of 10^6 – 10^9 $M^{-1} s^{-1}$ [8, 10].

They are also characterised by a little selectivity of attack which is a useful attribute for an oxidant used in wastewater treatment and for solving pollution problems. The versatility of AOP is also enhanced by the fact that they offer different possible ways for OH radicals production thus allowing a better compliance with the specific treatment requirements [8, 9].

Depending on the AOP, the hydroxyl radicals can be generated by any one or combination of the following methods [10]:

- a) chemical oxidation using hydrogen peroxide, ozone, hydrogen peroxide/ozone, Fenton's agent,

- b) radiation methods including ultraviolet (UV) radiation, γ -radiation, electronbeam, and ultrasonic waves,
- c) combination of any one of (a) with any of (b), in particular UV radiation or ultrasonication,
- d) photocatalysis using UV and titanium dioxide (TiO_2).

The aim of this labour was to verify in the model conditions possibility of utilization ozonization for phenanthrene elimination in the water solutions.

Material and methods

Devices:

- Ozonization device *DEZOSTER, HIVUS Ltd., Žilina*.
- UV-VIS Spectrophotometer *GENESYSTM 8*.
- pH & Conductivity Meter *JENWAY 3540*
- Analytical balance *Santorius BP 110 S*.

Materials:

For the preparation of calibration solutions, as well as for samples of ozonization were used methanol solution deposit of phenanthrene, which was prepared by soluble of powdered phenanthrene (p. a., MERCK) in methanol (p. a., Microchem Ltd., Pezinok) with the concentration 15 000 mg/l. Until the time of usage was the solution kept in the dark cold place. Calibration solutions, as well as samples for the ozonization were prepared nearly before the usage by mixing deposit solution with the distilled water.

Method of elimination of phenanthrene by ozonization in the flow reactor (Fig. 2):

- the reactor (3) was filled with 1000 ml water solution of phenanthrene,
- into sample was inserted aeration stones connected through rotameter (2) with ozonization device (1), by which the sample was ozonized,
- by pipes was the cell of the spectrophotometer (5) connected with the rotary pump (4) inserted into the sample,
- in time ozonization of phenanthrene sample was value of absorbance recorded by spectrophotometer into PC every 5 minutes in range of wave length 200 -351 nm,
- concentration of the phenanthrene c in the sample was counted from calibration curve.

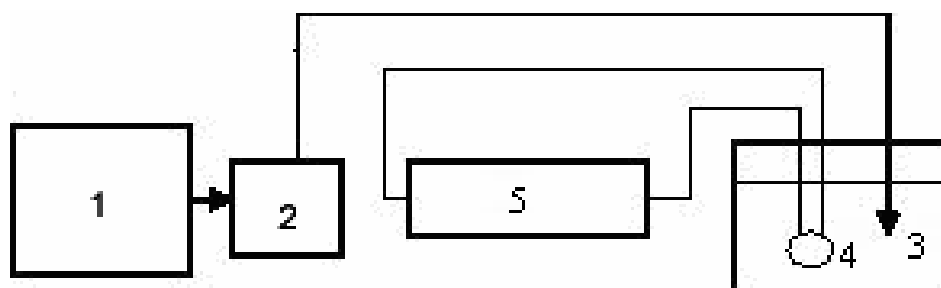


Fig. 2. Scheme of the equipment for continuous monitoring of phenanthrene elimination in water by ozonization.

1 – ozonization device, 2 – rotameter, 3 – reactor for ozonization (2 liter beak with 1000 ml sample, 1 bubble maker), 4 – pump for the sample circulation, 5 – spectrophotometer with flow cell connected with PC

For mathematical and statistical result processing were used OriginLab 8, professional data analysis and graphing software for scientists and engineers.

Results and discussion

Characterization of the method for determination of the phenanthrene contents in the water

For the study of the phenanthrene elimination possibility by ozonization were used as model samples of phenanthrene water solutions. For these types of samples appears as appropriate usage of UV spectrophotometry, while the knowledge about the UV radiation difference of ozone were used, of phenanthrene and water.

