

ADVANCED OXIDATION OF THE POLYCYCLIC MUSK FRAGRANCES WITH USING UV AND UV/H<sub>2</sub>O<sub>2</sub> PROCESSESEWA FELIS<sup>1</sup>, ALFREDO C. ALDER<sup>2</sup>, JOANNA SURMACZ-GÓRSKA<sup>1</sup>,  
KORNELIUSZ MIKSCH<sup>1</sup><sup>1</sup> Silesian University of Technology, Environmental Biotechnology Department  
ul. Akademicka 2, 44-100 Gliwice, Poland<sup>2</sup> Swiss Federal Institute for Environmental Science and Technology  
CH-8600 Dübendorf, Überlandstrasse 133, Switzerland**Keywords:** AHTN, HHCB, UV-radiation, UV/H<sub>2</sub>O<sub>2</sub>, the first order rate constant.

**Abstract:** The polycyclic musk fragrances AHTN (Tonalide) and HHCB (Galaxolide) are the most common components of cosmetics and detergents. Use of AHTN and HHCB per year (in the USA and in EU) was estimated at 1500 Mg and 3800 Mg, respectively. Because of their persistent character, musk compounds are introduced into environment mostly via urban sewage treatment plant effluents. The aim of the presented research was to assess the receptivity of AHTN and HHCB to the oxidation by means of UV-radiation and in the UV/H<sub>2</sub>O<sub>2</sub> process. The investigations were performed in the treated wastewater and the drinking water. After 8 minutes, in all experiments performed on drinking water, the degradations of AHTN and HHCB in the range of 99% were observed. The removal of HHCB from wastewater by means of UV radiation exceeded up 93% (after 8 minutes of the process), whereas the disappearance degree of this compound in wastewater, after only 3 minutes of UV/H<sub>2</sub>O<sub>2</sub> process, exceeded 99%. The degradation constant rate for AHTN in drinking water using UV radiation was equal to 0.764 min<sup>-1</sup> when the degradation rate of HHCB was estimated at 0.634 min<sup>-1</sup>. In the wastewater, the coefficient rate of HHCB degradation by means of UV/H<sub>2</sub>O<sub>2</sub> was nearly 4.5 times higher (1.580 min<sup>-1</sup>) in comparison to the value obtained by direct photolysis of HHCB (0.354 min<sup>-1</sup>).

## INTRODUCTION

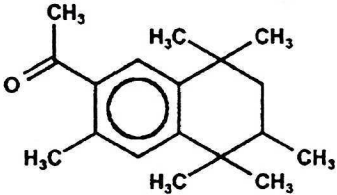
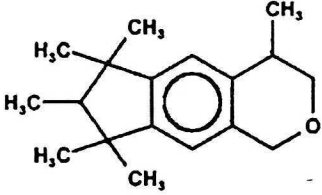
The polycyclic musk compounds are synthetic musks. The first polycyclic musk compound, AHDI, was synthesized in year 1951 [15]. After this date the production of polycyclic musk compounds developed on the industry-scale. Compared to other group of artificial nitro-free substances (e.g. macrocyclic musk), the polycyclic musks can be synthesized at relatively low costs [13]. Because of their characteristic fragrance proprieties and higher than nitro musk substances resistance to light, they are mainly used as component of cosmetics (especially perfumes) or detergents [7].

At the present moment AHTN (Tonalide) and HHCB (Galaxolide) are the most important representatives of polycyclic musks. Use of AHTN and HHCB per year (in the USA and in EU) was estimated at 1500 Mg and 3800 Mg, respectively [15]. It corresponds to about 95% general consumption of polycyclic musk compounds.

For the first time polycyclic musk fragrances were identified in surface water and fish samples from the River Ruhr (Germany) in the first half of the 1990s [2, 3]. Occurrence of AHTN and HHCB in the water sample from the River Elbe (Germany) was

reported in 1995 by Franke [5]. Nowadays prevalence of these compounds in different parts of environment is reported by many authors [e.g. 6, 7, 13, 17]. Because of their persistent character and biodegradation resistance, musk compounds are introduced into environment mostly via biological sewage treatment plant effluents [10]. Due to their physical-chemical properties they indicate lipophilic character. They are described as a new group of bioaccumulative and persistent xenobiotics. The most important polycyclic musks, AHTN and HHCB, can be accumulated not only in sediment and aquatic organisms but also in human milk, muscles and tissues [14]. Basic data on AHTN and HHCB are listed in Table 1.

Table 1. Basic data concerning AHTN and HHCB

	AHTN	HHCB
Chemical name	7-Acetyl-1,1,3,4,4,6-hexamethyl-tetrahydronaphthalene	1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-benzopyrane
Trade name	Tonalide*	Galaxolide*
Molecular formula	$C_{18}H_{26}O$	$C_{18}H_{26}O$
Chemical structure		
CAS No.	1506-02-1	1222-05-5

The aim of the presented research was to assess the receptivity of AHTN and HHCB to the oxidation by means of UV-radiation and in the UV/H<sub>2</sub>O<sub>2</sub> process. Additional aim of the study was to estimate the kinetic coefficients of the advanced oxidation of AHTN and HHCB in aquatic environment.

