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# Oxidation of bisphenol A from simulated and real urban wastewater effluents by UV, $O_3$ and UV/ $O_3$

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# ABSTRACT

Increased concentration of micropollutants in the aquatic environment triggers the necessity to develop more effective methods for their elimination. A variety of research has been devoted to similar subject matters regarding the efficiency of different advanced oxidation processes to eliminate micropollutants. On the basis of them, this study was undertaken so as to assess the efficiency of bisphenol A (BPA) elimination from both stimulated and real urban wastewater effluents by photolysis (UV), ozonation ( $O_3$ ) and UV/ $O_3$  processes. The obtained results were juxtaposed in terms of the efficiency of BPA elimination for deionised water. The physical and chemical composition of the solution differentiated BPA elimination efficiency in the investigated processes. BPA decomposition degree was higher for real wastewater effluents than for deionised water and stimulated effluents. It is probably connected with the presence of photosensitisers in the real effluent. It was established that the combination of photolysis and ozonation led to the highest level of compound decomposition (for real effluent >90%). In this research, a first-order reaction model was used to establish the reaction rate constant for BPA decomposition in a combined UV/ $O_3$  process. The half-life of the investigated compound was also identified.

*Keywords:* Micropollutants elimination; Bisphenol A; Wastewater effluent; Photolysis; Ozonation; Combined process

# 1. Introduction

The activated sludge process is one of the most common and most effective biological ways of urban wastewater treatment. However, its effectiveness in micropollutants elimination is very often insufficient. Micropollutants due to their structure (e.g. policyclicity, a variety of functional groups) and their physical and chemical properties (hydrophobicity, polarity, etc.), undergo biodegradation to a small extent. The micropollutants elimination from wastewater is connected with the phenomenon of compound adsorption on activated sludge flocs. Micropollutants frequently display toxicity against activated sludge biocenosis [1,2]. Thus, in the past 10 years the interest in the use of other unconventional wastewater treatment methods to remove micropollutants has significantly

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increased. First of all, the membrane techniques have been incorporated in this field [1–4]. The expansion of a wastewater treatment plant chain through the application of new technologies has also been taken into consideration. For example, advanced oxidation processes (AOPs) have been suggested to treat effluents from municipal wastewater treatment plants [3,4].

AOPs enable production of hydroxyl radicals in an amount sufficient to ensure efficient treatment of water streams [5]. Hydroxyl radicals have very high redox potential (2.8 V) which enables fast and nonselective oxidation of organic compounds which are toxic and difficult to biodegrade [6]. That is extremely important owing to the fact that wastewater is full of organic micropollutants of a multiple origin. We can differentiate natural micropollutants including toxins (e.g. ganistein, daidzein, zearaleonone and others) as well as chemical compounds produced by humans (different pharmaceutical, pesticides, alkylphenols and many other industrial chemical compounds) [1–6].

AOPs include first and foremost light-dependent reactions in which hydroxyl radicals are induced by electromagnetic radiation. Photolysis (UV) is the basic unit operation used in this process [7]. The mechanism of photolysis is based on the initiation of a pollutant molecule by photon absorption from the emission spectrum of an electromagnetic radiation beam. A wavelength is a significant parameter in a direct photolysis. If a wavelength is higher than 200 nm, the induced light does not generate hydroxyl radicals, and the observed pollutant changes are caused by the absorption of quantum of electromagnetic radiation. The efficacy of photolysis significantly depends on the type of the removed micropollutant. The studies by Esplugas et al. [8] proved that the removal degree of selected pharmaceuticals by direct photolysis varied between 5% for carbamazepine (a psychoactive drug) and to 91% for clofibric acid (a drug for a lipid disorders treatment). According to Neamtu and Frimmel [9], photolysis is rather inefficient for bisphenol A (BPA), which is a typical industrial compound, which leads to BPA degradation at the level of approximately 8%. However, when the conditions of the process undergo some changes, i.e. low pressure mercury lamp (15 W) is replaced with a metal-halide lamp (250 W), then BPA degradation reaches 40% [10]. The research outcomes prove the selectivity of the photolysis process. They also show that the process efficacy is subject to the selection of a proper radiation source.

