

# Oxidation of PAHs in water solutions by ultraviolet radiation combined with hydrogen peroxide

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**ABSTRACT.** The destruction of three polycyclic aromatic hydrocarbons (PAHs): benzo[a]pyrene, chrysene and fluorene in aqueous solution using advanced oxidation process  $\text{H}_2\text{O}_2/\text{UV}$  was investigated. The influence of pH, initial hydrogen peroxide and radical scavenger concentrations on the reaction rate was studied. The oxidation reactions most rapidly run in neutral and acidic solution at optimal hydrogen peroxide concentration (*ca.* 0.01 M). The degradation of benzo[a]pyrene and chrysene follows radical reaction, for fluorene the mechanism is not clear. The rate constants of the hydroxyl radicals and selected PAHs reaction were found to be  $2.53 \times 10^{10}$ ,  $9.82 \times 10^9$  and  $2.77 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  for benzo[a]pyrene, chrysene and fluorene, respectively.

## 1. INTRODUCTION

PAHs are ubiquitous in the ecosphere. They were found in the atmosphere [1], water [2], soil [3] as well as plants [4] and animals [2]. Their presence in drinking water was also detected [5]. Natural events such as forest fires, and cardinal anthropogenic activity, and first of all uncompleted combustion of fossil fuels are the main sources of PAHs emission. From the atmosphere or soil they are easily moved to surface waters. Increased attention has been paid to these compounds due to the mutagenic, teratogenic and carcinogenic character of some of these molecules even in very small doses [6]. So PAHs constitute an important, hazardous group of water micropollutants. With regard of their very low aqueous solubility classical methods of water purification are ineffective. Only oxidation or UV radiation can destroy these contaminants to some extent, leaving sometimes toxic by-products [7]. It seems that this type of processes combined with biological treatment are the most promising methods of PAHs elimination from water environment [8].

Processes based on the formation of highly reactive hydroxyl radicals to act as an oxidant have been designated as advanced oxidation processes (AOPs). Among different possibilities hydroxyl radicals can be generated by photolysis of hydrogen peroxide. This technique was widely used for destruction of various harmful compounds *e.g.* phenol [9], pentachlorophenol [10], halogenoalkanes [11], pesticides [12], surfactants [13]. PAHs were also the object of studies in the  $\text{H}_2\text{O}_2/\text{UV}$  system. Beltran *et al.* [14] widely investigated the dependence of initial hydrogen peroxide concentration and pH of reaction medium on the decomposition rate of acenaphthene, fluorene and phenanthrene in aqueous solutions. The influence of the hydroxyl radical scavenger-bicarbonate ion on reaction effectiveness was also studied. Surprisingly the presence of bicarbonate ion did not change the reaction course.

The kinetics of the degradation of the other PAHs set

were studied by Hautaniemi *et al.* [15]. The decomposition of naphthalene by  $\text{H}_2\text{O}_2$  alone and with UV radiation was investigated by Tuhkanen [16]. The influence of various parameters on reaction rate and the rate constants was determined [14-16].

The aim of present work was to study the benzo[a]pyrene (BAP), chrysene (CHR) and fluorene (FLU) degradation in aqueous solution in the presence of hydrogen peroxide and UV radiation. The influence of the pH of reaction solution and the presence of radical scavenger, *tert*-butyl alcohol (*t*-BuOH) was also investigated. Presented work is the second part of our study on application of different AOPs techniques for PAHs elimination from aqueous medium. The first part devoted to PAHs direct photolysis is now under preparation.

## 2. MATERIALS AND METHODS

The experiments were carried out in a  $1 \text{ dm}^3$  thermostated glass reactor equipped with the central well for immersion UV source and magnetic stirrer. The low pressure mercury lamp TNN 15/32 (Heraeus, Hanau) with the main emission wavelength of 254 nm was applied. Actinometric experiments with uranyl oxalate and potassium ferric oxalate [17] gave the intensity of radiation inside the reactor of  $2.49 \times 10^{18}$  quanta/s  $\text{dm}^3$ . The study was performed for three selected compounds: benzo[a]pyrene (98%, Sigma), chrysene (95%, Fluka) and fluorene (Sigma) without additional purification. Stock solutions of PAHs were prepared in ethanol (*p.a.*, 96%, Polmos). Reaction solutions were done by introducing proper volume of ethanol solution (usually tens of  $\mu\text{l}$ ) into distilled water treated in a Millipore Milli-Q Plus System. Earlier suitable quantity of hydrogen peroxide (30% POCh Gliwice) was added to water. The pH of reaction solution was adjusted by adding exact volume of sodium hydroxide (P.Ch. Lublin) or phosphoric acid (P.Ch. Lublin) solutions. As a radical scavenger *tert*-butyl alcohol (*p.a.*, Fluka) was used. The samples of reaction solution for analysis were diluted with methanol (HPLC reagent, Baker Anal-

