

The impact of 3,3',5,5'-tetrabromobisphenol-A (TBBPA) solution pretreatment by ozonolysis and photocatalysis on the activated sludge respirometric activity

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ABSTRACT

Tetrabromobisphenol-A (TBBPA) is a flame retardant widely used in the production of plastics, textiles, electronics, or electrical equipment. This compound was identified in environmental samples and the sewage sludge, thus its impact on biological processes in wastewater treatment plants is interesting. This work investigates the impact of advanced oxidation processes pretreatment of TBBPA and bisphenol-A (BPA) solutions on its toxicity to activated sludge. The highest efficiency of these micro-pollutants' removals (expressed by chemical oxygen demand), was observed for ozonolysis of BPA (32.3%), and the lowest for photocatalysis on micro-Fe₃O₄ (TBBPA – 32.8%; BPA – 17.3%). The concentration of biodegradable compounds increased the most after a photocatalysis on the micro-Fe₃O₄ (184% for TBBPA and 62.5% for BPA) and quite less for ozonolysis (71.8% and 50.3% respectively). The influence of the catalyst particle size on the photocatalytic pretreatment efficiency was determined based on the biological oxygen demand value measurements. It was found that all analyzed solutions had an adverse (toxic) effect on activated sludge respirometric activity.

Keywords: Tetrabromobisphenol-A (TBBPA); Bisphenol-A (BPA); Advanced oxidation processes (AOPs); Activated sludge; Oxygen uptake rate (OUR)

1. Introduction

The tetrabromobisphenol-A (TBBPA) is being one the major environmental pollutants, belonging to the category of POPs, that is, organic compounds that resist photolytic, biological, and chemical degradation. TBBPA affects various aspects of mammals physiology, also the human [1] – it is an endocrine system disruptor and shows other negative

effects inducing cytotoxicity, hepatotoxicity, nephrotoxicity and neurotoxicity.

TBBPA and its derivatives are considered as an alternative to some persistent and toxic brominated flame retardants, such as deca-BDEs and HBCD [2]. This compound combines a tendency to bioaccumulation and bioconcentration ($\log K_{ow} > 3$, BCF > 5000) together with potential toxic properties [3].

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Because of its intensive use as a flame retardant widely applied in the manufacturing of paper, textiles, plastics, electronics, and upholstered furniture and high persistency, TBBPA can be found in various environmental matrices: water, sediments, and various organisms [4–12]. TBBPA has the highest production volume out of all BFRs in the world, and its market size is forecasted to reach \$ 3.5 billion by 2025 [13]. As this compound was identified both in environmental samples and the sewage sludge (Table 1), thus the scale of its impact on biological processes in wastewater treatment plants (WWTPs) must be considered.

Under natural conditions, the degradation of TBBPA seems to be problematic. Water and soil contamination removal techniques usually require complex procedures, whereas thermal treatment is a classic approach to TBBPA decomposition [14]. One of the major drawbacks of TBBPA combustion or pyrolysis relies on highly toxic PBDDs and PBDFs [15]. In contrast, the ozonolysis or photocatalysis has been considered as a promising technique for TBBPA degradation, free from above-mentioned derivatives. Ozonolysis leads to the almost complete removal of bromine from TBBPA and the formation of bisphenol-A (BPA). This process may occur directly in the atmosphere and water solutions [16]. Unfortunately, formation of BPA during the process is a serious disadvantage. The BPA is a genuine threat to living species not only due to the estrogenic activity and sperm count reduction but also such adverse effects as genotoxicity and carcinogenicity. Whereas the photocatalysis process causes the disruption of the TBBPA and formation of small molecule compounds.

The activated sludge process is one of the most common biological wastewater treatment method; however, it is not designed specifically to remove or degrade xenobiotic organic chemicals and micropollutants. Hence, the pre-treatment of wastewater containing such organic compounds by advanced oxidation processes seems to be promising in solving the problem of wastewater contaminated by POP's. Moreover, it is believed that the combination of advanced oxidation processes (AOPs) with biological processes is practically feasible and economically viable

for wastewater treatment. Although the activated sludge is usually used for municipal wastewater treatment, the occasional presence of residual wastewater originating from industrial activities in influents of MWWTPs is also very common. However, this could create several operational problems, especially in the biological stage of the treatment. The admixture of selected chemical compounds present in industrial wastewater could have an inhibitory effect on activated sludge, manifested in the reduction of removal efficiency of organic matter or nitrogen [17]. The oxygen uptake rate is one of the most important indicators for controlling the activated sludge activity. The oxygen uptake rate (OUR) assay conducted according to standard methods reflects changes in the availability, concentration, and composition of carbon sources, but may be also used as a toxicology test [18].

The main routes for decompose toxic compounds in natural surface water involves biodegradation and photodegradation. Photodegradation is an important mechanism for the decomposition of aromatic hydrocarbons, chlorinated aromatic hydrocarbons, chlorinated phenols, and many pesticides [19] Biological degradation refers to the elimination of the pollutant by the metabolic activity of living organisms, usually microorganisms and in particular bacteria and fungi that occur in the environment [20]. The compounds discussed in the study are classified as xenobiotics, having no analogs in the environment, hence conventional biological processes do not always provide satisfactory results. Therefore, the only possible solution to this problem seems to be the use of AOPs before the biological process. The chemical processes, especially advanced oxidation processes, can effectively break down some of the structurally complex organic compounds and bio-inhibitory compounds. AOPs are one of the favored techniques to remove refractory pollutants involving hydroxyl radicals [21], a powerful oxidant.

This work investigates the impact AOPs pretreated water solutions of TBBPA and BPA on the activated sludge respirometric activity with comparison to the effect of starting compounds solutions (not degraded). The water solution of

Table 1
Examples of TBBPA concentrations in environments

Medium	Location	TBBPA content ng/g (dry weight)	References
Soil	China, Shandong	7,758	[5]
Soil	Vietnam, Bui Dau	2,900	[6]
Soil	Israel	50,000	[7]
Water	England, County Durham, River Skerne	9,800	[8]
Water	Netherlands, unidentified river	130	[8]
Water	South Korea, Nakdong River	150	[9]
Water	USA, Detroit River	1,840	[10]
WWTPs sludge	China	259	[11]
WWTPs sludge	England	112	[8]
WWTPs sludge	Ireland, Cork	192	[8]
WWTPs sludge	Netherland	600	[8]
WWTPs sludge	Spain	472	[12]
WWTPs sludge	Canada/USA	2.98–196	[10]

BPA and TBBPA has been subjected to the ozonolysis and photocatalysis processes. The starting compounds (BPA, TBBPA) solutions and AOPs pretreated solutions were used as a substrate for activated sludge. The measurements of the activated sludge respirometric activity allowed the evaluation of the effectiveness of the solutions' pre-treatment methods.

2. Materials and methods

2.1. Chemical reagents and catalyst

3,3',5,5'-Tetrabromobisphenol-A (97%) was purchased from Alfa Aesar, bisphenol-A (>98%) from Sigma-Aldrich, and both forms of Fe₃O₄ catalyst from Sigma-Aldrich: magnetite micropowder (micro-Fe₃O₄), with declared by manufacturer particle size under 5 μm, $d = 4.8\text{--}5.1\text{ g cm}^{-3}$ and nanopowder (nano-Fe₃O₄), with declared particle size under 50 nm (derived from TEM), $d = 3.9\text{ g cm}^{-3}$, 98% trace metals basis.