For attest thereof assumption were analyzed absorbent strips of water solution phenanthrene (45 mg/l) and saturation solution of ozone at water. Measured out absorbent strips for both samples are listed on Fig. 3. By the mathematical interpretation through the software OriginLab 8 was find out, that solution phenanthrene shows eminent maximal absorption band near twiddle length 351 nm, when already ozone solution don't absorb UV radiance (it's maximal absorption band near twiddle length is 256 nm). Usage of the absorbing strips of phenanthrene by the twiddle lengths stay's the object of next analyses and study in the future periods.

Based on the previous knowledge was for the estimate concentration of ozone in model samples elected spectrophotometric method, by measurement of the absorption radiance near 351 nm. For creation of absorption dependence from the phenanthrene concentration at the water were prepared sets of solutions with the concentration 0 - 75 mg/l, at those was again measurement of absorption done at twiddle scale selected 200 - 360 nm. Results of the measurement are presented in the Fig. 4.

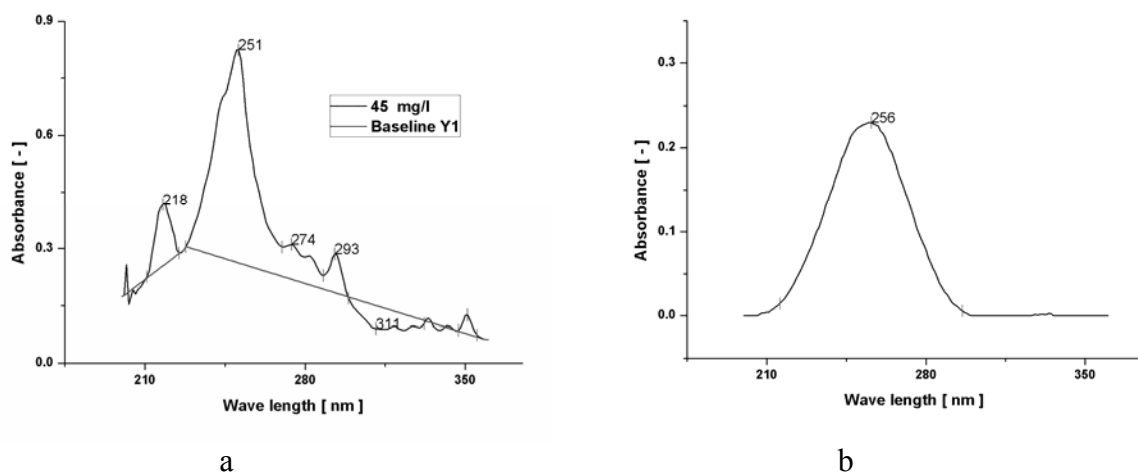


Fig. 3. UV absorption spectrums of water solution of phenanthrene (a) and ozone saturated water (b)

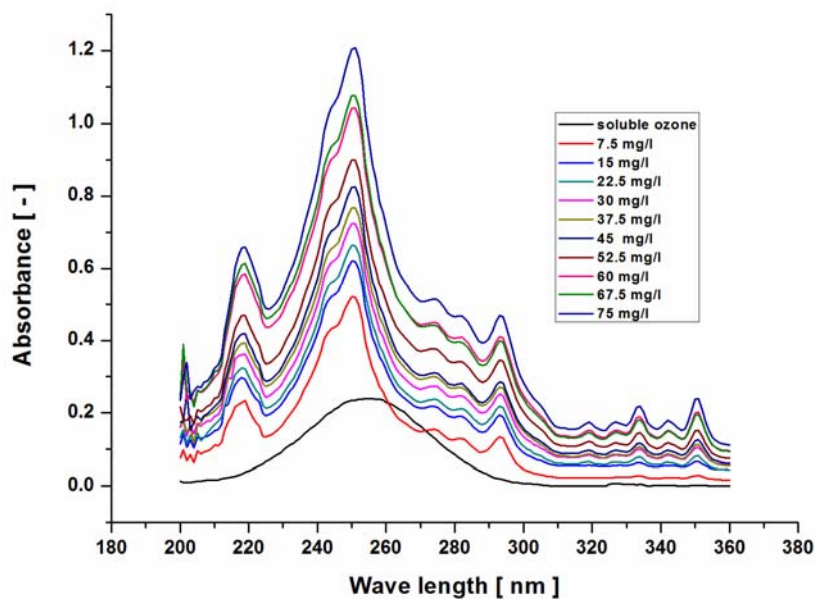


Fig. 4. Absorption spectrums of the phenanthrene water solutions with various concentrations