## MATERIALS AND METHODS

### Chemicals

AHTN (Tonalide) and HHCB (Galaxolide) were purchased as 100 µg/cm<sup>3</sup> – solutions (Certan<sup>®</sup>) in cyclohexane from Promochem GmbH, Germany. Surrogate standard, AHTN (Tonalide) – D3, was purchased as 100 µg/cm<sup>3</sup> – solution in isooctane (2,2,4-trimethylpentane) from Dr. Ehrenstorfer GmbH, Germany. All solvents used for solid phase extraction (SPE) were of the highest grade commercially available and they were purchased from Merck. The solid phase extraction cartridges were purchased from Supelco. Hydrogen peroxide (30%) was purchased from Fluka.

### *Analytical methods*

All GC/MS analyses were performed according to Ternes and Joss [9, 16]. The water or wastewater samples (contained AHTN and HHCB) were filtered through glass fiber filter (GF 8, Schleicher & Schuell, Dassel, Germany). The AHTN – D3 was spiked into each sample as surrogate standard. The samples were sucked through the SPE cartridges containing a solid phase material (conditioned by flushing with hexane p.a., acetone p.a., methanol p.a. and deionized water at neutral pH) at a flow rate of  $\approx 20 \text{ cm}^3/\text{min}$ . As the solid phase material, the 0.5 g RP – C<sub>18</sub> Bulk Sorbent (from Separtis GmbH, Grenzahll-Wyhlen, Germany) was used. Before elution the cartridges were completely dried by a gentle stream of nitrogen. The analytes were eluted with methanol p.a. and the samples were evaporated to dryness using nitrogen. The analytes were solved on hexane containing PBC Nr. 30 (as instrumental standard). Identification of AHTN and HHCB was performed by GC/MS in single-ion monitoring (SIM) without derivatization. GC/MS measurements were performed on a gas chromatograph HP 5890 (equipped with auto-sampler HP 7673), coupled with mass spectrometer HP 5971. Restek XTI-5 (30 m x 0.25 mm x 0.25  $\mu\text{m}$ ) as GC-column was used. The injector temperature was 215°C (injection volume =  $3 \cdot 10^{-6} \text{ dm}^3$ ). The temperature program was as follows: 50°C (isothermic) for 0.75 min.; 20°C/min. up to 160°C; 4°C/min. up to 280°C; 20°C/min. up to 300°C; 300°C (isothermic) for 10 min. Quantification was done by comparing the ratios of the peak areas from the analytes and the surrogate standard to an external calibration curve.

### *Experimental set-up*

The experiments were performed with wastewaters from sewage treatment plant and drinking water containing AHTN and HHCB standards. The grab samples of wastewater were taken from urban sewage treatment plant of Klotten Opfikon (Switzerland) on 7–8 June 2004. The sewage treatment plant of Klotten Opfikon (total population equivalents about 55 000) treats the wastewater from two towns (Klotten and Opfikon) and from an airport. The mechanical part of the STP consists of a screen, an aerated grit-removal tank and a primary clarifier. The primary effluent is directed to the activated sludge system for denitrification and nitrification. The effluent after a secondary clarifier and two-layer sand filter is introduced to the receiving water [9]. Phosphorus removal is obtained by simultaneous precipitation with the addition of Fe(II)chloride. The wastewater for the investigation was tertiary effluent taken after the sand filter. The experiments were conducted at real concentrations of AHTN and HHCB in the wastewater (the concentration of AHTN  $\cong 0.52 \pm 0.06 \mu\text{g}/\text{dm}^3$  and HHCB  $\cong 2.12 \pm 0.25 \mu\text{g}/\text{dm}^3$ ). In the wastewater the average COD concentration was equal to 29 mg O<sub>2</sub>/dm<sup>3</sup> and the average suspended solid (SS) concentration was equal to 50 mg/dm<sup>3</sup>. Drinking water solutions were prepared by spiking the required volume of standard solution of AHTN and HHCB (in cyclohexane) into the drinking water (taken from a water supply system). The initial concentrations of HHCB in prepared drinking water solution were  $2.42 \pm 0.14 \mu\text{g}/\text{dm}^3$  in the experiments with UV and  $2.13 \pm 0.17 \mu\text{g}/\text{dm}^3$  in the experiments with UV/H<sub>2</sub>O<sub>2</sub>. The initial concentrations of AHTN (in both processes) were equal to  $1.91 \mu\text{g}/\text{dm}^3$ .