2.2. Catalyst characterization

The crystal structure of the materials was studied using X-ray diffraction (XRD) (D8 Advance, BRUKER) with a graphite monochromator using CuKα radiation ($\lambda = 1.5406\text{ \AA}$), within 20–80 2θ. The catalyst morphology was observed using a SU-8010 scanning electron microscope (SEM) (Hitachi, Tokyo, Japan). The catalysts' optical properties were investigated using the Cary series UV-Vis-NIR spectrophotometer (Agilent Technology, MA, USA) in the range of 180–1,200 nm.

2.3. Degradation procedure

2.3.1. Photocatalytic degradation of bisphenols

An aqueous solution of bisphenol (TBBPA or BPA) (750 cm³, $2.0 \times 10^{-4}\text{ mol L}^{-1}$), with the pH adjusted to the value of 8 ± 0.1 using 0.1 mol L^{-1} NaOH solution, next 0.07% w/v of semiconductor-catalyst powder was dispersed. The suspension was stirred for 30 min in the dark. The photocatalytic degradation was performed using a Heraeus LRS2 photoreactor in open air conditions. The illumination was effected with the excimer lamp TQ150 (150 Watt, with forced water cooling down to 25°C, of ca. 47 Watt light energy flux integrated over the 200–600 nm range, and power density of $0.004696\text{ W cm}^{-2}$ measured by digital lux meter Peak Tech 5025, what gives light intensity ca. 7.88×10^{19} photons/s) operated by utilizing a vertically arranged immersion tube, submerged into the

continuously stirred reaction suspension. The photocatalytic reaction was performed up to 60 min.

2.3.2. Ozonolysis

The ozonolysis experiment was performed as follows: the reaction solution prepared as above, was constantly flushed with an ozone solution in the air. The reaction was developed using Viaken Vairo-2186 ozone generator. Ozone concentration in the solution phase was $12.73\text{ mg L}^{-1}\text{ h}^{-1}$ measured following the iodometric method [22].

2.3.3. Assessment of treatment products impact on respirometric activity of activated sludge

The concentration of organic compounds expressed as chemical oxygen demand (COD), biological oxygen demand (BOD₅) and total organic carbon (TOC) was determined in BPA and TBBPA solutions and post-reactions mixtures according to relevant standards [23–25]. The removal efficiency was calculated according to Eq. (1):

$$E = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

where C_0 – concentration of the pollution indicator in the initial solution (BPA, TBBPA) (mg L^{-1}); C_e – concentration of the pollution indicator in the solution after AOPs (mg L^{-1}).

The respirometric activity tests were carried out according to the standard procedure PN EN ISO 8192 [18] for assessing the AOPs pretreatment impact on subsequent biological treatment. Activated sludge, was taken from the municipal WWTP in Rzeszów (PE ≈ 200 k, II° nitrification tank). Immediately after delivery to the laboratory, the sludge was twice rinsed, what included: gentle mixing, sedimentation, decantation of supernatant and refilling with fresh tap water collected after 5 min of draining, then the sludge was aerated for 24 h. At the same time, a liquid nutrient solution was prepared with the composition of 100 fold concentrated synthetic wastewater according to OECD [26]. During the tests both the BPA and TBBPA solutions and AOPs treated solutions were added to the 1 L glass reactors previously topped up with activated sludge suspended to the final concentration of 3 g L^{-1} (by weighting method $105^\circ\text{C}/550^\circ\text{C}$) in water solution of standard medium, then mixed and aerated continuously for 30 min at constant temperature ($20^\circ\text{C} \pm 0.2^\circ\text{C}$). In the samples taken from each reactor the rates of dissolved oxygen concentration changes were measured (Elmetron) immediately and after 10 min without aeration. The measurement was repeated after the 140 min (which gives 180 min in total). Based on the obtained results the oxygen uptake rate (OUR) [$\text{mg L}^{-1}\text{ h}^{-1}$] was calculated according to Eq. (2):

$$\text{OUR} = \frac{\rho_1 - \rho_2}{\Delta t} \times 60 \quad (2)$$

where ρ_1 – the oxygen concentration at t_0 (mg L^{-1}); ρ_2 – the oxygen concentration at $t_{10\text{ min}}$ (mg L^{-1}); Δt – the time interval between measurements (min).

Table 2

Catalyst particle sizes declared and estimated by SEM measurement (Fig. 2)

Catalyst	Size declared (nm)	Size range by SEM (nm)
mikro-Fe ₃ O ₄	500	100–400
nano-Fe ₃ O ₄	50	25–100

Statistical analyzes were performed using the Kruskal-Wallis nonparametric test of multiple comparisons of the mean rank for all samples (assuming the significance level of $\alpha = 0.05$) (Statistica 13).

3. Results and discussion

The characterization of used catalysts was conducted by SEM, XRD, and UV-Vis analysis. Zeta potentials measurements was provided in earlier work [27]. The phase identification of magnetite structure was carried out by powder X-ray diffractometer (Fig. 1). XRD patterns showed that the diffraction peaks surrounding at $2\theta = 30.2^\circ, 35.3^\circ, 43.7^\circ, 53.9^\circ, 57.1^\circ,$ and 62.7° (Fig. 1) had good agreement with Fe_3O_4 (Reference code 01-089-3854); they belonged to the cubic structure system, corresponding to (220), (311), (400), (422), (511), and (440) facets of Fe_3O_4 [28].

The morphology of Fe_3O_4 catalysts is shown in Fig. 2. Images show agglomerates of nanocrystals, the particle size of the agglomerates was in the range of 100–400 nm (Fig. 2a, Table 2) for micro catalyst, and 25–100 nm (Fig. 2b, Table 2, nano- Fe_3O_4).

The absorption spectra in the range of 180–1,000 nm are similar for both catalysts (Fig. 3). Hence the higher degradation efficiency of nano catalyst was caused by surface properties.

The catalyst's adsorption capacity strongly depends on the specific surface area. The surface area of used catalysts was estimated in the paper by Kisala et al. [27] and was $30.80 \text{ m}^2 \text{ g}^{-1}$ for nano- Fe_3O_4 and $0.0245 \text{ m}^2 \text{ g}^{-1}$ for micro- Fe_3O_4 . As the nanocatalyst was characterized by a higher specific surface area, thus the adsorption of substrates on its surface is more likely. The environment in which particles were utilized essentially affected their surface composition. Magnetite surface in aqueous media possesses acid-base properties with the pK values 4.4 (pK_1) and 9.0 (pK_2) [29]. At acidic conditions Fe_3O_4 dissolves whereas, at $\text{pH} > 7$ the effect of hydrolysis is expected to be negligible [30].