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ysed), so the final solvent composition was 50/50 vol. water/methanol. The addition of methanol stabilised the samples preventing PAHs deposition onto walls of flasks. The spectrofluorimetric analysis of reaction mixture was carried out [18] using Perkin Elmer LS50B apparatus. All experiments were performed at temperature 20 °C.

### 3. RESULTS AND DISCUSSION

**3.1. Influence of parameters.** The primary experiments were carried out without UV radiation to determine the participation of “dark” PAHs degradation under the influence of hydrogen peroxide at the concentration of 0.1 M. After 30 min of reaction time no depletion in BAP, CHR and FLU concentration was observed. After the next 10 min 20% of BAP and CHR converted into products, but FLU concentration remained unchanged. Other PAHs were also found to be recalcitrant towards oxidation by hydrogen peroxide alone [14, 16].

The next step of our study was focused on determination of the optimal  $H_2O_2$  concentration in the reaction medium. For generation of hydroxyl radicals by hydrogen peroxide photolysis (1) a relatively high dosage of  $H_2O_2$  is required. When comparing



to the  $\cdot OH$  radicals formation in the  $O_3/UV$  system, the photolysis of hydrogen peroxide is about 50 times slower than that of ozone [19]. High  $H_2O_2$  concentration in turn effectively quenches hydroxyl radicals (2) causing inhibition of next reactions [20].

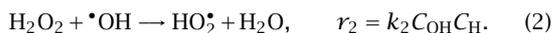


Figure 1 presents the evolution of BAP's relative concentration versus time for various hydrogen peroxide concentrations. The most effective conversion was observed for  $H_2O_2$  content about 0.01 M (Figure 2). The same results were obtained for the other two PAHs.

The different pH of reaction solution can influence the reaction rate changing on the one hand the acid-base equilibrium of  $H_2O_2$  (3) and modifying target molecule conformation on the other hand.



The latter induces among others, the alteration of extinction coefficient, which in our case was observed for CHR (Figure 3) and BAP. In acidic solutions a sharp increase of the absorption was noticed.

The degradation of PAHs was studied at three pH values: 2.5, 7 and 11.7. During reactions the changes of pH were not observed, probably due to very low concentrations of acidic products. Figure 4 presents the evolution in normalised CHR concentration during reaction for various pH values. The highest rate of conversion took place in neutral and next in acidic solutions. In alkaline mixture the reaction rate explicitly decreased. The same relation was observed for FLU, but for BAP

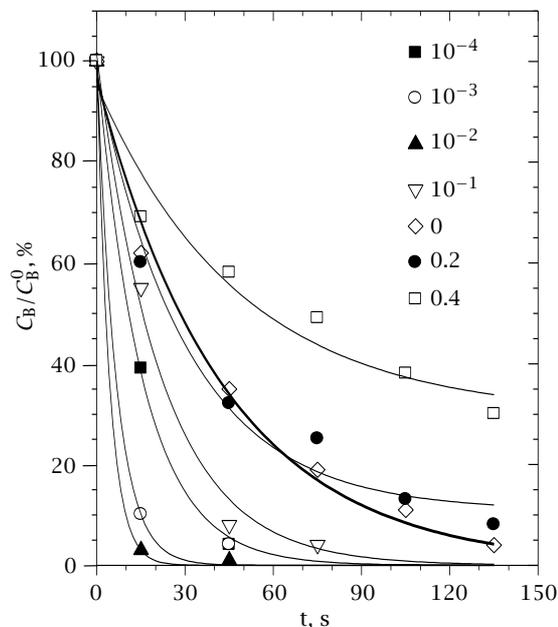


Figure 1. Evolution of relative BAP concentration versus time for various hydrogen peroxide concentrations;  $C_H^0, M$ .  $pH = 7$ ,  $C_B^0 = 4.76 \times 10^{-9} M$ .