The experiments of the AHTN and HHCB oxidation by using UV and UV/H<sub>2</sub>O<sub>2</sub> processes were carried out in a reactor UVILab P400 (Vita Tech GmbH, Germany) equipped with 400 W medium-pressure mercury lamp with a broad radiation spectrum 200–280 nm. The light source in a quartz casing was immersed in a glass reactor (the volume of

reactor = 350 cm<sup>3</sup>). All experiments were performed using a half of the maximal lamp power ( $P = 200$  W). The average path length of a light through the solution was equal 5 to mm. Figure 1 shows a scheme of an experimental reactor. The wastewater from sewage treatment plant effluent (or drinking water containing AHTN and HHCB standards) was introduced into the feeding tank (1). From feeding tank (1) the medium was pumped into the reaction chamber (3) equipped with cooling system (4). The retention time in reaction chamber (so-called "irradiation time") was set up by a flow rate of a medium (the flow rate ranging between 44 and 350 cm<sup>3</sup>/min). For example, the flow rate by the irradiation time = 8 min was equal to 44 cm<sup>3</sup>/min. The water peroxide solution (by UV/H<sub>2</sub>O<sub>2</sub> oxidation) was introduced into the reaction chamber from the water peroxide tank by a peristaltic pump (5). The UV/H<sub>2</sub>O<sub>2</sub> experiments were conducted at overdosed concentrations of H<sub>2</sub>O<sub>2</sub> – the wastewater from sewage treatment plant effluent was oxidized by H<sub>2</sub>O<sub>2</sub> concentration  $\cong 1$  g H<sub>2</sub>O<sub>2</sub>/dm<sup>3</sup> and the drinking water containing AHTN and HHCB standards was oxidized by concentration of H<sub>2</sub>O<sub>2</sub>  $\cong 1$  mg H<sub>2</sub>O<sub>2</sub>/dm<sup>3</sup>. The experiments were performed at pH  $\cong 7$  and at room temperature (23–25°C).

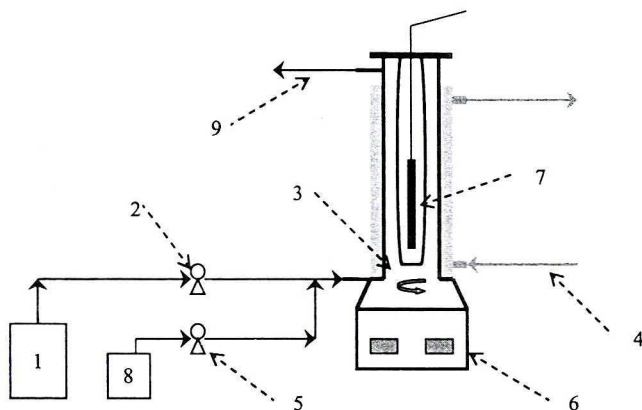


Fig. 1. Scheme of the experimental reactor: 1 – feeding tank, 2 – feeding pump, 3 – reaction chamber, 4 – cooling system, 5 – peristaltic pump, 6 – magnetic stirrer, 7 – UV lamp, 8 – H<sub>2</sub>O<sub>2</sub> chamber – option by UV/H<sub>2</sub>O<sub>2</sub> process, 9 – reactor effluent

## RESULTS AND DISCUSSION

### *UV oxidation (photolysis experiments)*

The removal of AHTN and HHCB from the aquatic environment by UV-radiation is shown in Figure 2 (drinking water) and in Figure 3 (wastewater effluent). After 8 min. of the photolysis process in drinking water, the removal of AHTN and HHCB reached a range of 99%. The concentrations of AHTN and HHCB in water samples after 8 min. UV – oxidation were below limit of detection (LOD = 20 ng/dm<sup>3</sup>). Data showed degradation of AHTN within 3 min. by the UV oxidation process in the wastewater samples. Even after 8 min. of the oxidation process in the same conditions, HHCB was not completely removed from the wastewater sample – the reduction rate reached 93%. The difference between reduction rate of AHTN and HHCB in the wastewater samples can be explained by the fact that initial concentrations of these two compounds in the wastewater were

different. The concentration of AHTN was at the level of  $0.52 \pm 0.06 \mu\text{g}/\text{dm}^3$ , whereas the concentration of HHCB was four times higher and was equal to  $2.12 \pm 0.25 \mu\text{g}/\text{dm}^3$ . The investigations at real concentrations of AHTN and HHCB in the wastewater were performed. The similar distribution of concentrations between AHTN and HHCB was observed very often in the aquatic environment. For instance, a proportion 4:1 between concentrations of HHCB and AHTN in effluents from sewage treatment plant was reported by Fromme [6].