Taking into account that for many years electromagnetic radiation has been incorporated on a technical scale for drinking water or wastewater disinfection, a variety of research has been conducted to increase the efficacy of photolysis in order to eliminate micropollutants by cumulating it with other processes in a variety of configurations, e.g. photolysis and hydrogen peroxide oxidation (UV/H<sub>2</sub>O<sub>2</sub>), photolysis catalysed with titanium dioxide TiO<sub>2</sub>, so called photocatalysis (UV/TiO<sub>2</sub>), photolysis with ozonation (UV/O<sub>3</sub>). Thus, reusing existing installations and minor system modifications might make it possible to efficiently eliminate different types of pollutants including low-molecular weight micropollutants [11].

According to many researchers [12-14], the incorporation of hydrogen peroxide during photolysis increases the efficiency of micropollutants removal in a significant way in contrast to the reaction conducted as a separate process. When exposed to UV radiation, the direct photolysis of hydrogen peroxide takes place, and as a consequence hydroxyl radicals are generated. In the studies carried out by Esplugas et al. [8], the addition of  $H_2O_2$  in the concentration of 10 mg/L to the solution increased the elimination degree of carbamazepine to the level of 99%, whereas it was almost non-degradable in the process of a separate photolysis. The investigations confirmed that the combination of both processes resulted in a synergistic effect of different oxidisers. According to Konstantinou and Albanis [15], the application  $TiO_2$  during electromagnetic radiation also leads to a synergy process. A huge advantage of TiO<sub>2</sub> is its non-toxicity, low price and quite significant vulnerability to degradation. According to Sakkas et al. [16], the concentration of salbutamol (a compound belonging to a group of pharmaceuticals) decreased to about 90% in the process of photocatalysis with the use of  $TiO_2$  at a dosage of 500 mg/L after a 30 min radiation time. During photocatalysis with the use of TiO<sub>2</sub> certain intermediate products of high toxicity were produced. This phenomenon is common while conducting the oxidation processes. A complete mineralisation of salbutamol (a pharmaceutical substance used in drugs for the relief of bronchospasm) as well as other by-products produced during its oxidation were obtained long after 24 h process performance.

Comparing the above-mentioned methods of AOPs, the combination of photolysis and ozonation  $(UV/O_3)$  seems to be the most promising one. In their investigations, Pengxiao et al. [17] contrasted photolysis, ozonation and a combined process of  $UV/O_3$  in terms of removal of selected antibiotics from wastewater. The results obtained in these investigations revealed that photolysis proved completely ineffective against antibiotics removal. The efficiency of ozonation dependant on the ozone and water contact time. Satisfactory results of antibiotics removal were observed after a 30 min process. On the other hand, in the case of the cumulative process of  $UV/O_3$ , after 10 min the degree of antibiotics removal reached approximately

90%. Moreover, in this cumulative process a significant decrease in wastewater toxicity was observed (approximately 58%).

BPA is a common micropollutant characterised by potential toxicity and some dangerous biological activity [9]. On the basis of the gathered information, this study was undertaken to assess the elimination efficiency of BPA from urban wastewater effluents by UV,  $O_3$  and UV/ $O_3$  processes. Both the simulated and real effluents were taken under investigation. The obtained results were compared against their BPA removal efficiency for deionised water. In this research, a first-order reaction model was used to identify the reaction rate constant for BPA decomposition in a combined UV/ $O_3$  process. The half-life of the investigated compound was also established.