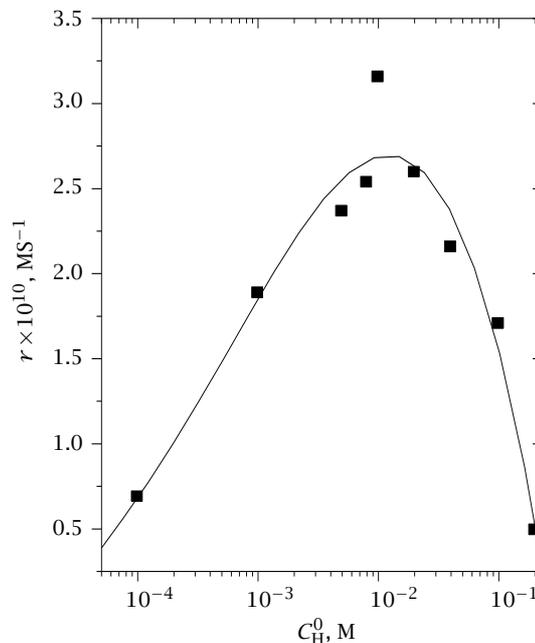


Figure 2. Dependence of CHR degradation rate on hydrogen peroxide concentration.  $pH = 7$ ,  $C_C^0 = 5.12 \times 10^{-9} M$ .

the best conditions for its degradation were noticed at  $pH = 2.5$ .

The PAHs in the  $H_2O_2/UV$  system disappear due to direct photolysis and to their reaction with hydroxyl radicals. In alkaline solution part of the light absorbed by hydrogen peroxide, exactly its ionic form-hydroperoxide anion (3), increases since the extinction coefficient increases from  $19 M^{-1} cm^{-1}$  for  $H_2O_2$  [21] to

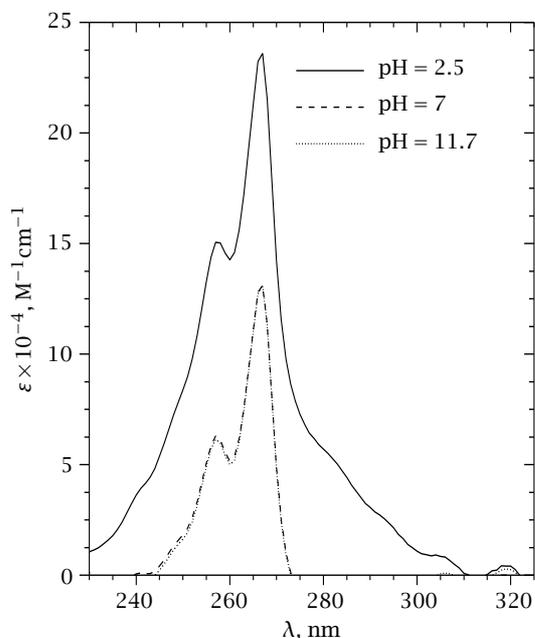


Figure 3. Absorption spectra of CHR for different pH in 50/50 vol. methanol/water solution  $C_C = 1.14 \times 10^{-6} M$ .

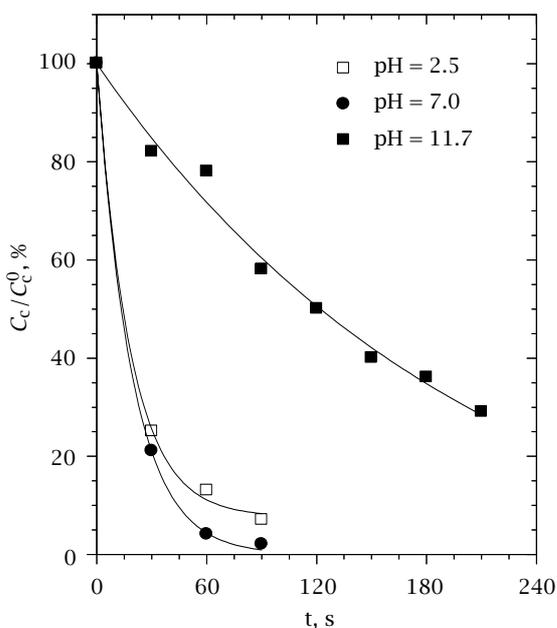
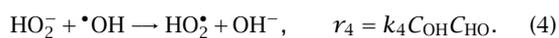


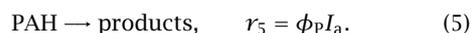
Figure 4. Variation of relative CHR concentration versus time in acidic, neutral and alkaline solutions.  $C_C^0 = 5.12 \times 10^{-9} M$ ,  $C_H^0 = 1 \times 10^{-3} M$ .