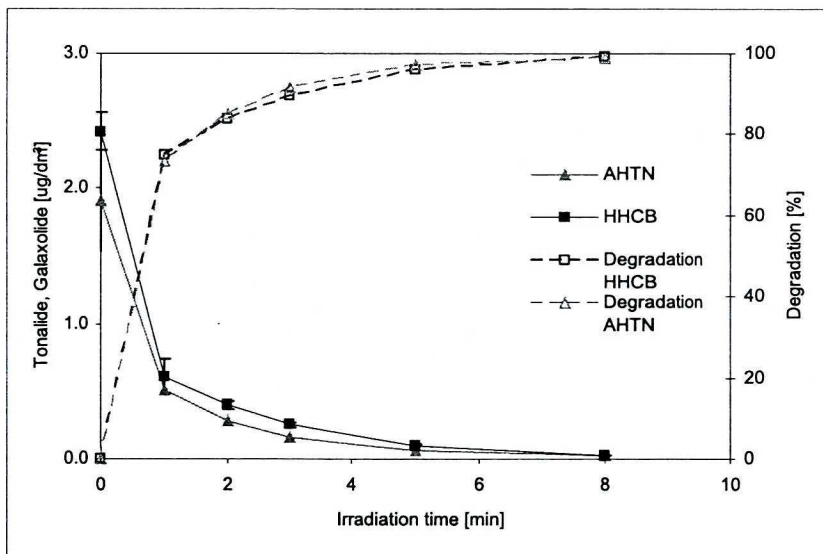


Fig. 2. The degradation of AHTN and HHCB from drinking water using UV-radiation

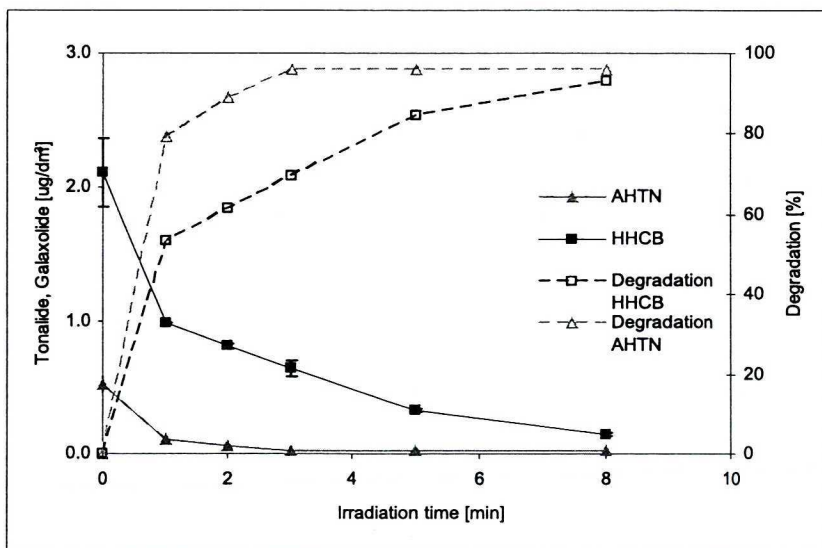


Fig. 3. The degradation of AHTN and HHCB from wastewater effluent using UV-radiation

The first order rate constants ( $k$ ) of a direct photolysis (via UV radiation) of AHTN and HHCB in the water and the wastewater samples were calculated using a graphic method. The first order reaction can be described by a mathematic model:

$$-\frac{d[C]}{dt} = k \cdot [C] \quad (1)$$

After the variables separation and integration of equation (1) at the limits of an integration:  $[C] = [C_0]$  and  $[C] = 0$ ;  $t = 0$  and  $t = t$ , a relationship has been established:

$$k \cdot t = \ln \frac{[C_0]}{[C]} \quad (2)$$

The equation (2) can be shown in a diagram as a plot of the  $\ln$  of the substrate concentration changes ( $\ln \frac{[C_0]}{[C]}$ ) versus time (Fig. 4). When the reaction order equals 1,

then the plot is a straight line. The first order rate constant ( $k$ ) can be calculated as a slope of the plotted straight line. Table 2 comprises the first order rate constants ( $k$ ) of photolytic oxidation of AHTN and HHCB in drinking water and wastewater. The first order rate constants of photolytic oxidation of AHTN and HHCB in drinking water were comparable and they were equal to  $0.762 \text{ min}^{-1}$  and  $0.634 \text{ min}^{-1}$ , respectively. The wastewater matrix reduced the photodegradation rate of HHCB (by an increase UV-light absorption) and the rate of HHCB disappearance in samples from sewage treatment plant effluent was two times slower than in drinking water (Tab. 2). In the case of photolysis of AHTN in wastewater, the first order rate constant was determined only for the first three minutes of reaction – after this time the AHTN removal was complete and the reaction was finished. The rate of AHTN disappearance in wastewater was equal to  $1.127 \text{ min}^{-1}$  and it was about 1.5 times higher than the disappearance rate of AHTN in the water. In order to explain this behavior of AHTN in the water and wastewater two hypotheses were put forward. The