By the statistical processing of absorbance solutions (351 nm) about various concentration of phenanthrene were using the software OriginLab 8 evaluated calibration curve (Fig. 5), which were used in next study for valuation of the phenanthrene elimination by ozone. It was find out, that the optimal scale of concentration is in area 0 - 45 mg/l.

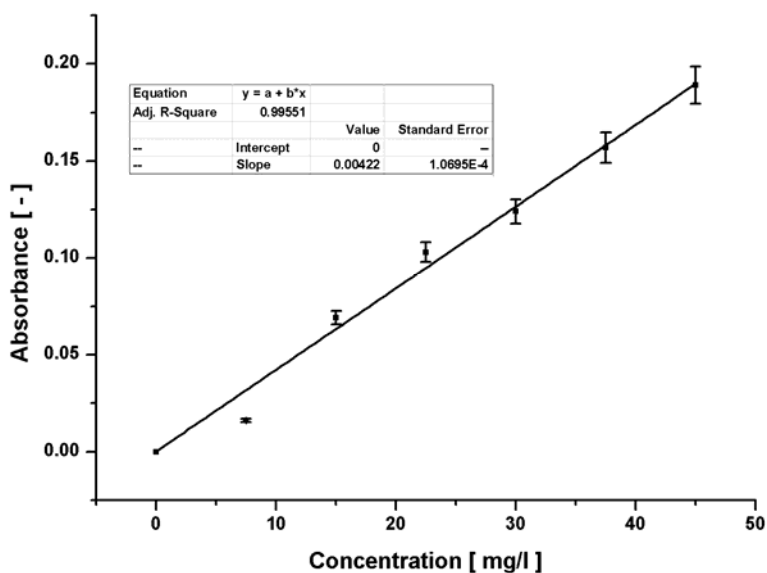


Fig. 5. Calibration curve of water solutions of phenanthrene at 351 nm

The study of the ozonized air exploitation for the phenanthrene elimination in water

Despite of low water solubility, PAH represents a serious risk of water pollution - upper as well as ground and drinking water. Concentrated streams containing PAH are also important due to their transport to the various elements of the living environment, especially to the soil where it can deposit and concentrate. On the other hand, the water usage as the PAH solvent and eliminator brings more advantages that are related to the AOP kinetics and effectiveness as well as to the price and availability of water.

Phenanthrene was chosen for verification of PAH elimination by the ozone application. Phenanthrene exists on large scale in the living environment. The reduction of phenanthrene content was studied in lab. The study was done in model water solutions of different concentration under effect of bubble ozonized air. The study was supposed to verify the next research direction in this area.

By the ozonizator device utilization were by above described procedures ozonized water solutions of phenanthrene within concentration scale 7,5 - 37,5 mg/l. Results of the measurements are showed in the graph on figure 6, where there are listed elimination graphics of the phenanthrene at samples, i.e. dependences of phenanthrene content changes in various solutions in relation from time of ozonization. For the influence arbitration of oxygen on phenanthrene elimination was feasible experiment by the aeration of selected solution only with the air, by the equal condition performance like in ozonization. Result of the measurement with air is presented in the Fig. 6, included with elimination results by the ozonized air.