# 2. Materials and methods

# 2.1. Materials and reagents

The BPA analytical standard with the percentage of purity greater than 98 by Sigma-Aldrich was applied. N-methyl-n-(trimethylsilyl)trifluoroacetamide (MSTFA) by Sigma-Aldrich was used as a derivate in the derivatisation reaction introduced as a preparation phase before the application of GC–MS technique. Moreover, in the investigations both methanol with 99.5% of purity and acetonitrile with over 99.5% of purity by Avantor were used. For solid phase extraction (SPE) Supelclean<sup>™</sup> ENVI-18 cartridges (volume 6 mL, solid phase 1.0 g) by Supelco as well as the SPE chamber from the same company were applied.

# 2.2. Solutions compositions

The solutions were prepared from deionised water. Both simulated and real effluents after a biological purification with BPA in a constant concentration  $500 \ \mu g/L$  underwent purification by UV, O<sub>3</sub> and UV/O<sub>3</sub> processes. The physical and chemical characteristics of the investigated solutions are presented in Table 1.

The real effluent was taken from an urban wastewater treatment plant working in the mechanicalbiological system, and located in western Poland. The simulated effluent was prepared on the basis of a dry stock, casein peptone, NH<sub>4</sub>Cl, NaCl, CaCl<sub>2</sub>·6H<sub>2</sub>O, MgSO<sub>4</sub>·7H<sub>2</sub>O, K<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub>. Absorbance measurement in UV<sub>254</sub> made it possible to establish a diversity regarding the levels concentration of highmolecular weight organic compounds among the investigated effluents.

# 2.3. Oxidation processes

Photolysis was conducted in the temperature of 20°C in the batch reactor (capacity in 700 mL) by Heraeus equipped with the medium pressure mercury vapour lamp of 150 W. The light exposure was conducted in a constant manner throughout 30 min. On the other hand, ozone was introduced to the reactor through a ceramic diffuser before the light exposure. In the case of single series, ozone was applied with a time delay when compared to the radiation time. This delay was introduced so as to compare the efficiency of a separate photolysis process of the solution against the efficiency of a combined process (photolysis and ozonation). Ozone was generated by the air in Ozoner FM500 generator (ozone output 0.14 mg/s) by WRC Multiozon. The ozone dosage, depending on the research stage, varied from 1 to 20 mg/L, whereas the contact time between the oxidiser and solution was constant and lasted for 1 min.

# 2.4. Kinetic evaluation of UV/O<sub>3</sub> process

On the basis of the information gathered from literature, in order to describe the combined process  $UV/O_3$ , in a simple way a first-order reaction model can be applied in accordance with the following equation [21]:

Table 1The physical and chemical characteristics of the investigated solutions containing BPA

Type of solutions	рН <sup>а</sup>	Conductivity (mS/cm)	Absorbance in $UV_{254}$ (1/cm)	Total organic carbon (TOC, mg/L)
Deionised water Simulated effluent	7.0	0.005 0.793 0.985	0.000 0.055 0.218	0.00 24.41 33.01

<sup>a</sup>Correction of solution pH was made using of 0.1 mol/L HCl or 0.2 mol/L NaOH.

 $r = k \cdot c \tag{1}$ 

where k—reaction rate constant, c—BPA concentration.

Taking into consideration a proper mixture of the investigated substance, it can be assumed that:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -kc \tag{2}$$

After division of variables and the integration of the equation, the following dependency is obtained:

$$\ln c = k \cdot t + \ln a \tag{3}$$

At the same time, the disappearance of substrates in this process can be described by the exponential function:

$$c = a \cdot e^{-kt} \tag{4}$$

# 2.5. Analytical procedures

# 2.5.1. HPLC (UV) analysis

BPA determination was conducted using the following methodology:

- (1) compound separation from the solution by means of a SPE,
- (2) elution of analyte by a mixture of acetonitrile and methanol (40/60, v/v),
- (3) a quantitative–qualitative analysis of the compound by HPLC (UV) technique.