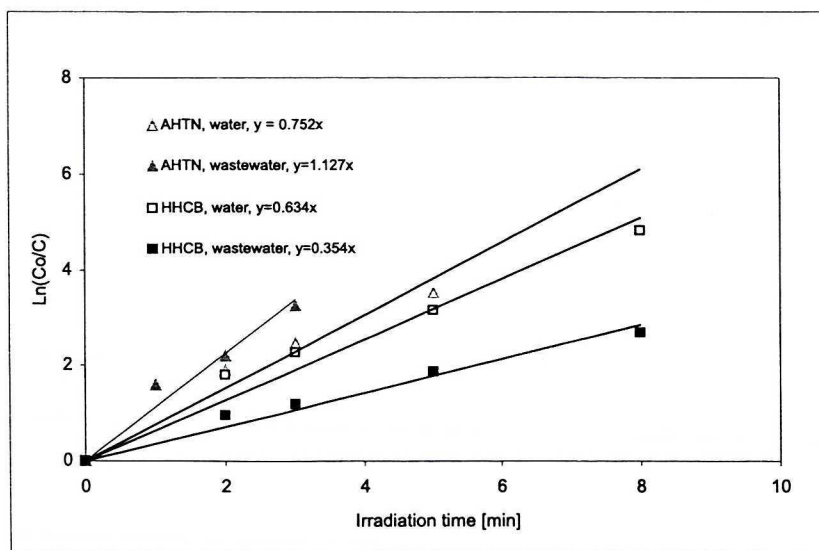


Fig. 4. The changes of substrates concentration during UV oxidation process

first hypothesis is that in the wastewater a substance was present which was a photosensibiliser only of AHTN photodegradation. It means that the photosensibiliser absorbing the UV-radiation accelerated only the photodegradation of AHTN. The alternative hypothesis is that AHTN molecules (when the concentration of this compound in the wastewater was not high) were able to absorb more than one energy quantum per molecule. The additional energy allowed for acceleration of the degradation rate of AHTN.

Table 2. The first order rate constants ( $k$ ) of photolytic oxidation of AHTN and HHCB in drinking water and wastewater

Compounds	$k$ [ $\text{min}^{-1}$ ]	$R^2$
AHTN (in water)	0.752	0.959
AHTN (in wastewater)	1.127	0.961
HHCB (in water)	0.634	0.959
HHCB (in wastewater)	0.354	0.970

### UV/H<sub>2</sub>O<sub>2</sub> process

The addition of H<sub>2</sub>O<sub>2</sub> in the UV oxidation experiments should increase the efficiency of micropollutants removal from aquatic environment. When a H<sub>2</sub>O<sub>2</sub> molecule is attacked by UV ray (direct photolysis of H<sub>2</sub>O<sub>2</sub> at  $\lambda \leq 400$  nm is possible), then two molecules of hydroxyl radicals (OH $\cdot$ ) from one H<sub>2</sub>O<sub>2</sub> are generated [4]. These generated during direct photolysis of H<sub>2</sub>O<sub>2</sub> hydroxyl radicals can be significant accelerator of UV oxidation process. Additionally, H<sub>2</sub>O<sub>2</sub> is an oxidant ( $E^0 = 1.77$  V), which can directly oxidize the micropollutants.

The Figures 5 and 6 present the removal of AHTN and HHCB using UV/H<sub>2</sub>O<sub>2</sub> from drinking water and from wastewater, respectively. Both compounds in the drinking water were oxidized within 8 minutes to the detection limits. The removal of HHCB from wastewater samples (to the detection limit) followed after 3 minutes. Because of low concentration of AHTN, its complete removal from wastewater was observed within 2 minutes of UV/H<sub>2</sub>O<sub>2</sub> process.

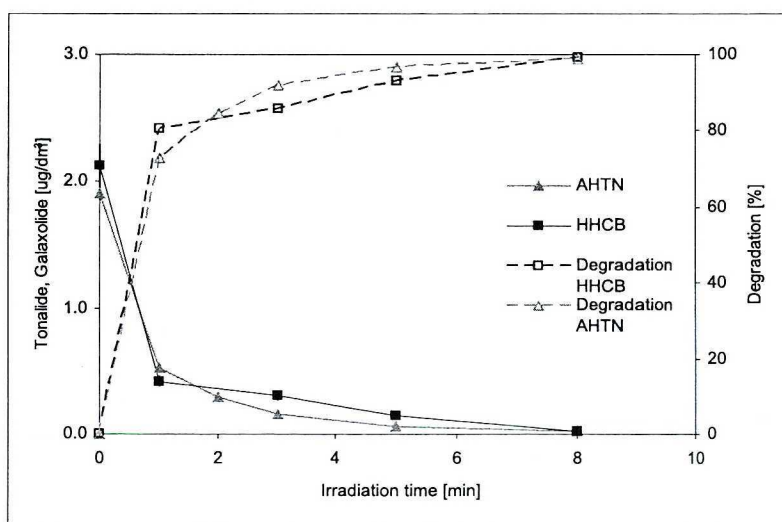


Fig. 5. The degradation of AHTN and HHCB from drinking water using UV/H<sub>2</sub>O<sub>2</sub>