Measurements of zeta potential of the catalysts surface at $\text{pH} = 8$ suggest deprotonation the surface hydroxyl ($\equiv\text{Fe(II,III)O}$; $\zeta = -0.37 \text{ V}$) for $\mu\text{-Fe}_3\text{O}_4$, whereas for $n\text{-Fe}_3\text{O}_4$ protonated surface species are dominant ($\equiv\text{Fe(II,III) OH}_2^+$; $\zeta = +14.4 \text{ V}$). TBBPA under reaction conditions also is negatively charged, so the positively charged surface of nano- Fe_3O_4 improves the degradation efficiency.

Advanced oxidation processes have received increasing attention in the research and development of wastewater treatment technologies in the last decades. These processes (e.g., cavitation, photocatalytic oxidation, Fenton's chemistry, ozonation) have been applied successfully for the complete removal of refractory pollutants, or used as a pre-treatment to convert them into a shorter-chain compounds that can be consequently treated by conventional or biological methods. Ozonation classified as a AOPs technique, was widely applied to treat wastewater containing such specific organic compounds as anti-inflammatory drugs, hormones or pesticides. The ozone promotes the production of large amounts of powerful oxidative species, that immediately oxidating target compounds. The rate of ozonation is additionally accelerated in alkaline media because hydroxide ion catalyzes the decomposition of ozone and produces hyperactive hydroxyl radical ($\cdot\text{OH}$). However, the assessment of ozonation efficiency in alkaline conditions is difficult because of reaction complexity caused by the competition between self-decomposition of ozone, reaction of the resultant hydroxyl radical with substrate, or reaction of ozone with free radicals produced during the ozonation [31].

TBBPA is a hydrophobic compound, and its solubility in aqueous solutions depends on pH. At pH above its pK_a ($\text{pK}_{a1} = 7.5, \text{pK}_{a2} = 8.5$) [32], TBBPA is soluble, which reduces the mass transfer resistance, and accelerating the reaction rate. The half-life of ozone in water ($\text{pH} = 7$) is very low (about 20 min [33]) thus the $\cdot\text{OH}$ radical dominate in the system as reaction intermediate.

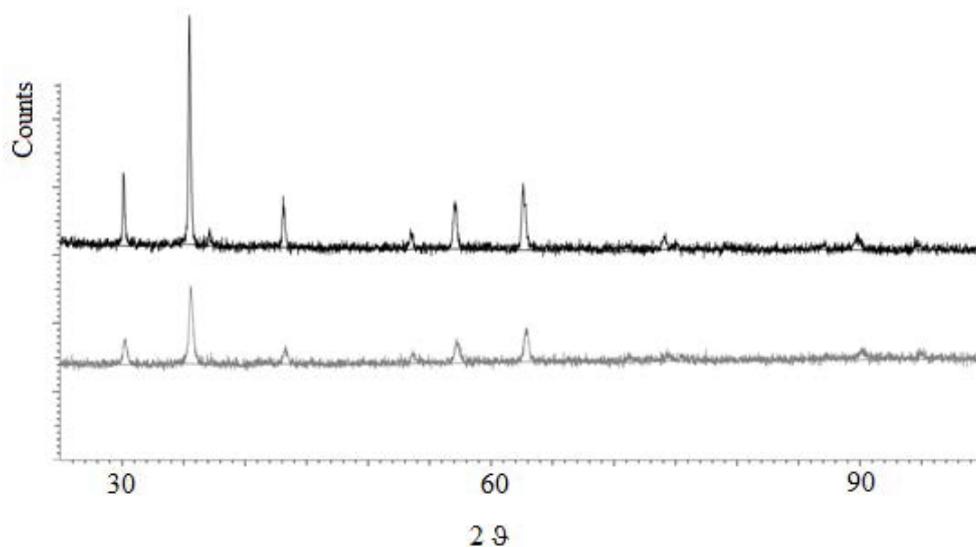
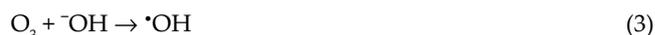


Fig. 1. X-ray diffraction measurements of micro- Fe_3O_4 (black), nano- Fe_3O_4 (gray).

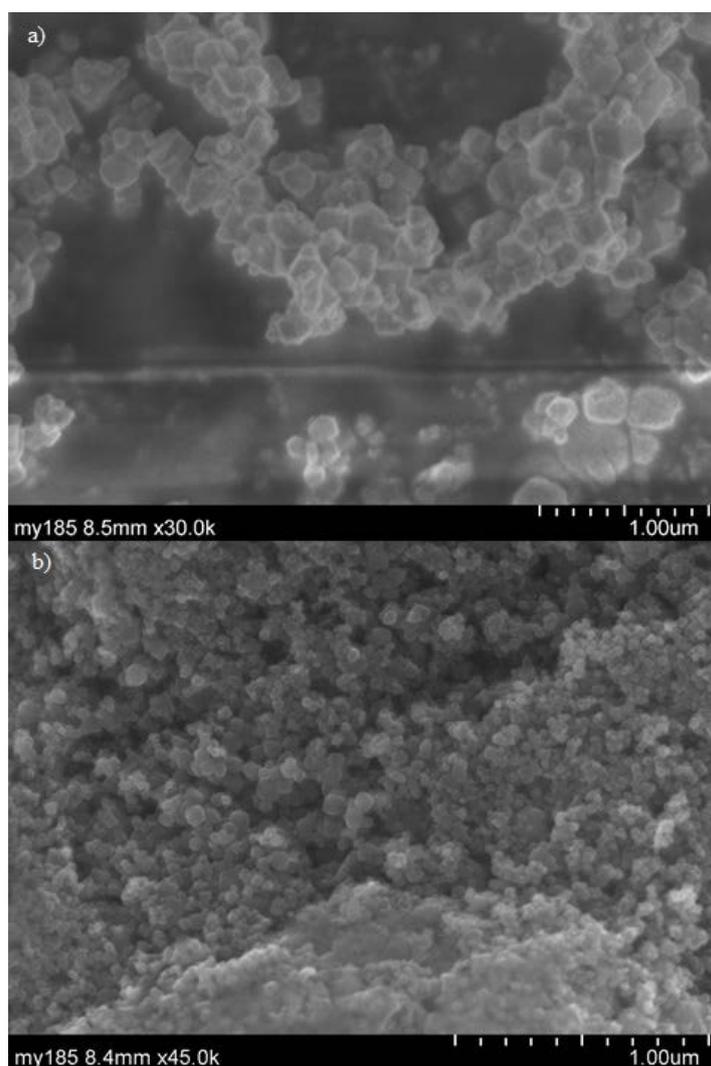


Fig. 2. SEM image of catalysts: (a) micro-Fe₃O₄ and (b) nano-Fe₃O₄.



Therefore, degradation of BPA occurred with $\cdot\text{OH}$ radicals, while molecular ozone can be ignored.

In this experiment, the pH value was chosen due to the hydrolytic stability of the catalyst. This issue was considered more widely in the paper by Kisala et al. [27]. The tested TBBPA concentration was higher than in the environment, but such a value was necessary to assess the yield of degradation. The intermediate products of BPA decomposition during photocatalytic degradation include p-isopropenylphenol, hydroquinone, 4-isopropenylphenol, glycolic acid acetate, tartaric acid, and formic acid [34,35]. Aliphatic acids as intermediates are formed by the further oxidation of quinone derivatives [36]. It is known that phenol is photocatalytically mineralized *via* the generation of quinone derivatives and organic acids as intermediates. Photocatalytic decomposition of BPA may produce similar intermediates. In this paper formation of a low molecular fraction has been observed during the photocatalytic

decomposition of BPA (summarized in Table 3) and its mineralization. However, the process efficiency was not satisfactory enough, when only 50% of substrate was converted after 60 min.