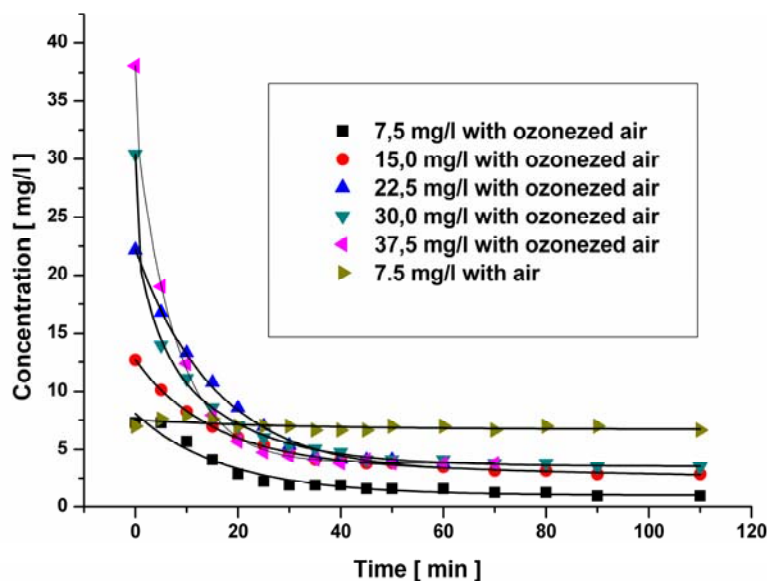


Fig. 6. Change of the phenanthrene concentration at water in dependence of the ozonization time (the capacity samples 1 000 ml, flow of the ozonized air 2,4 l/min, flow of the ozone at the air 3,29 mg/min, temperature 23 -25 °C, pH 7,007 - 7,00)

From the results is able to see, that the impact of ozonized air on aqueous solutions of phenanthrene tend to uniform decreasing his concentration, when middling after 30 min was already the concentration meaningly invariable. By utilization of the software OriginLab 8

was find out, that concentration decreasing of phenanthrene is possible mathematically describe by formulas in the form:

$$y = A_1 \cdot e^{-y/t_1} + A_2 \cdot e^{-y/t_2} + A_3 \cdot e^{-y/t_3} + y_0 \quad (1)$$

The coefficient values of the formula y_0 , A_1 , t_1 , A_2 , t_2 , A_3 , t_3 for tested phenanthrene concentrations, as well as coefficient determinants R^2 (Adjusted coefficients of determination R^2) they are listed in the following table (on Fig. 6 there are formulas in graphical representation by full lines):

Concentration [mg/l]	7,5	15,0	22,5	30,0	37,5
y_0	1.01276	1.86647	2.97959	3.54152	3.78882
A_1	2.34651	2.27275	6.41772	7.44215	5.01443
t_1	17.97766	123.97667	15.68713	0.15232	0.03348
A_2	2.34651	3.16217	6.41772	7.43254	13.70647
t_2	17.97766	14.70105	15.68713	3.85897	7.01992
A_3	2.34651	5.37918	6.41772	12.01949	15.53937
t_3	17.97792	14.69679	15.68684	16.65288	8.47946
R^2	0.93166	0.99817	0.99304	0.99822	0.99907

On the Fig. 7 there are results of the elimination expressed in the form of phenanthrene efficiency reduction opposite the initial content at the beginning of ozonization. Neither in a single case was proofless entire removal of phenanthrene, what can be because of the spectrophotometric method of the organic stuff designation, when the product degradations can be in interference by electromagnetic radiance near given twiddle length. This assumption could to be attested by exploitation HPLC analyses.

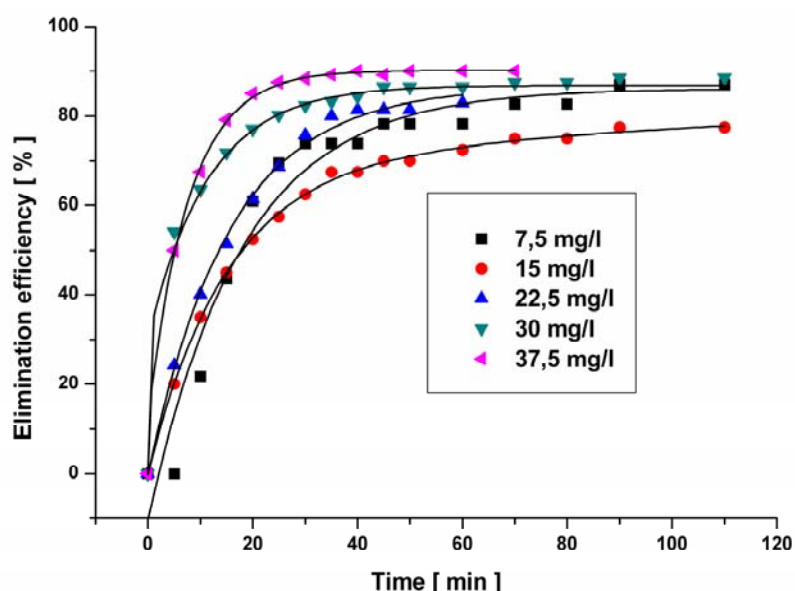


Fig. 7. Efficiency elimination during the ozonization time of the sample with the various phenanthrene concentration