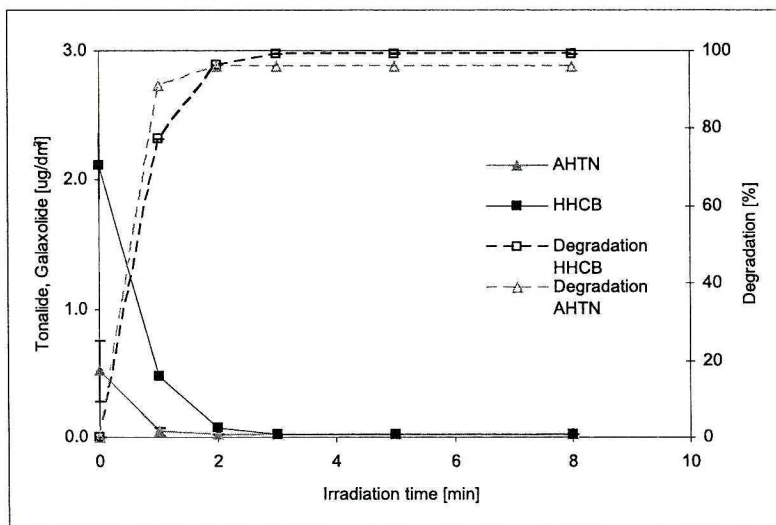


Fig. 6. The degradation of AHTN and HHCB from wastewater samples using UV/H<sub>2</sub>O<sub>2</sub>

The oxidation reactions with using hydroxyl radicals as second order reactions are described by many author [8, 11]. However, when the hydroxyl radicals (in UV/H<sub>2</sub>O<sub>2</sub> process) are present in overdosed concentration in comparison to substrate concentration and the substrate occurs in middle concentration, the reactions of substrate oxidation under definite conditions can proceed as first order reactions [1, 4, 18]. The orders of AHTN and HHCB oxidation reaction using UV/H<sub>2</sub>O<sub>2</sub> were estimated using graphic methods. When the reaction is the first order reaction, then the plot of  $\ln \frac{[C_0]}{[C]}$  versus time is a straight line. When the reaction is the second order reaction, then the plot of reverse of substrate concentration ( $1/[C]$ ) versus time is a straight line [12]. Two diagrams ( $\ln \frac{[C_0]}{[C]}$  versus time and  $1/[C]$  versus time) were constructed. Next, the linear trend functions were performed and the correlation coefficients ( $R^2$ ) of these trend functions were calculated. The result of coefficients ( $R^2$ ) comparison indicated that the UV/H<sub>2</sub>O<sub>2</sub> oxidation reactions of AHTN and HHCB under the conditions adapted in the present study were the first order reactions (except of AHTN oxidation in wastewater). In view of very low concentration of AHTN in wastewater, we observed the substance disappearance to its limit of detection after 2 minutes of UV/H<sub>2</sub>O<sub>2</sub> process. It means that we obtained only 2 measure points (without point "zero" for the determination of reaction order. To precisely determine the reaction order and rate constants, we need at least 3 measure points. For this reason, the determined order of reaction and the calculated value of the rate constant (in the case of oxidation AHTN in wastewater) should be treated only as estimated quantities. The values of coefficients  $R^2$  by oxidation AHTN in wastewater using UV/H<sub>2</sub>O<sub>2</sub> process were higher in the case of the second order reaction in comparison to the value  $R^2$  of the first order reaction, but both coefficients exceeded the value of 0.900. On the basis of the data received, the order of the above-mentioned reaction can not be unequivocally defined.



The first order rate constant of UV/H<sub>2</sub>O<sub>2</sub> oxidation HHCB in the wastewater samples reached the value of 1.580 min<sup>-1</sup> (Tab. 3). The addition of H<sub>2</sub>O<sub>2</sub> highly accelerated the reaction of the HHCB decomposition in the wastewater. The value of the rate constant received during UV/H<sub>2</sub>O<sub>2</sub> oxidation is nearly 4.5 times higher in comparison to the value obtained by direct photolysis of HHCB in wastewater. In drinking water, the calculated rate constants of AHTN and HHCB disappearance reached 0.754 min<sup>-1</sup> and 0.577 min<sup>-1</sup>, respectively. These values are very similar to the values of the rate constant obtained by direct photolysis reactions of AHTN and HHCB. It means that addition of H<sub>2</sub>O<sub>2</sub> did not significantly increase the degradation rates of both musks. It is probably an effect of the presence of cyclohexane in the drinking water solutions – the drinking water solutions were prepared by spiking the standard solutions of AHTN and HHCB which were dissolved in cyclohexane. There is a strong possibility that the present in drinking water solutions of cyclohexane could substantially increase the scavenging of the hydroxyl radical. It means that the degradation rate of the investigated compounds induced by hydroxyl radical could be strongly decreased with respect to the same water (or wastewater) without cyclohexane.