Direct photolysis of halogenated aromatic compounds in water proceeds *via* dehalogenation [37] although the subsequent reactions/rearrangements depend on the position of substituents. For BPA and TBBPA, the major primary photochemical reaction involves cleavage between one of the benzene rings and the isopropyl group. The TBBPA degradation mainly includes debromination, hydroxylation and demethylation by both oxidation and reduction processes [38]. The intermediate products of BPA/TBBPA decomposition during photocatalytic degradation include low molecular fraction formation and its subsequent mineralization. The exception is the TBBPA degradation process on Fe₃O₄-micro catalyst, where mainly the debromination process takes place (Table 3).

The concentration of organic compounds was determined as COD, BOD₅, and TOC for all analyzed solutions.

Table 3
Decomposition products of BPA and TBBPA arranged according to pre-treatment process

Substrate	Pretreatment process/designation	Post-reaction mixture composition	Degradation efficiency [%] ^a
BPA	Ozonolysis/BPAc	BPA low molecular fraction: phenol, quinones, carboxylic acids, ketones, aldehydes CO ₂ , H ₂ O	41
TBBPA	Ozonolysis/TBBPAc	TBBPA, BPA low molecular fraction: phenol, quinones, carboxylic acids, ketones, aldehydes CO ₂ , H ₂ O, Br ⁻	51
BPA	Photocatalytic micro-Fe ₃ O ₄ /TBBPAa	BPA low molecular fraction: phenol, quinones, carboxylic acids, ketones, aldehydes CO ₂ , H ₂ O	33
TBBPA	Photocatalytic micro-Fe ₃ O ₄ /TBBPAa	BPA CO ₂ , H ₂ O, Br ⁻	63
BPA	Photocatalytic nano-Fe ₃ O ₄ /BPAb	BPA low molecular fraction: phenol, quinones, carboxylic acids, ketones, aldehydes CO ₂ , H ₂ O	36
TBBPA	Photocatalytic nano-Fe ₃ O ₄ /TBBPAb	Aliphatic products: carboxylic acids, ketones, aldehydes CO ₂ , H ₂ O, Br ⁻	48

^aDegradation efficiency was calculated according to Eq. (2).

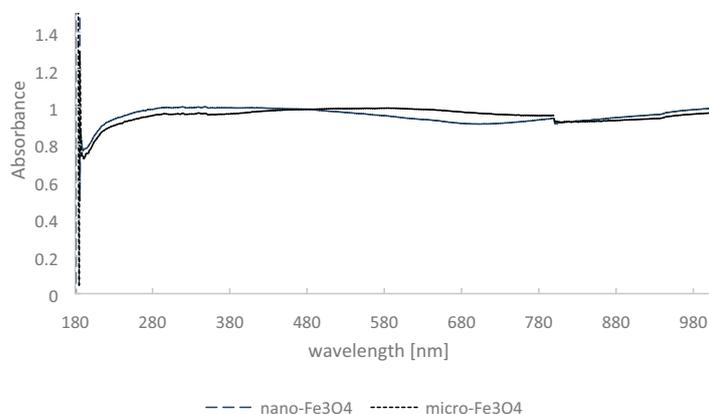


Fig. 3. UV-Vis spectra of nano- (dotted) and micro-Fe₃O₄ (dashed).

The COD values corresponds approximately to the amount of oxygen needed to oxidize carbon in organic compounds, nevertheless the presence of reduced inorganic compounds may also influence the result. The BOD₅ shows the amount of molecular oxygen consumed during 5 d for the degradation of organic compounds by microorganisms under normal conditions. These parameters are mainly used to test the contamination of drinking water or sewage by organic matter. The BOD₅ value and the dynamics of the biological process result from (i) the presence of compounds susceptible to microbiological degradation in the sample, (ii) the activity of microorganisms, (iii) the presence of compounds

inhibiting the growth of microorganisms and/or their biochemical activity in the system. The value of TOC directly relates to the carbon content of organic compounds.

In this work, we examined solutions containing only the starting substrates (TBBPA and BPA) and mixtures resulting from AOPs pretreatment (photocatalysis, ozonolysis).

The AOPs pretreatment resulted in a significant decrease in COD value in all experimental layouts. Simultaneously, the increase in BOD₅ was observed for all samples (Fig. 4). It can be explained by the formation during ozonolysis and photocatalysis processes the organic products that are accessible to biodegradation. The BOD₅ value for

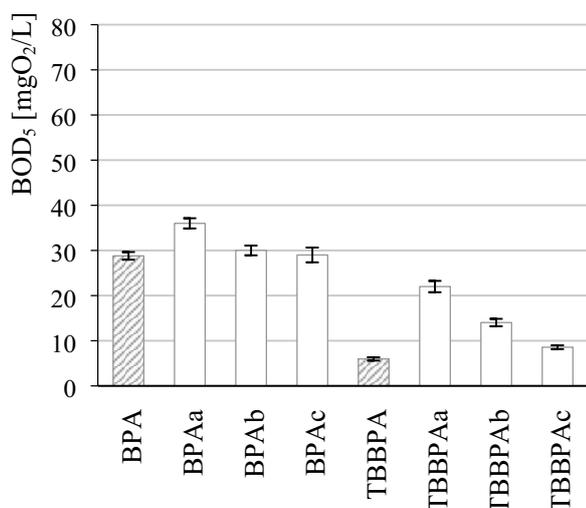


Fig. 4. Concentration of organic compounds in solutions of raw BPA and TBBPA (slashed bars) and products of AOPs treatment (a – photocatalysis on micro-Fe₃O₄, b – photocatalysis on nano-Fe₃O₄, c – ozonolysis) expressed as a biological oxygen demand (BOD₅).

the photocatalytic pretreatment on the micro catalyst was slightly lower than that of the starting BPA solution (Fig. 4). This may be due to the presence of bromide ions in the TBBPAa system. A significantly lower BOD₅ value for the TBBPA starting solution than for the BPA starting solution indicates a slower biodegradation of TBBPA and/or its inhibitory effect.

The efficiency (expressed as TOC value reduction) of pretreatment methods is relatively low. The best result was for photocatalytic TBBPA degradation on micro-Fe₃O₄ (TBBPAa; 63%). Ozonolysis of TBBPA (TBBPAC) had a 51% degradation efficiency, whereas the remaining processes were below 50%.

The efficiency of COD removal depended on the size of the catalyst, it was higher for nano-Fe₃O₄ than for micro-Fe₃O₄ (Fig. 5). The efficiency of removing easily degradable compounds was measured as the BOD₅ parameter. The value of the BOD₅ parameter for the BPA solution was higher than for TBBPA (28.8 and 5.97 mg L⁻¹, respectively). Pre-treatment of AOPs increased the concentration of easily decomposing organic substances and the efficiency of organic matter removal for TBBPA solutions.