$240 M^{-1} cm^{-1}$  for  $HO_2^-$  [11]. This diminishes the formation of hydroxyl radicals according to equation (1). Additionally,  $\cdot OH$  radicals can be consumed not only in reaction (2) but also in the following reaction, which in these circumstances become very important.



Moreover, if the concentration of  $H_2O_2$  is low, then part of the light absorbed by PAHs attains a consider-

able value, BAP and CHR quench smaller light quantity as their extinction coefficient decreases at high pH. So the reaction of direct photolysis is also retarded.



In conclusion, when pH is increased the oxidation rate of PAHs in  $H_2O_2/UV$  system decreases.

The study of the PAHs degradation using hydrogen peroxide and UV radiation was also performed with the addition of *t*-BuOH, known as hydroxyl radical scavenger [22]. The decomposition rate of BAP and CHR decreased as the concentration of *t*-BuOH in reaction solution increased, which is shown in Figure 5. The relationship observed for radical reaction seems to be obvious, however in the case of FLU no influence of the scavenger on reaction rate is reported. The same phenomena for FLU, acenaphthene and phenanthrene were presented by Beltran *et al.* [14] in their work with the use of bicarbonate ion as a radical quencher. But their explanation is unapplicable to our case. Probably, the degradation of FLU occurred according to the mechanism other than the radical one. However, a detailed explanation requires more experimental data.

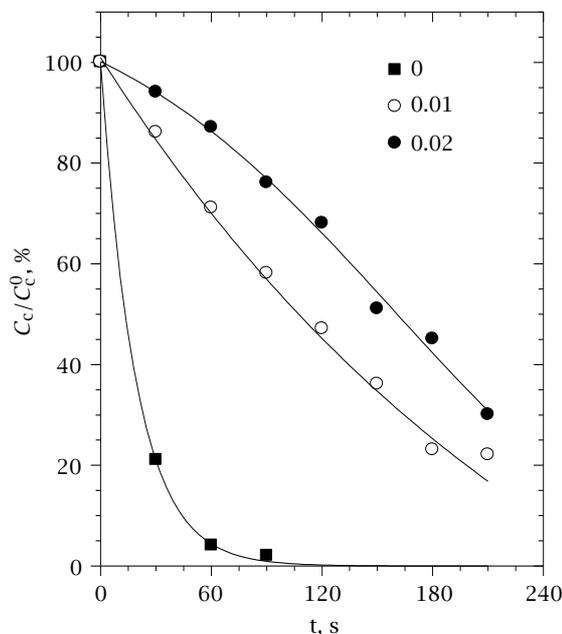


Figure 5. The influence of radical scavenger concentration  $C_t^0$ , M on the CHR degradation rate. pH = 7,  $C_C^0 = 5.12 \times 10^{-9} M$ ,  $C_H^0 = 1 \times 10^{-3} M$ .

**3.2. Kinetic computing.** The oxidation of PAHs by hydrogen peroxide combined with UV radiation can be treated as the process consisting of direct photolysis (5) and reaction of hydroxyl radicals:



According to the above, the rate of this AOP can be written down as:

$$r = -\frac{dC_P}{dt} = r_{UV} + k_6 C_{OH} C_P \quad (7)$$

The rate of photolysis follows the Lambert-Beer law:

$$r_{UV} = \phi_P I_0 f_P \left[ 1 - \exp\left(-2.303b \sum \varepsilon_i C_i\right) \right] \quad (8)$$

where  $f_P$  is the fraction of radiation absorbed by a given PAH:

$$f_P = \frac{\varepsilon_P C_P}{\sum \varepsilon_i C_i}. \quad (9)$$

When reaction is carried out at high  $H_2O_2$  concentration it practically absorbs total light flux ( $f_H = 1$ ) and direct PAHs photolysis can be neglected. Simultaneously, the hydrogen peroxide concentration in the initial stage of reaction can be treated as constant [14, 16]. For these conditions equation (7) simplifies to the form:

$$-\frac{dC_P}{dt} = k_z C_P \quad \text{where } k_z = k_6 C_{OH}. \quad (10)$$

$k_z$  is the pseudo-first order rate constant, so the plot of integrated form of equation (10) should follow a straight line in the coordinates system  $\ln(C_P^0)/C_P$ -t. The verification of this relationship is shown in Figure 6.