Table 3. The first order rate constants of AHTN and HHCB during UV/H<sub>2</sub>O<sub>2</sub> oxidation in drinking water and wastewater

Compounds	$k$ , min <sup>-1</sup>	R <sup>2</sup>
AHTN (in water)	0.754	0.955
AHTN (in wastewater)*	1.789	0.910
HHCB (in water)	0.577	0.992
HHCB (in wastewater)	1.580	0.997

\* – the order of oxidation reaction AHTN in wastewater using UV/H<sub>2</sub>O<sub>2</sub> cannot be unequivocally defined. The value of coefficients R<sup>2</sup> was higher in the case of the second order reaction in comparison to the value R<sup>2</sup> of the first order reaction. The second order rate constant obtained  $k_{II} = 6.303 \mu\text{M}^{-1} \cdot \text{s}^{-1}$  by R<sup>2</sup> = 0.991. However, it was calculated basing on only 2 measure points.

## CONCLUSIONS

The polycyclic musk compounds AHTN and HHCB were effectively degraded using UV and UV/H<sub>2</sub>O<sub>2</sub> methods. In all experimental sessions performed in drinking water environment, after 8 minutes of treatment, the AHTN and HHCB degradation rates reached a range of 99% and the concentrations of investigated compounds were below their detection limit.

The removal of HHCB from wastewater by UV radiation exceeded 93% when the disappearance degree of this compound in wastewater samples after only 3 minutes of UV/H<sub>2</sub>O<sub>2</sub> process obtained 99%. Due to very low concentration of AHTN in wastewater, the degradation to a concentration below its limit of detection reached 3 minutes by UV oxidation and 2 minutes by UV/H<sub>2</sub>O<sub>2</sub> process.

The orders of AHTN and HHCB oxidation reactions using UV and UV/H<sub>2</sub>O<sub>2</sub> method were determined. In all cases (except of AHTN in wastewater by UV/H<sub>2</sub>O<sub>2</sub> process) the oxidation reaction under described conditions proceeded as a first order reaction. Based on the data received, the reaction order of AHTN oxidation in wastewater by UV/H<sub>2</sub>O<sub>2</sub> process cannot be unequivocally defined.

The first order rate constants of investigated compounds at the neutral pH were estimated. The degradation constant rate for AHTN in drinking water using UV radiation reached  $0.764 \text{ min}^{-1}$  when the degradation rate of HHCB was estimated at the range of  $0.634 \text{ min}^{-1}$ . In all performed experiments AHTN degradation rate constants were higher in comparison to the rate constant of HHCB. These regularities can be confirmed by the fact that the moiety of HHCB consists of three closing carbon rings whereas the AHTN moiety consists only of two closing rings. It can suggest that for the AHTN moiety destruction, the less energy than for HHCB destruction is needed and the reaction of AHTN destruction can proceed faster than the reaction of HHCB destruction.

The addition of  $\text{H}_2\text{O}_2$  in the experiment of HHCB degradation in the wastewater samples effectively accelerated this process. The coefficient rate of HHCB degradation using UV/ $\text{H}_2\text{O}_2$  was nearly 4.5 times higher ( $1.580 \text{ min}^{-1}$ ) in comparison to the value obtained by direct photolysis of HHCB in the wastewater ( $0.354 \text{ min}^{-1}$ ). In the investigations performed in drinking water, the addition of  $\text{H}_2\text{O}_2$  did not accelerate the oxidation reaction of AHTN and HHCB. It could be effected by the presence of cyclohexane which is a hydroxyl radical scavenger and which could strongly decrease the degradation rate of investigated compounds induced by the hydroxyl radicals.

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#### REFERENCES

- [1] Beltran F.J., M. Gonzalez, J.F. Gonzalez: *Industrial wastewater advanced oxidation. Part I: UV radiation in the presence and absence of hydrogen peroxide*, Water Res., **31**, 2405–2414 (1997).
- [2] Eschke H.-D., H.-J. Dibowski, J. Traud: *Studies on the occurrence of polycyclic musk fragrances in different environmental compartments, 2. communication* (in German), UWSF. – Z., Umweltchem. Oekotoxikol., **7**, 131–138 (1995).
- [3] Eschke H.-D., J. Traud, H.-J. Dibowski: *Studies on the occurrence of polycyclic musk fragrances in different environmental compartments, 1. communication* (in German), UWSF. – Z., Umweltchem. Oekotoxikol., **6**, 183–189 (1994).
- [4] Esplugas S., J. Gimenez, S. Contreras, E. Pascual, M. Rodriguez: *Comparison of different advanced oxidation processes for phenol degradation*, Water Res., **36**, 1034–1042 (2002).
- [5] Franke S., S. Hildebrandt, J. Schwarzbauer, M. Link, W. Francke: *Organic compounds as contaminants of the River Elbe and its tributaries, part II: GC/MS screening for contaminants of the Elbe water*, Fresenius J. Anal., **353**, 3949 (1995).
- [6] Fromme H., Th. Otto, K. Pilz: *Polycyclic musk fragrances in different environmental compartments in Berlin (Germany)*, Water Res., **35**, 121–128 (2001).
- [7] Heberer Th.: *Occurrence, fate, and assessment of polycyclic musk residues in the aquatic environment of urban areas – a review*, Acta Hydrochim. Hydrobiol., **30**, 227–243 (2002).
- [8] Huber M., S. Canonica, G.-Y. Park, U. Gunten von: *Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes*, Environ. Sci. Technol., **37**, 1016–1024 (2003).
- [9] Joss A., E. Keller, A. Alder, A. Goebel, Ch. McArdell, Th. Ternes, H. Siegrist: *Removal of pharmaceuticals and fragrances in biological wastewater treatment*, Water Res., **39**, 3139–3152 (2005).
- [10] Llompart M., C. Garcia-Jares, C. Salgado, M. Polo, R. Ccla: *Determination of musk compounds in sewage treatment plant sludge samples by solid-phase microextraction*, J. Chromatogr. A, **999**, 185–193 (2003).
- [11] Packer J., J. Werner, D. Latch, K. McNeill, W. Arnold: *Photochemical fate of pharmaceuticals in the environment: Naproxen, diclofenac, clofibric acid and ibuprofen*, Aquat. Sci., **65**, 342–351 (2003).
- [12] Pigon K., Z. Ruziewicz: *Chemia fizyczna*, PWN, Warszawa 1980.
- [13] Rimkus G.: *Polycyclic musk fragrances in the aquatic environment*, Toxicol. Lett., **111**, 37–56 (1999).