The concentration of biodegradable compounds increased the most in case of photocatalysis on micro-Fe₃O₄ (62.5% for BPA and 184% for TBBPA), and significantly less after ozonolysis (50.3% for BPA and 71.8% for TBBPA). The effect of catalyst particle size on the efficiency of photocatalysis, measured as BOD₅, was also observed. The BOD₅ increase was less for nano catalyst than for a micro-size. The differences in the values of COD and BOD₅ for both BPA and TBBPA solutions and the pre-treated mixtures by the photocatalytic process on micro-Fe₃O₄ were statistically significant ($p = 0.013$). The BOD₅/COD ratio is often used as a measure of biodegradability. However, its value strongly depends on the type of tested wastewater

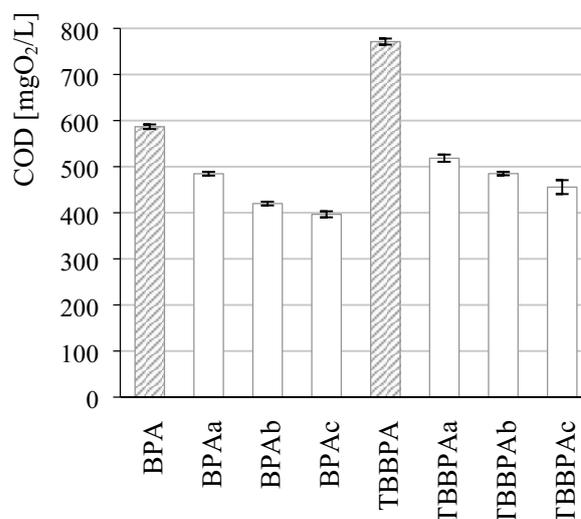


Fig. 5. Concentration of organic compounds in solutions of raw BPA and TBBPA (slashed bars) and products of AOPs treatment (a – photocatalysis on micro-Fe₃O₄, b – photocatalysis on nano-Fe₃O₄, c – ozonolysis) expressed as a chemical oxygen demand (COD).

(e.g., in municipal ones this ratio is high and usually amounts to ca. 0.7, in contrast old landfill leachate does not exceed 0.1). In these studies the BOD₅/COD ratio was at the level of 0.05 and 0.01, in the BPA and TBBPA solutions respectively. The biodegradability of the organics has increased, as expected, after pre-treatment (for BPA, up to 0.07 regardless of the AOPs system; and for TBBPA up to 0.04). The highest BOD₅/COD ratio of 0.04 was obtained for TBBPAa system (Fig. 6).

The COD values are usually in the range of 1.3–1.5 times the BOD₅ in the case of biodegradable organics. Our COD tests results are more than twice that of the BOD₅, so it could be concluded that a significant portion of the organic material in the samples was still refractory.

It was found that the initial value of TOC parameter was higher for TBBPA – 68.07 mg L⁻¹ (BPA – 59.4 mg L⁻¹). AOPs pre-treatment caused a decrease in TOC concentration for both analyzed compounds. However, the carbon oxidation efficiency for TBBPA was higher regardless of the AOPs method used. The TOC removal efficiency was comparable for each of the pretreatment methods (the lowest for photocatalysis on micro-Fe₃O₄ – 3.31%, and the highest for ozonolysis – 4.16% of BPA). The statistical analysis of the results showed significant differences between the pure substances and the sample after photocatalysis on micro Fe₃O₄ ($p = 0.013$). The catalyst's particle size used in photocatalysis influenced the TOC removal efficiency, for BPA the effect was better on nano-Fe₃O₄ and for TBBPA on micro-Fe₃O₄. TOC removal efficiency for TBBPA was the highest for photocatalysis on micro-Fe₃O₄ (63.2%), and the lowest for ozonation (50.7%) (Fig. 7). These differences may result from the course of the catalytic process. BPA will bond to nano-Fe₃O₄ surfaces more easily than to micro. However, the opposite effect is seen with TBBPA. It is related to the surface properties of the catalysts (zeta potential) and the pKa of organic

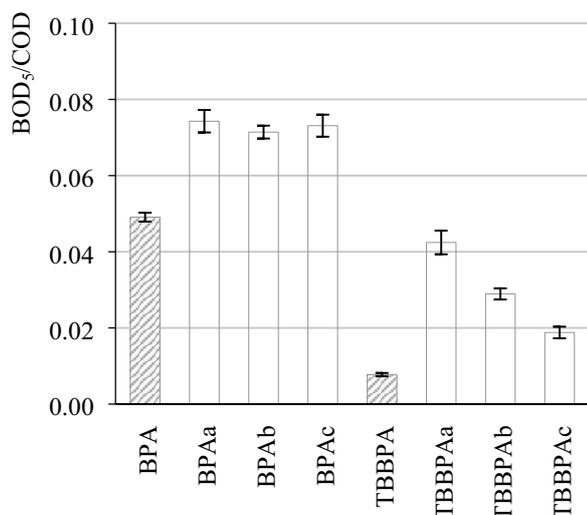


Fig. 6. Biodegradation potential as a ratio of BOD₅ to COD in starting solutions and products of AOPs (a – photocatalysis on micro-Fe₃O₄, b – photocatalysis on nano-Fe₃O₄, c – ozonolysis).

compounds. Moreover, BPA is more readily biodegradable than TBBPA (BOD₅ values).

The TOC/COD value determines the amount of oxygen that is needed to oxidize organic substances in relation to the carbon content in their chemical structure. Since the end product of the oxidation of carbon in organic compounds under aerobic conditions is a carbon dioxide molecule, the reference point for this ratio is value 2.66 (the ratio of the mass of oxygen to carbon in CO₂). The value of the TOC/COD ratio depends on the structure of organic compounds present in the solution, including the oxygen content in a molecule. Theoretically, the O/C values in a molecule should vary from 0.5 for carbon dioxide to 0 for hydrocarbons. Eq. (3) [39] describes the TOC/COD value depending on the atomic ratio O/C:

$$\frac{\text{TOC}}{\text{COD}} = \frac{1}{2\left(2 - \frac{O}{C}\right)} \quad (5)$$

In the present work, the TOC/COD ratios for BPA and TBBPA were similar and amounted to 0.1 and 0.09, respectively. After the AOPs pretreatment, this proportion decreased the most for the photolysis process on micro-Fe₃O₄ (BPA – 0.08; TBBPA – 0.05). The photocatalysis on the nano-Fe₃O₄ and ozonolysis processes resulted in a reduction of the TOC/COD ratio to 0.09 for BPA and 0.07 for TBBPA (Fig. 8). This could mean that subjecting BPA and TBBPA to AOPs increases oxygen demand.

TOC/COD ratio is a function of the oxidation state of carbon in the compound. The lower is the oxidation state, the lower is the TOC/COD ratio. Hence, the photocatalysis on micro-Fe₃O₄ caused rise of more oxidized compounds for both BPA and TBBPA. The formation of more oxidized compounds results in their easier biodegradation, which can be observed as the BOD₅ values (the BPAa and TBBPAa systems, Fig. 4).