In order to enable the identification analysed by HPLC water samples of a volume 100 mL (pH 7), the investigated compound was separated through SPE. Before separation, the stationary phase was conditioned with acetonitrile (5 mL) and methanol (5 mL), and then rinsed with deionised water (5 mL). The separated compounds were eluted with a mixture of acetonitrile and methanol (40/60, v/v) of volume 1 mL. Further on, the extract was dried with a faint stream of nitrogen, and then dissolved in 100  $\mu$ L of methanol and underwent a chromatographic analysis.

For the above identifications an HLPC unit by Varian with the UV detector (wavelength  $\lambda = 220$  nm) equipped with Hypersil GOLD column by Thermo Scientific, of 25 cm length, diameter 4.6 mm, particle size 5 µm was applied. A mobile phase consisted of a

mixture of acetonitrile/water with ratios 85:15 (v/v). Sample injections were performed manually with a microsyringe of  $50 \mu$ L by Hamilton.

# 2.5.2. GC-MS (EI) analysis

In the case of solutions with increased concentration of high-molecular weight organic substances (real effluent), which hindered the chromatographic measurement, the GC–MS analysis was incorporated.

The identification of the investigated pollutant was performed applying the following methodology:

- (1) separation of BPA form the solution through SPE,
- (2) elution of analyte by a mixture of acetonitrile and methanol (40/60, v/v),
- (3) derivatisation of the investigated compound to a trimethylsilyl derivative,
- (4) a quantitative–qualitative analysis of a BPA derivative by GC–MS (EI) technique.

The procedure of SPE of BPA from water before its determination by GC–MS was conducted similarly to the analytical procedure using HPLC (UV) technique. Without doubt, the inclusion of the derivatisation process was an essential preparatory measure. Hence, the extracts obtained after the sample drying with a faint stream of nitrogen underwent the process of derivation with a silylating reagent MSTFA (volume 30  $\mu$ L). After a 30 min reaction time at the temperature of 55°C, the obtained trimethylsilil derivative of the investigated compound was analysed chromatographically. In a simple way, the reaction of generating the trimethylsilil derivative of BPA was conducted in accordance with the scheme introduced in Fig. 1.

These identifications were conducted with the use of a gas chromatograph coupled with a mass detector (GC–MS) with electron ionisation EI-type Saturn 2100 T by Varian. The extract was divided in the column SLB<sup>TM-5</sup> ms by Supelco, dimensions 30 m × 0.25 mm × 0.25 µm, using the temperature of the column oven program 80°C (1 min), 20°C/min till 300°C (3.5 min). The remaining temperature parameters were as follows: injector 300°C, ion trap 180°C, ion source 290°C. Helium constituted a mobile phase (flow 1.4 mL/min). Sample injections (volume 1–3 µL) were performed manually with a microsyringe volume 10 µL by Hamilton. The mass detector was working in the ion record mode from 70 to 400 m/z.

The recovery of BPA for both methods exceeded 66%. The value of this parameter in the slightest degree depended on the physical and chemical

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Fig. 1. The reaction scheme of BPA derivatisation.

composition of the investigated solutions. The limit of the compound detection depended on the analytical method, in the case of HPLC (UV) it reached  $0.3 \mu g/L$  and for GC–MS (EI) 20 ng/L.

# 2.5.3. Analysis of selected wastewater pollutant indicators

The physical and chemical characteristics of the solutions before and after the treatment processes were determined on the basis of the following measurements:

- (1) general parameters describing the properties of the investigated water, i.e. pH and temperature;
- (2) parameters connected with the presence of organic substances in water (absorbance in UV<sub>254</sub> and total organic carbon (TOC));
- (3) parameters connected with the presence of inorganic substances (conductivity).

Laboratory pH-meter CP-505 by Elmetron was incorporated to measure general parameters and conductivity. Absorbance was measured by 240 nm wavelength by means of UV VIS Cecil 1000 by Jena AG, whereas the concentration of the TOC was determined by HiPerToc analyser by Thermo Electron.