- [14] Rimkus G., M. Wolf: *Polycyclic musk fragrances in human adipose tissue and human milk*, Chemosphere, **33**, 2033–2043 (1996).
- [15] Sommer C.: *The role of Musk and Musk Compounds in the Fragrance Industry. Synthetic Musk Fragrances in the Environment*, The Handbook of Environmental Chemistry, vol. 3, part X, 1–16, Springer Verlag, Berlin – Heidelberg 2004.
- [16] Ternes Th., M. Bonerz, N. Herrmann, D. Loeffler, E. Keller, B. Lacida, A. Alder: *Determination of pharmaceuticals, iodinated contrast media and musk fragrances in sludge by LC/tandem MS and GC/MS*, J. Chromatogr. A, **1067**, 213–223 (2005).
- [17] Ternes Th., N. Herrmann, M. Bonerz, Th. Knacker, H. Siegrist, A. Joss: *A rapid method to measure the solid-water distribution coefficient ( $K_d$ ) for pharmaceuticals and musk fragrances in sewage sludge*, Water Res., **38**, 4075–4084 (2004).
- [18] Vogna D., R. Marotta, A. Napolitano, R. Andreozzi, M. d'Ischia: *Advanced oxidation of the pharmaceutical drug diclofenac with UV/H<sub>2</sub>O<sub>2</sub> and ozone*, Water Res., **38**, 414–422 (2004).

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#### ZAAWANSOWANE UTLENIANIE POLICYKLICZNYCH ZWIĄZKÓW PIŻMA W PROCESACH UV I UV/H<sub>2</sub>O<sub>2</sub>

AHTN (Tonalid) i HHCB (Galaksolid) są najczęściej stosowanymi substancjami zapachowymi z grupy policyklicznych związków piżma. Używane są zwykle jako składniki perfum lub detergentów. W krajach Unii Europejskiej i w Stanach Zjednoczonych (łącznie) roczne zużycie AHTN szacowane jest na 1500 Mg, a HHCB na 3800 Mg. Ze względu na swoje właściwości, substancje te nie są usuwane w biologicznych procesach oczyszczania ścieków i wraz ze ściekami oczyszczonymi przedostają się do środowiska. Celem prezentowanych badań było określenie podatności AHTN i HHCB na utlenienie za pomocą promieniowania UV i w procesie UV/H<sub>2</sub>O<sub>2</sub>. Badania prowadzone były w ściekach oczyszczonych i w wodzie pitnej. We wszystkich eksperymentach prowadzonych w wodzie pitnej, już po 8 minutach procesu, obserwowano rozkład AHTN i HHCB na poziomie 99%. W ściekach, po 8 minutach utleniania HHCB promieniami UV, stopień rozkładu tej substancji przekroczył 93%. Podczas utleniania HHCB w procesie UV/H<sub>2</sub>O<sub>2</sub>, już po 3 minutach, stopień rozkładu tego związku przekroczył 99%. Wartość stałej szybkości rozkładu AHTN w wodzie pitnej pod wpływem promieniowania UV wyniosła 0,764 min.<sup>-1</sup>, a wartość stałej szybkości rozkładu HHCB wyniosła 0,634 min.<sup>-1</sup>. W ściekach wartość stałej szybkości rozkładu HHCB w procesie UV/H<sub>2</sub>O<sub>2</sub> była prawie 4,5 razy większa (1,580 min.<sup>-1</sup>) w porównaniu z wartością stałej szybkości rozkładu tego związku w procesie fotolizy bezpośredniej (0,354 min.<sup>-1</sup>).