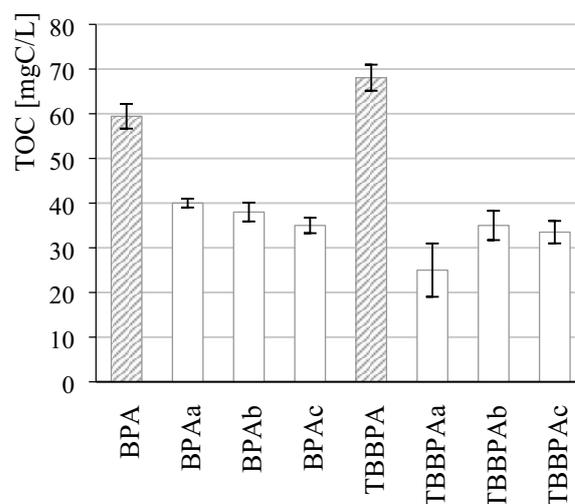


Fig. 7. Concentration of organic compounds in solutions of raw BPA and TBBPA (shaded bars) and products of AOPs treatment (a – photocatalysis on micro-Fe₃O₄, b – photocatalysis on nano-Fe₃O₄, c – ozonolysis) expressed as a total organic carbon.

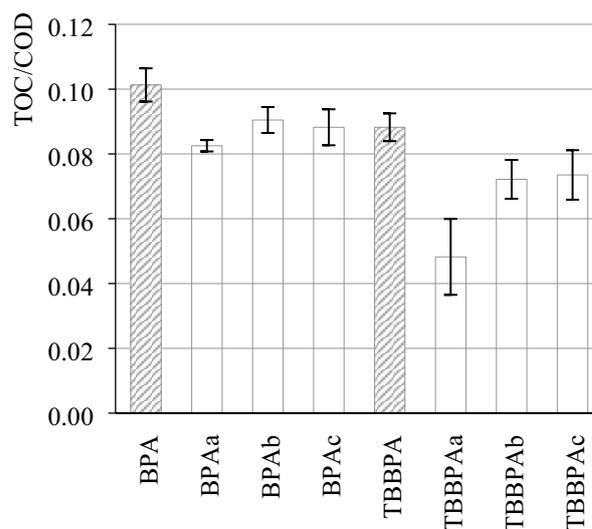


Fig. 8. Biodegradation potential as a TOC/COD ratio in starting solutions and products of AOPs (a – photocatalysis on micro-Fe₃O₄, b – photocatalysis on nano-Fe₃O₄, c – ozonolysis).

The process of aerobic biodegradation of organic matter could be determined by measuring the rate of oxygen uptake by microorganisms [40]. OUR tests are useful tool to evaluate biological process performance [41,42]. There are two components of OUR: exogenous and endogenous respiration. In the exogenous phase, the microorganisms use the supplied substrate, which comprises the medium and the test substance, while in the endogenous phase, the organic matter in the activated sludge itself is consumed [17]. Oxygen demand values obtained in respirometric tests represents a direct measure of the activity of microorganisms present in aerobic activated sludge. Furthermore, since

respiration of the activated sludge is inhibited in the presence of toxicants, it can be used as an efficient tool for the measurement of acute toxicity on microbial population of biological WWTP sludge [43,44].

The OUR measurement was performed after 30 and 180 min to of activated sludge exposition for the mixtures. It was found that all analyzed solutions had an adverse (toxic) effect on activated sludge. The TBBPA solutions (basic, and after pre-treatment) caused the higher decrease in respiratory activity than BPA solutions (Fig. 9).

AOPs pretreatment of solutions resulted in a significant increase in respirometric activity compared to the raw bisphenols solutions. The products of photocatalytic degradation on micro- Fe_3O_4 are characterized by the lowest negative impact. Statistical analysis showed significant differences in OUR between the pure substances and the samples after photocatalysis in the presence of micro- Fe_3O_4 ($p = 0.013$). The decrease in oxygen consumption after 180 min of aeration informs about the progress of organics consumption. At $\text{OUR} < 9.0 \text{ mg O}_2 \text{ L}^{-1} \text{ h}^{-1}$, the microorganisms are believed to enter the endogenous respiration phase, indicating that all (or most) of the organic substances present in the solution are consumed by vital processes. AOPs pretreatment of TBBPA solutions resulted in OUR lower than $9 \text{ mg O}_2 \text{ L}^{-1} \text{ h}^{-1}$ after both 30 and 180 min. It may indicate the immediate consumption of substrates by microorganisms and the negative (toxic) effect of the analyzed compounds on microorganisms. The pre-treatment methods only slightly improved the bioavailability of the solutions.

Ricco et al. [45] studied the toxicity of four xenobiotic compounds using the simple respirometric procedure and Microtox assay. A comparison of the EC_{50} data obtained by the two methods showed very good agreement. The authors demonstrated that the OUR could be useful for toxicity detection. Although the Microtox assay is more sensitive than the OUR test, it can be used to estimate the acute toxicity effect on activated sludge.

The BOD_5/COD ratios that valued from 0.1 (TBBPA) to 0.04 (TBBPA solution after photocatalytic decomposition

on micro- Fe_3O_4), testify the low bioavailability of the analyzed organic matter, which leads to considering the toxic effects of these solutions. This has been found in research of Ko et al. [46] and Le Bonté et al. [47]. They showed that toxic wastewater causes an instant drop of OUR below the value of endogenous respiration, which shows inhibition of microorganism activity or even sanitization effect. The respiratory activity of the activated sludge in the presence of pre-treated BPA solutions initially decreases compared to the reference sample (activated sludge with a nutrient solution only, $\text{OUR}_{30} = 17.95 \text{ mg O}_2 \text{ L}^{-1}$, $\text{OUR}_{180} = 47.34 \text{ mg O}_2 \text{ L}^{-1}$). On the other hand, the BPA degradation products showed no negative effects. It is supported by BOD_5/COD ratio value. OUR is proportional to the microorganism concentration and depends on the quality of the incoming wastewater. Thus, this parameter is very suitable for monitoring and control of the activated sludge system.