# 3. Results

# 3.1. Ozonation process

Fig. 2 shows the interdependence between the ozone dosage and a decrease in BPA concentration for three different solutions, i.e. deionised water, both simulated and real effluents after a biological treatment. A BPA concentration decreased with an increase in ozone dosage. This interdependence was noticed for all above-mentioned types of solutions. In the case of deionised water and the oxidiser dosage of  $1 \text{ mg O}_3/\text{L}$ , a decomposition of the compound reached approximately 40%. On the other hand, for the simulated effluent and the real effluent, decomposition reached 8–15%, respectively. Moreover, when the ozone dosage was increased five times (5 mg O<sub>3</sub>/L), the compound decomposition for deionised water reached



Fig. 2. The influence of ozone dosage on the decrease of BPA concentration in the ozonation process of the investigated solutions.

approximately 70%, whereas for the real effluent approximately 43%. In the case of the simulated effluent, a minor decrease in BPA concentration was noticed for the dosage of  $1 \text{ mg O}_3/\text{L}$ . The highest level of BPA decomposition was reported for the dosage of  $10 \text{ mg O}_3/\text{L}$ . For the real effluent it reached over 90%.

Ternes et al. [18] and Huber et al. [19] reported that application of ozone dosages from 5 to  $10 \text{ mg O}_3/\text{L}$ made it possible to decompose majority of organic micropollutants in wastewater from 90 to 99%, which is confirmed by the results obtained in this research. On the basis of these results it can be also deduced that the efficiency of the ozonation process is to a large extent subject to the physical and chemical composition of the treated solution (Table 1). These results are also confirmed by the studies of Beltran [20] and Gottschalk et al. [12]. In the case of the simulated effluent, the removal of BPA was the lowest and amounted from approximately 5% for the oxidant dosage of  $1 \text{ mg O}_3/\text{L}$  to approximately 30% for the dosage of  $10 \text{ mg O}_3/\text{L}$ . Therefore, higher ozone dosages were applied in the next phase of the study (Fig. 3), i.e. 15 and  $20 \text{ mg } O_3/L$ , respectively. In the case of the dosage of  $20 \text{ mg O}_3/\text{L}$ , the BPA concentration decreased to approximately 43%. A similar level of the investigated compound decomposition was obtained for deionised



Fig. 3. The influence of the ozone dosage on BPA decomposition in the simulated effluent ozonation process.

water with 20 times lower ozone dosage, whereas for the real effluent with four times lower reagent dosage.

# 3.2. Photolysis

In the photolysis process along with the increased water radiation time, the BPA concentration decreased for all of the three investigated solutions (Fig. 4). The highest concentration decrease was observed at the initial radiation time, in the ranges 0–10 min. Moreover, despite further illumination of the two solutions the investigated compound concentration both for deionised water and the simulated effluent

was maintained at a similar level (for deionised water approximately 60%, for simulated effluent about 85%). On the other hand, after 20 min illumination time, the BPA concentration for the real effluent decreased to approximately 95% and after 30 min to more than 98%. The observed higher degree of BPA decomposition for the real effluent in comparison to deionised water and the simulated effluent was also observed by Neamtu and Frimmel [9]. These authors presumed that this phenomenon could be a result of chemical substances, which are present in wastewater after a biological treatment, and exhibit activity similar to photosensitisers. These compounds possess the ability to capture electromagnetic radiation energy and return it to other substances that take part in photochemical reactions.