In literature [11] is described that removal of the organic compounds in water can be fit by the pseudo-first-order kinetic equation:

$$\ln\left(\frac{c_0}{c}\right) = k \cdot t \quad (2)$$

where c_0 and c are the concentrations of phenanthrene at the initial time (mg/l) and at the reaction time t , respectively, and k is the pseudo-first-order reaction rate constant (min^{-1}) obtained by least square method. The linear regression equation is $y = k \cdot x$

Calculated elimination velocity constants of the phenanthrene water solutions by ozonized air included with graphical expression straight lines they are listed on the Fig. 8.

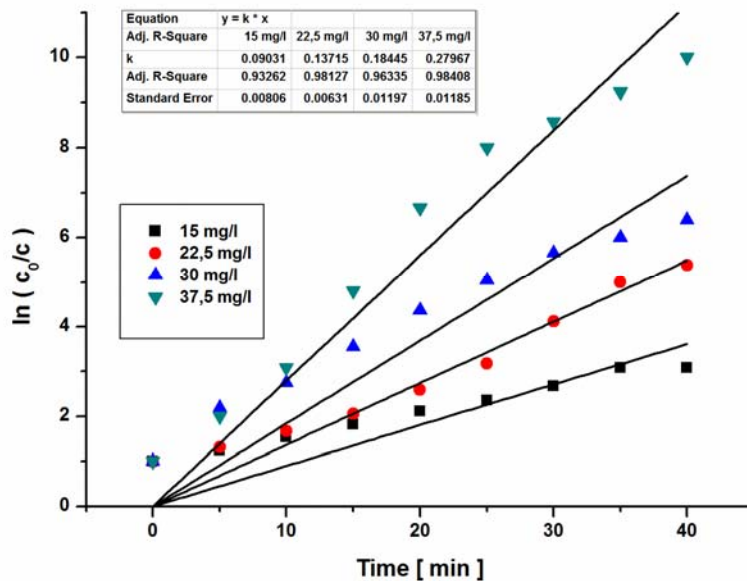


Fig. 8. Velocity constants of the phenanthrene elimination at the samples within concentration scale 15 - 37,5 mg/l

From results issue, that in the solutions with the higher content of phenanthrene overshoot process of the elimination quicker and in investigated concentration scale is possible express accrual of the velocity constant from the initial concentration formula presented on Fig. 9. It is assumed, that near given ozonization conditions, is possible to reach fast reduction of the phenanthrene also in the sample up of the concentration 37,5 mg/l, which is indeed to attest using other methodic of estimation. In the next work is also recommended study of temperature influence, of the pH solutions and ozonized air flow on speed phenanthrene elimination, as well as exploitation of the combination with other AOP, e.g. ultrasound.