4. Conclusions

The tetrabromobisphenol-A is considered being one of the major environmental pollutants, belonging to the category of Persistent Organic Pollutants. However, POPs transformation products could have a serve impact on the ecosystem and human health. Using AOPs as a pre-treatment method, the highest efficiency of micropollutants removal, expressed as TOC removal efficiency was observed for pre-treated TBBPA solutions (48%–62%). This indicates the tested pre-treatment methods are more suitable for TBBPA degradation than BPA. The values of BOD_5 showed the formation in AOPs compounds assessable to biodegradation. BPA solution and pre-treated solutions are easier biodegradable than TBBPA solutions. The biodegradable substance concentration is assessed with the pre-treatment method. It significantly increased after photocatalysis on micro- Fe_3O_4 (for BPA up to 62.5% and up to 184% for TBBPA), and quite less for ozonolysis (50.3% and 71.8%, respectively). The impact of the catalyst grain size was also noticed by the BOD_5 increase (for nano-catalyst this increase was lower than for micro-catalyst). The difference between the COD and BOD_5

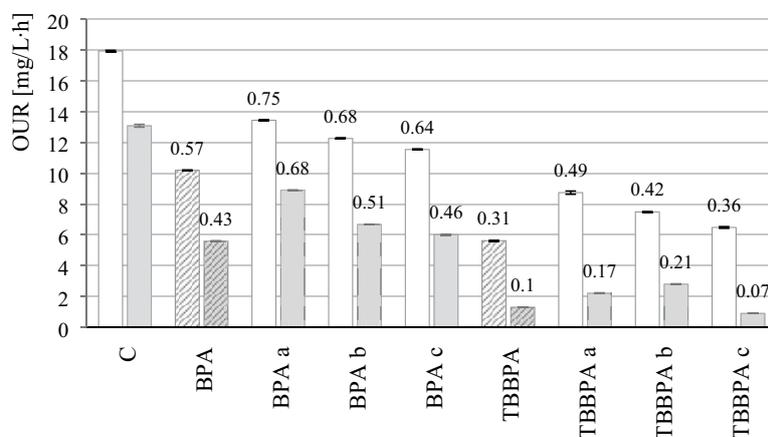


Fig. 9. Respirometric activity of activated sludge in control samples (C) and samples exposed to raw BPA or TBBPA (slashed bars) and products of their treatment (a – ozonolysis, b – photocatalysis with micro- Fe_3O_4 and c – photocatalysis nano- Fe_3O_4) expressed as an oxygen uptake rate (OUR) measured after 30 (white bars) and 180 min (grey bars). Whiskers indicate the standard deviation, labels – relative change to the control samples.

values for pure substances and pre-treated solutions in the presence of micro-Fe₃O₄ was statistically significant for both BPA and TBBPA. Oxygen uptake rate tests are a simple tool for tracking the activity of microorganisms responsible for removal of organic pollutants from wastewater. This test may be used as an acute toxicity estimation. It was found that all analyzed solutions had an adverse (toxic) effect on activated sludge, although TBBPA and products of its AOPs pretreatment were more toxic than BPA and its degradation products. The pre-treatment improved biodegradability of all samples.

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Symbols and abbreviations

C_0	–	Concentration of the pollution indicator in the initial solution (BPA, TBBPA), mg L ⁻¹
C_e	–	Concentration of the pollution indicator in the solution after AOPs, mg L ⁻¹
ρ_1	–	Oxygen concentration at t_0 , mg L ⁻¹
ρ_2	–	Oxygen concentration at $t_{10 \text{ min}}$, mg L ⁻¹
Δt_i	–	Time interval between measurements, min
AOPs	–	Advanced oxidation processes
BPA	–	4,4'-isopropylidenebisphenol, bisphenol-A
BFRs	–	Brominated flame retardants
BOD	–	Biological oxygen demand
COD	–	Chemical oxygen demand
Deca-BDEs	–	Decabromodiphenyl esters
HBCD	–	Hexabromocyclodecane
MWWTPs	–	Municipal wastewater treatment plants
OUR	–	Oxygen uptake rate
PBDDs	–	Polybrominated dibenzo-p-dioxins
PBDFs	–	Polybrominated dibenzofurans
POPs	–	Persistent organic pollutants
SEM	–	Scanning electron microscopy
TBBPA	–	4,4'-isopropylidenebis(2,6-dibromophenol), 3,3',5,5'-tetrabromobisphenol A
TOC	–	Total organic carbon
WWTPs	–	Wastewater treatment plants
XRD	–	X-ray diffractometry

References

- [1] T. Colnot, S. Kacew, W. Dekant, Mammalian toxicology and human exposures to the flame retardant 2,2',6,6'-tetrabromo-4,4'-isopropylidenediphenol (TBBPA): implications for risk assessment, *Arch. Toxicol.*, 88 (2014) 553–573.
- [2] A. Liu, Z. Zhao, G. Qu, Z. Shen, J. Shi, G. Jiang, Transformation/degradation of tetrabromobisphenol A and its derivatives: a review of the metabolism and metabolites, *Environ. Pollut.*, 243 (2018) 1141–1153.
- [3] P.H. Howard, D.C.G. Muir, Identifying new persistent and bioaccumulative organics among chemicals in commerce, *Environ. Sci. Technol.*, 44 (2010) 2277–2285.
- [4] A. Covaci, S. Voorspoels, M.A.-E. Abdallah, T. Geens, S. Harrad, R.J. Law, Analytical and environmental aspects of the flame retardant tetrabromobisphenol-A and its derivatives, *J. Chromatogr. A*, 1216 (2009) 346–363.
- [5] Z.-C. Zhu, S.-J. Chen, J. Zheng, M. Tian, A.-H. Feng, X.-J. Luo, B.-X. Mai, Occurrence of brominated flame retardants (BFRs), organochlorine pesticides (OCPs), and polychlorinated biphenyls (PCBs) in agricultural soils in a BFR-manufacturing region of North China, *Sci. Total Environ.*, 481 (2014) 47–54.
- [6] H. Matsukami, N.M. Tue, G. Suzuki, M. Someya, L.H. Tuyen, P.H. Viet, S. Takahashi, S. Tanabe, H. Takigami, Flame retardant emission from e-waste recycling operation in northern Vietnam: environmental occurrence of emerging organophosphorus esters used as alternatives for PBDEs, *Sci. Total Environ.*, 514 (2015) 492–499.
- [7] S. Arnon, Z. Ronen, A. Yakirevich, Evaluation of soil flushing potential for clean-up of desert soil contaminated by industrial wastewater, *Chemosphere*, 62 (2006) 17–25.
- [8] S. Morris, C.R. Allchin, B.N. Zegers, J.J.H. Haftaka, J.P. Boon, C. Belpaire, P.E.G. Leonards, S.P.J. van Leeuwen, J. de Boer, Distribution and fate of HBCD and TBBPA brominated flame retardants in North Sea estuaries and aquatic food webs, *Environ. Sci. Technol.*, 38 (2004) 5497–5504.
- [9] I.S. Lee, H.H. Kang, U.J. Kim, J.E. Oh, Brominated flame retardants in Korean river sediments, including changes in polybrominated diphenyl ether concentrations between 2006 and 2009, *Chemosphere*, 126 (2015) 18–24.
- [10] S.C. Quade, M. Alaei, C. Marvin, R. Hale, K.R. Solomon, N.J. Bunce, A.T. Fisk, Determination of tetrabromobisphenol-A in Detroit River sediment and sewage sludge, *Organohalogen Compd.*, 62 (2003) 327–330.
- [11] S. Song, M. Song, L. Zeng, T. Wang, R. Liu, T. Ruan, G. Jiang, Occurrence and profiles of bisphenol analogues in municipal sewage sludge in China, *Environ. Pollut.*, 186 (2014) 14–19.
- [12] M. Gorga, E. Martínez, A. Ginebreda, E. Eljarrat, D. Barceló, Determination of PBDEs, HBB, PBEB, DBDPE, HBCD, TBBPA and related compounds in sewage sludge from Catalonia (Spain), *Sci. Total Environ.*, 444 (2013) 51–59.
- [13] industryarc.com/Research/Tetrabromobisphenol-A-Market-Research-501611 (assessed 17.08.2021).
- [14] F. Barontini, V. Cozzani, K. Marsanich, V. Raffa, L. Petarca, An experimental investigation of tetrabromobisphenol A decomposition pathways, *J. Anal. Appl. Pyrolysis*, 72 (2004) 41–53.
- [15] G. Söderström, S. Marklund, PBCDD and PBCDF form incineration of waste containing brominated flame retardants, *Environ. Sci. Technol.*, 36 (2002) 1959–1964.
- [16] S.K. Han, P. Bilski, B. Karriker, R.H. Sik, C.F. Chignell, Oxidation of flame retardant tetrabromobisphenol A by singlet oxygen, *Environ. Sci. Technol.*, 42 (2008) 166–172.
- [17] A. Kossay, Z. Fakhri, Effect of type of wastewater on the oxygen uptake rate in batch reactor, *J. Duhok Univ.*, 15 (2012) 25–36.
- [18] EN ISO 8192 Water Quality – Test for Inhibition of Oxygen Consumption by Activated Sludge for Carbonaceous and Ammonium Oxidation (ISO 8192:2007).
- [19] R. Andreozzi, M. Raffaele, P. Nicklas, Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment, *Chemosphere*, 50 (2003) 1319–1330.
- [20] A. Katsoyiannis, C. Samara, Persistent organic pollutants (POPs) in the conventional activated sludge treatment process: fate and mass balance, *Environ. Res.*, 97 (2005) 245–257.
- [21] I. Skoczko, J. Piekutin, Photo-Fenton method usage to organic compounds degradation, *Desal. Water Treat.*, 52 (2014) 3837–3842.
- [22] Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, American Water Works Association, Water Environment Federation, Washington DC, USA, 2005.
- [23] PN-ISO 6060:2006 Water Quality – Determination of Chemical Oxygen Demand.