# 3.3. The combination of photolysis and ozonation

In the third stage of the study after the initial radiation time (10 min), ozone was introduced to a reactor (dosage of  $3 \text{ mg O}_3/\text{L}$ ). The results of this process are shown in Fig. 5. The delayed introduction of ozone to the reactor was performed to enable the comparison of efficiency of a separate photolysis process with combined processes of photolysis and ozonation. As a consequence, after 20 min of this experiment it was observed that the degree of decrease in BPA concentration raised for deionised water and the real effluent to 75 and 98%, respectively. On the other hand, for the simulated effluent, the investigated compound concentration was maintained at a similar level of approximately 64%. These results prove that the combined



Fig. 4. The influence of radiation time on a decrease in BPA concentration in the photolysis of the investigated solutions.



Fig. 5. The influence of the radiation time on BPA decomposition in a combined process of photolysis and ozonation of the investigated solutions.

process of photolysis and ozonation make it possible to reach a higher level of BPA elimination when compared to the level observed for a separate process of photolysis (Fig. 4) for deionised water and the real effluent. Most of the studies described in the literature with regard to the application of AOPs proved higher efficiency level for the combined UV/O<sub>3</sub> processes than for other processes performed separately, i.e. either photolysis or ozonation [21-24]. However, the investigations conducted e.g. by Esplugas et al. [8] are contrary to the above-mentioned opinion since the synergistic effect of different oxidation processes was not observed in that study. These authors claimed that none of the combination oxidation processes applied by them  $(O_3/H_2O_2, UV/O_3 \text{ and } O_3/UV/H_2O_2)$ increased the degradation rate of phenol. Thus, the efficiency of any process is subject to many factors, such as pH, composition of the investigated solutions, or the physical and chemical characteristics of the reagent itself [12].

In the studies of the kinetics of the combined process of UV/O<sub>3</sub>, further experiments were conducted in such a way as to apply ozone before simulated effluent radiation. This way of conduct was the most common in similar research papers. Ozone dosages were applied from 3 to 20 mg O<sub>3</sub>/L. Fig. 6 shows the dependence of BPA concentration on time for the ozone dosage 15 mg O<sub>3</sub>/L and the radiation time of 30 min.

For the investigated cases related to the BPA decomposition from the simulated effluent in the combined process  $UV/O_3$ , the equations of the regression function adjusted to the measuring points are presented in Table 2.



Fig. 6. The decrease of BPA concentration in a cumulative process (ozone dosage of  $15 \text{ mg O}_3/\text{L}$ ).

In all the investigated cases the coefficient of determination  $R^2$  exceeded 0.82, which proves that the measuring points were properly adjusted to the model. In the next stage, a half-life of the investigated compound was determined. The half-life of the BPA decreased along with an increase in the ozone dosage in the combined processes of UV/O<sub>3</sub>. For example, the increase in the ozone dosage of five times resulted in half-life shortening nearly twice (Table 2).

On the other hand, the values of first-order reaction rate constants of BPA were determined by means of a graphic method, i.e. by drawing a linear relationship ln ( $C_0/C$ ) in the time function (Fig. 7). In Table 3, the established values for BPA decomposition reaction rate constants in a combined process UV/O<sub>3</sub> were juxtaposed and they were presented in L/mol s for both simulated and real effluents.

The obtained results have proved that the reaction rate of BPA decomposition increases with an increase in the ozone dosage in a combined process UV/O<sub>3</sub>. On the basis of the literature data [25], the values of reaction rate constants for ozone with organic substances range from 0.1 to approximately  $7 \times 10^5$  L/mol s. The data gathered for the cumulative process can also be included in these ranges. However, it must be highlighted that the values of reaction rate constants are dependant on the pH and the physical and chemical composition of the solution and the conditions of the process conduct. For example, Ning et al. in [26] estimated that the reaction rate constant for nonylphenol (a compound used as a substrate for the synthesis of polyethoxylates surface active agents, motor oils etc. [27]), in an ozonation process performed in an acidic solution (pH 2) reached  $3.90 \times 10^4 \text{ L/mol s}$ , whereas for a neutral pH (pH 7.3) reached by firstorder of magnitude for  $1.09 \times 10^5 \text{ L/mol s}$ . On the other hand, in this investigation a significantly higher reaction rate was reported for the real effluent, which compared to the simulated effluent differed by means of the physical and chemical characteristics, and first and foremost the concentration of high molecular weight organic substances determined by the absorbance measurement in UV<sub>254</sub> (Table 1). This phenomenon was explained in the previous parts of this paper. On the basis of the obtained data it can be deduced that BPA is relatively prone to decomposition under the influence of ozone and electromagnetic radiation, which was applied in a cumulative process.