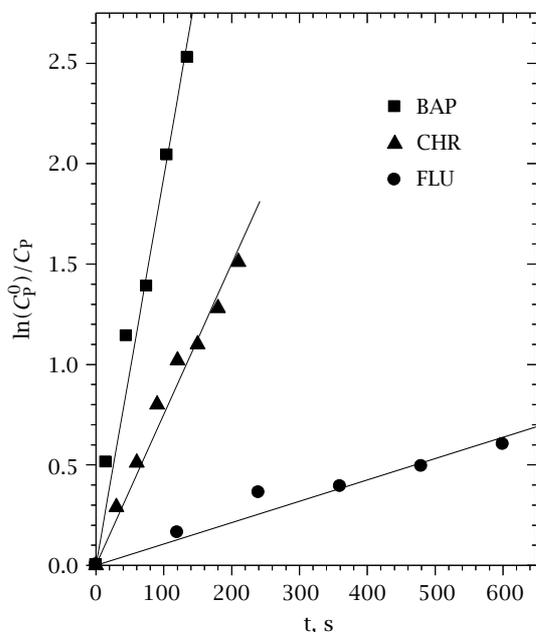


Figure 6. Determination of pseudo-first order rate constants  $k_z$  (equation 10) of PAHs decomposition. pH = 7,  $C_B^0 = 4.76 \times 10^{-9} M$ ,  $C_C^0 = 5.12 \times 10^{-9} M$ ,  $C_H^0 = 0.2 M$  and  $C_F^0 = 5.42 \times 10^{-6} M$ ,  $C_H^0 = 0.4 M$ .

Considering the reaction scheme described by reaction pathways (1), (2), (3), (4), (5) and (6) and assuming that other possible reactions of  $\cdot OH$  disappearance can be refused, the stationary state for hydroxyl radicals is described by  $r_1 = r_2 + r_4 + r_6$  and after expansion:

$$2\phi_H I_0 f_H \left[ 1 - \exp\left(-2.303b \sum \varepsilon_i C_i\right) \right] = k_2 C_{OH} C_H + k_4 C_{OH} C_{HO} + k_6 C_{OH} C_P. \quad (11)$$

This equation is useful in computing the concentration of hydroxyl radicals:

$$C_{OH} = \frac{2\phi_H I_0 f_H \left[ 1 - \exp\left(-2.303b \sum \varepsilon_i C_i\right) \right]}{k_2 C_H + k_4 C_{HO} + k_6 C_P}. \quad (12)$$

The concentration of hydroperoxide anion  $C_{HO}$ , which effectively quenches hydroxyl radicals (4) is pH dependent and it is calculated from the equilibrium constant (3):

$$C_{HO} = \frac{K C_H^0}{\exp(-2.303pH) + K} \quad \text{and } C_H^0 = C_{HO} + C_H. \quad (13)$$

Combining equations (12) and (10) and determining  $k_z$  (Figure 6) it is possible to calculate the rate constant of the reaction of PAH with hydroxyl radical. The values of  $k_2 = 2.7 \times 10^7 M^{-1} s^{-1}$  and  $k_4 = 7.5 \times 10^9 M^{-1} s^{-1}$  were taken from literature [20]. For studied PAHs the average rate constants  $k_6$  were found to be:  $2.53 \times 10^{10}$ ,  $9.82 \times 10^9$  and  $2.77 \times 10^9 M^{-1} s^{-1}$  for BAP, CHR and FLU, respectively.

Equation (12) permits to compute the concentration of hydroxyl radicals using determined  $k_6$  rate constant. The selected results of our experiments and calculations are collected in Table 1. It is seen that hydroxyl radical concentration increases with an increase of hydrogen peroxide content to an optimal value, and then it falls down. In alkaline reaction mixture one can see the decrease of  $\cdot OH$  radicals concentration in relation to neutral or acidic solutions. The results of these calculations confirm the validity of the reaction model proposed.