- [24] DIN EN 1899-1/EN 1899-2 Determination of Biochemical Oxygen Demand After n Days (BOD_n).
- [25] PN-EN 1484:1999 Water Quality – Guidelines for the Determination of Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC).
- [26] OECD, Test No. 209: Activated Sludge, Respiration Inhibition Test (Carbon and Ammonium Oxidation), OECD Guidelines for the Testing of Chemicals, Section 2, OECD Publishing, Paris 2010, <https://doi.org/10.1787/9789264070080-en> (assessed 15.10.21).
- [27] J. Kisala, A. Tomaszewska, D. Pogocki, 4,4'-Isopropylidenebis (2,6-dibromophenol) photocatalytic debromination on nano- and micro-particles Fe_3O_4 surface, *J. photocatalysis*, 1 (2020) 61–66.
- [28] S. Kabekkodu, PDF-4+ 2015 (Database), International Centre for Diffraction Data, Newtown Square (PA), 2015.
- [29] A.E. Regazzoni, M.A. Blesa, A.J.G. Maroto, Interfacial properties of zirconium dioxide and magnetite in water, *J. Colloid Interface Sci.*, 91 (1983) 560–570.
- [30] A.F. White, M.L. Peterson, M.F. Hochella Jr., Electrochemistry and dissolution kinetics of magnetite and ilmenite, *Geochim. Cosmochim. Acta*, 58 (1994) 1859–1875.
- [31] S. Imamura, H. Umena, N. Kawabata, M. Teramoto, Ozonation of organic compounds in alkaline aqueous media, *Can. J. Chem. Eng.*, 60 (1982) 853–858.
- [32] pubchem.ncbi.nlm.nih.gov (assessed 17.08.2021).
- [33] K. Barbusiński, Zaawansowane utlenianie w procesach oczyszczania wybranych ścieków przemysłowych, (In English): Advanced Oxidation in the Treatment of Selected Industrial Wastewater, Silesian University of Technology, Monograph 2013.
- [34] Q. Huang, W.J. Weber, Transformation and removal of bisphenol A from aqueous phase via peroxidase-mediated oxidative coupling reactions: efficacy, products, and pathways, *Environ. Sci. Technol.*, 39 (2005) 6029–6036.
- [35] K. Lin, W. Liu, J. Gan, Oxidative removal of bisphenol A by manganese dioxide: efficacy, products, and pathways, *Environ. Sci. Technol.*, 43 (2009) 3860–3864.
- [36] C. Wang, L. Zhu, C. Song, G. Shan, P. Chen, Characterization of photocatalyst $Bi_{3.84}W_{0.16}O_{6.24}$ and its photodegradation on bisphenol A under simulated solar light irradiation, *Appl. Catal., B*, 105 (2011) 229–236.
- [37] J. Eriksson, S. Rahm, N. Green, A. Bergman and E. Jakobsson, Photochemical transformations of tetrabromobisphenol A and related phenols in water, *Chemosphere*, 54 (2004) 177–126.
- [38] Y. Bao, J. Niu, Photochemical transformation of tetrabromobisphenol A under simulated sunlight irradiation: kinetics, mechanism and influencing factors, *Chemosphere*, 134 (2015) 550–556.
- [39] T. Kowalski, Analiza chemicznych i biochemicznych właściwości zanieczyszczeń występujących w ściekach, (In English): Analysis of Chemical and Biochemical Properties of Pollutants Present in Wastewater, *Ochrona środowiska*, 38 (1998) 13–16.
- [40] F. Garcia-Ochoa, E. Gomez, V.E. Santos, J.C. Merchuk, Oxygen uptake rate in microbial processes: an overview, *Biochem. Eng. J.*, 49 (2010) 289–307.
- [41] F. Hussain, H.-W. Yu, K. Chon, Y.-G. Lee, H. Eom, K.-J. Chae, S.-E. Oh, Real-time biomonitoring of oxygen uptake rate and biochemical oxygen demand using a novel optical biogas respirometric system, *J. Environ. Manage.*, 277 (2021) 111467, doi: 10.1016/j.jenvman.2020.111467.
- [42] P. Piechna, M. Zubrowska-Sudoł, Respirometric activity of activated sludge and biofilm in ifas-MBBR system, *J. Ecol. Eng.*, 18 (2017) 145–151.
- [43] E. Strade, D. Kalnina, Cost effective method for toxicity screening of Pharmaceutical Wastewater Containing Inorganic salts and harmful organic compounds, *Environ. Clim. Technol.*, 23 (2019) 52–63.
- [44] I. Oller, S. Malato, J.A. Sanchez-Perez, Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination – a review, *Sci. Total Environ.*, 409 (2011) 4141–4166.
- [45] G. Ricco, M. Concetta Tomei, R. Ramadori, G. Laera, Toxicity assessment of common xenobiotic compounds on municipal activated sludge: comparison between Respirometry and Microtox, *Water Res.*, 38 (2004) 2103–2110.
- [46] J. Ko, H. Woo, B.J. Copp, S. Kim, C. Kim, Evaluation of several respirometry-based activated sludge toxicity control strategies, *Water Sci. Technol.*, 45 (2002) 143–150.
- [47] S. Le Bonté, O. Potier, M.-N. Pons, Toxic event detection by respirometry and adaptive principal components analysis, *Environmetrics*, 16 (2005) 589–601.