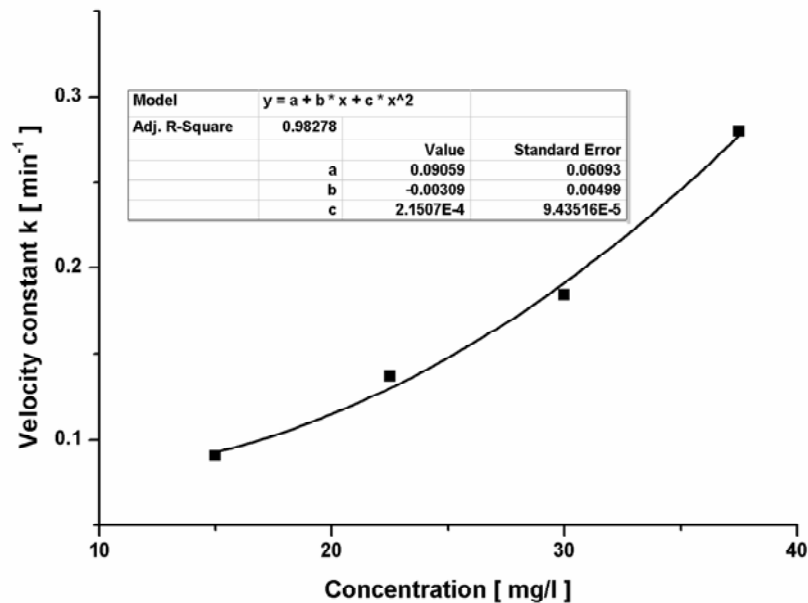


Fig. 9. Dependence of the phenanthrene velocity constant change by the ozonized elimination air from concentration

Conclusion

By the phenanthrene water solution ozonization study within the scale of concentration 7,5 - 37 mg/l it was prove favourable effect on his elimination, when it was already after 30 min of activity the maximum effect reached by 95 %. From the elimination velocity constants (near conditions of the ozonization: flow of the ozonized air 2,4 l/min, flow of the ozone at the air 3,29 mg/min, temperature 23 -25 °C, pH 7,007 - 7,009) it is expected achievement of the reduction also in the higher phenanthrene concentrations at water solutions. In the next study is recommended to continue with the usage of the ozonization combination with other AOP, especially by the ultrasound.

References:

- [1] LIU LI-BIN et al. Development of analytical methods for polycyclic aromatic hydrocarbons (PAHs) in airborne particulates: A review. In *Journal of Environmental Sciences*, 2007, 19, pp. 1-11.
- [2] ARODI BERNAL-MARTINEZ, DOMINIQUE PATUREAU, JEAN-PHILIPPE DELGENČS, HÉLČNE CARRČRE. Removal of polycyclic aromatic hydrocarbons (PAH) during anaerobic digestion with recirculation of ozonated digested sludge. In: *Journal of Hazardous Materials*, 2009, 162, pp.1145–1150.
- [3] STANLEY E. MANAHAN: *Environmental Chemistry*. Eighth Edition. Taylor & Francis, Inc. 2004, p. 816. ISBN 9781566706339
- [4] T. VO-DINH, J. FETZER, A.D. CAMPIGLIA. Monitoring and characterization of polyaromatic compounds in the environment. In *Talanta*, 1998, 47, pp. 943–969.
- [5] ARODI BERNAL-MARTINEZ et al. Ozone pre-treatment as improver of PAH removal during anaerobic digestion of urban sludge. In *Chemosphere*, 2007, 68, pp. 1013–1019.

- [6] ZHENG LI et al. Concentration and profile of 22 urinary polycyclic aromatic hydrocarbon metabolites in the US population. In *Environmental Research*, 2008, 107, pp. 320–331.
- [7] JAMES F. LAWRENCE. *Liquid Chromatography in Environmental Analysis* (Contemporary Instrumentation and Analysis). Humana Press; 1 edition: 1984, 385 p. ISBN 978-0896030459
- [8] ROBERTO ANDREOZZI, VINCENZO CAPRIO, AMEDEO INSOLA, RAFFAELE MAROTTA. Advanced oxidation processes (AOP) for water purification and recovery. In *Catalysis Today*, 53, 1999, pp. 51–59.
- [9] ELISA FERRARESE, GIANNI ANDREOTTOLA, IRINA AURA OPREA. Remediation of PAH-contaminated sediments by chemical oxidation. In *Journal of Hazardous Materials*, 152, 2008, pp. 128–139.
- [10] LAWRENCE K. WANG et al. *Advanced Physicochemical Treatment Processes* (Handbook of Environmental Engineering). Humana Press; 1 edition: 2006, 712 p. ISBN 978-1588293619
- [11] XU XIAN-WEN, SHI HUI-XIANG, WANG DA-HUI. Ozonation with ultrasonic enhancement of *p*-nitrophenol wastewater. In *J Zhejiang Univ SCI* 2005, 6B(5), pp. 319-323.