#### 4. CONCLUSIONS

The experiments performed on PAHs elimination from aqueous solution using  $H_2O_2/UV$  system make it possible to draw the following conclusions.

According to literature data [14, 16, 19] we found that beneficial doses of hydrogen peroxide which maximally accelerate the degradation equal to about 0.01 M for all studied PAHs.

The rate of PAHs disappearance is pH dependent. The smallest rates were achieved in alkaline reaction mixtures.

The comparison of reactions carried out in the presence and absence of *tert*-butyl alcohol enables us to state that BAP and CHR decomposition follows radical reactions. In the case of FLU no influence of *t*-BuOH on reaction rate was observed which could indicate another pathway of its decomposition. The lack of inhibiting effect on the FLU degradation in the presence of bicarbonate ion was also noticed in the work of Beltran *et al.* [14].

The verified kinetic model, experimental and literature data enable computation of the rate constants of PAHs reaction with hydroxyl radicals. The obtained values are of the same order of magnitude as those cited in the literature [14, 15] and equal to  $2.53 \times 10^{10}$ ,  $9.82 \times 10^9$  and  $2.77 \times 10^9 M^{-1} s^{-1}$  for BAP, CHR and FLU, respectively.

Table 1. The concentration of hydroxyl radicals  $C_{OH}$  computed according to equation (13)

No.	$C_H^0$ M	$r \times 10^{10}$ Ms <sup>-1</sup>	$f_H$	$C_{HO}$ M	$C_{OH} \times 10^{12}$ M
BENZO[A]PYRENE		$C_B^0 = 4.76 \times 10^{-9}$ M		$k_6 = 2.53 \times 10^{10}$ M <sup>-1</sup> s <sup>-1</sup>	
1	10 <sup>-3</sup>	6.51	0.988	1.58 × 10 <sup>-8</sup>	22.9
2	10 <sup>-2</sup>	7.18	0.988	1.58 × 10 <sup>-7</sup>	12.1
3	0.2	1.16	0.999	3.16 × 10 <sup>-6</sup>	0.76
4 <sup>a</sup>	10 <sup>-3</sup>	2.00	0.988	4.99 × 10 <sup>-9</sup>	23.0
5 <sup>b</sup>	10 <sup>-3</sup>	0.63	0.988	4.42 × 10 <sup>-4</sup>	0.19
FLUORENE		$C_F^0 = 5.42 \times 10^{-6}$ M		$k_6 = 2.77 \times 10^9$ M <sup>-1</sup> s <sup>-1</sup>	
6	10 <sup>-3</sup>	1273	0.186	1.58 × 10 <sup>-8</sup>	10.6
7	10 <sup>-2</sup>	1380	0.696	1.58 × 10 <sup>-7</sup>	10.0
8	0.2	162.6	0.958	3.16 × 10 <sup>-6</sup>	0.73
9	0.4	90.30	0.989	6.32 × 10 <sup>-6</sup>	0.38
10 <sup>a</sup>	10 <sup>-3</sup>	1000	0.186	4.99 × 10 <sup>-9</sup>	10.6
11 <sup>b</sup>	10 <sup>-3</sup>	321.0	0.186	4.42 × 10 <sup>-4</sup>	0.13
CHRYSENE		$C_C^0 = 5.125 \times 10^{-9}$ M		$k_6 = 9.81 \times 10^9$ M <sup>-1</sup> s <sup>-1</sup>	
12	10 <sup>-3</sup>	1.88	0.985	1.58 × 10 <sup>-8</sup>	22.9
13	10 <sup>-2</sup>	3.15	0.998	1.58 × 10 <sup>-7</sup>	12.3
14	0.2	0.48	0.999	3.16 × 10 <sup>-6</sup>	0.36
15 <sup>a</sup>	10 <sup>-3</sup>	1.74	0.985	4.99 × 10 <sup>-9</sup>	23.4
16 <sup>b</sup>	10 <sup>-3</sup>	0.27	0.985	4.42 × 10 <sup>-4</sup>	0.19

<sup>a</sup>pH = 2.5;    <sup>b</sup>pH = 11.7

#### ACKNOWLEDGEMENTS

The study was sponsored by the Polish Committee for Scientific Research, Grant No.3T09C 02412. The authors are grateful to the Foundation for Development of Polish Science for purchasing Perkin Elmer spectrofluorimeter LS50B.