The efficiency of high-molecular weight organic compounds determined by the absorbance measurement in  $UV_{254}$  was also subject to the type of the treated effluent. For example, for the oxidiser dosage of 3 mg O<sub>3</sub>/L and radiation time of 10 min, the values of this parameter in the combined  $UV/O_3$  process

Table 2

Ozone dosage $(mg O_3/L)$	Exponential function equation	Coefficient of determination $R^2$	Half-life of the compound (min)
3	$y = 0.0014 e^{-0.075t}$	0.88	3.27
5	$y = 0.0013 e^{-0.073t}$	0.86	2.35
10	$y = 0.0013 e^{-0.076t}$	0.83	2.25
15	$y = 0.0013 e^{-0.090t}$	0.90	1.91
20	$y = 0.0010e^{-0.094t}$	0.82	0.97

Equations of the regression function adjusted to the measuring points determining a decrease in BPA concentration in time in the  $UV/O_3$  process for the simulated effluent



Fig. 7. Graphic representation of first-order reaction rate constants of BPA decomposition in a combined process  $UV/O_3$  for the simulated effluent (ozone dosage of 15 mg  $O_3/L$ ).

Table 3

Reaction rate constants of BPA decomposition in a combined process for the simulated and the real effluents

Simulated effluent				
Ozone dosage $(mg O_3/L)$	Reaction rate constant (L/mol s)			
3	$2.857 \times 10^{5}$			
5	$2.861 \times 10^{5}$			
10	$2.888 \times 10^{5}$			
15	$3.398 \times 10^{5}$			
20	$3.565 \times 10^{5}$			
Real effluent				
3	$6.008  imes 10^5$			

reached approximately 45% for the simulated effluent and 26% for the real effluent. An increase in the elimination efficiency of the high-molecular weight organic compounds was observed when the radiation time of the solution was increased. It was also determined that the elimination efficiency of the high-molecular weight organic compounds was significantly lower than in the case of low-molecular weight BPA. This phenomenon is frequently observed and is caused by different sensibility to the decomposition process among substances of different physical and chemical properties.

# 4. Conclusions

On the basis of the investigations on the BPA elimination in the oxidation processes it was proved that the cumulative application of photolysis and ozonation is more profitable than applying these processes separately.

The BPA decomposition during the real effluent treatment in the combined UV/O3 process exceeded 90%. For a separate photolysis process, a long radiation rate was necessary to obtain high efficiency of BPA decomposition. On the other hand, in the ozonation process a decrease in the investigated compound concentration was subject to the oxidising agent dosage. The efficiency of BPA elimination in the investigated processes was also subject to the physical and chemical composition of the treated solution. The degree of BPA decomposition was higher in the case of the real effluent (with the highest concentration of pollutants) rather than for the solutions of deionised water and the simulated effluent. It is probably connected with the presence of photosensitisers in the real effluent, which facilitates BPA decomposition. The obtained results in this aspect require further investigation in order to identify substances that facilitate/ inhibit micropollutants oxidation. On the other hand, the elimination degree of high-molecular weight organic compounds (determined through absorbance measurement in UV<sub>254</sub>) was significantly lower than for low-molecular weight BPA.

The application of the first-order reaction model to describe the combined process of  $UV/O_3$  made it possible to identify reaction rate constants for BPA decomposition. The identification of this parameter was highly dependent on the ozone dosage.

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