#### NOMENCLATURE

*b*-light path*C*-concentration*f*-fraction of absorbed radiation*I*<sub>0</sub>-intensity of incident radiation*I*<sub>a</sub>-intensity of absorbed radiation*k*-rate constant*k*<sub>z</sub>-pseudo-first order rate constant*K*-equilibrium constant*r*-reaction rate*t*-time

#### Greek letters

ε-extinction coefficient

λ-wavelength

Φ-quantum yield

#### Subscripts

B-benz[a]pyrene

C-chrysene

F-fluorene

H-hydrogen peroxide

HO-hydroperoxide anion

OH-hydroxide radical

P-PAHs

t-*tert*-butyl alcohol**Superscript**

0-initial value

#### REFERENCES

- [1] I. G. Karanassios, V. I. Georgakilas, E. S. Lahaniatis, and G. A. Pilidis, *Fresenius Envir. Bull.* **3** (1994), 511.
- [2] A. Saber, G. Morel, L. Paturel, J. Jarosz, M. Martin-Bouyer, and M. Vial, *Fresenius J. Anal. Chem.* **339** (1991), 716.
- [3] A. Eschenbach, M. Kästner, R. Bierl, G. Schaefer, and B. Mahro, *Chemosphere* **28** (1994), 683.
- [4] K. Krenzel-Rothensee, *BioEngineering* **9** (1993), 13.
- [5] D. Maier, M. Maier, B. Lloyd, and I. P. Toms, *Ozone Sci. & Eng.* **18** (1997), 517.
- [6] B. Fouillet, P. Chambon, M. Castegnaro, and N. Weill, *Bull. Environ. Contam. Toxicol.* **47** (1991), 1.
- [7] A. Kornmüller, M. Cuno, and U. Wiesmann, *Wat. Sci. Tech.* **35** (1997), 57.
- [8] C. E. Cerniglia, *Journal of Industrial Microbiology & Biotechnology* **19** (1997), 324.
- [9] A. K. De, S. Bhattacharjee, and B. K. Dutta, *Ind. Eng. Chem. Res.* **36** (1997), 3607.
- [10] D. W. Sundstrom, B. A. Weir, and H. E. Klei, *Environ. Prog.* **8** (1989), 6.

- [11] E. Tace, *Etude cinétique de la dégradation de chloroethanes et de s-triazines en milieux aqueux par irradiation UV en absence et en présence de peroxyde hydrogène*, Ph.D. thesis, Université de Poitiers, France, 1992.
- [12] F. J. Beltran, G. Ovejero, and B. Acedo, *Water Res.* **27** (1993), 1013.
- [13] M. E. Sigman, A. C. Buchanan III, and S. M. Smith, *J. Adv. Oxid. Technol.* **2** (1997), 415.
- [14] F. J. Beltran, G. Ovejero, and J. Rivas, *Ind. Eng. Chem. Res.* **35** (1996), 883.
- [15] M. Hautaniemi, J. Kallas, R. Munter, M. Trapido, and Y. Veressinina, vol. 82, p. 1, Lappeenranta University of Technology, Finland, 1997.
- [16] T. Tuhkanen, *Oxidation of Organic Compounds in Water and Waste Water with the Combination of Hydrogen Peroxide and UV Radiation*, Ph.D. thesis, University of Kuopio, Finland, 1994.
- [17] S. L. Murov, I. Carmichael, and G. L. Hug, *Handbook of Photochemistry*, 2nd ed., 1993, M. Dekker.
- [18] J. S. Miller, *Anal. Chim. Acta.* **388** (1999), 27.
- [19] J. Hoigne, *Chemistry of Aqueous Ozone and Transformation of Pollutants by Ozonation and Advanced Oxidation Processes*, The Handbook of Environmental Chemistry (Berlin, Heidelberg) (J. Hrubec, ed.), Springer-Verlag, 1998.
- [20] H. S. Christensen, H. Sehested, and H. Corfitzan, *J. Phys. Chem.* **86** (1982), 15.
- [21] I. Nicole, J. De Laat, M. Dore, J. Duguet, and C. Bonnel, *Water Res.* **24** (1990), 157.
- [22] J. Staehelin and J. Hoigne, *Environ. Sci. Technol.* **19** (1985), 1206.



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