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UV/O_3 and UV/H_2O_2 processes in the decomposition on waste streams generated during membrane filtration of laundry wastewater

Edyta Kudlek

Faculty of Energy and Environmental Engineering, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland, Tel. +48 32 237-24-78; email: edyta.kudlek@polsl.pl

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ABSTRACT

One major disadvantage of membrane processes is the generation of a waste stream – retentate, which must be treated or disposed in a separate process. The study assesses the effectiveness of the retentate treatment, obtained after the filtration of laundry wastewater, in the UV/O_3 and UV/H_2O_2 processes. The experiments were carried out using two UV radiation sources – a mono- and a polychromatic UV lamp (15 and 150 W, respectively). The UV/O_3 process was carried out for O_3 doses ranging from 2 to 10 mg/dm^3, while the H_2O_2 dose during the UV/H_2O_2 process ranged from 3 to 12 mg/dm^3. The process's effectiveness was assessed based on changes in the total organic carbon (TOC), cationic and anionic surfactants and triclosan concentrations. Both, UV/O_3 and UV/H_2O_2 processes lead to an over 60% reduction of the TOC concentration. Higher removal degrees of triclosan and surfactants were observed in the processes carried out with the use of a polychromatic UV lamp. The UV/O_3 process allowed for the complete removal of triclosan after 30 min of process duration (at the O_3 = 5 mg/dm^3). The toxicological analysis showed a significant decrease in the toxicity of solutions subjected to the implemented process.

Keywords: Oxidation processes; Retentate; Organic micropollutants; Surfactants; Toxicity

1. Introduction

Membrane processes are one of the most commonly described in the literature technology for the treatment of different types of water streams [1]. Membrane techniques are becoming a competing method for other in-depth treatment technologies due to the continuous reduction in the size of membrane modules and installations, energy requirement, and low capital cost [2]. Among the numerous advantages of these constantly evolving techniques for the effective treatment of water streams, one significant disadvantage should be mentioned, which is the generation of a waste stream called retentate. The retentate is a kind of concentrate of all undesirable compounds separated from the treated water streams. This highly polluted water stream is considered to be a dangerous hazardous waste, which should be disposed of. Especially retentates coming from the membrane treatment of industrial water streams like laundry wastewater [3] should be subjected to effective treatment processes.

The chemical composition of laundry wastewater is strictly dependent on the types of chemicals used during the washing procedures and the type of contamination of the laundry going to the washing devices. In general, this type of wastewater stream is characterized by a high content of organic compounds easily and hardly biodegradable, high concentration of solid particles, as well as proteins, starch, fats, lubricants, and disinfectants [4].

In addition, industrial laundries serving hospitals generate wastewater with a high microbial load, which contains a wide range of pharmaceutical compounds [5]. Special attention should be paid to the presence of surfactants in wastewater which, due to the type of hydrophilic group, can be divided into non-ionic, anionic, cationic, or amphoteric [6]. A large number of surfactants can have a negative impact on living organisms and some of them for example sodium dodecyl sulfate and dodecyl dimethyl benzyl ammonium chloride are classified as toxic substances [7] and have to be removed from water streams that are going to be introduced into the environment. Therefore it is necessary to search for effective methods for their removal, which can be applied without the risk of the formation of biological active decomposition by-products.

The most commonly used laundry wastewater treatment processes include classic coagulation [8], electrochemical coagulation and flotation [9], adsorption [10], filter bed filtration [11], and membrane filtration [12], as well as sequential or hybrid systems combining these processes [5] which might be additionally supplemented with biological processes [13]. An alternative to these processes and a promising solution for the retentate treatment may be advanced oxidation processes characterized by high purification efficiency of complex water matrices containing difficult-to-biodegrade compounds [14,15].

The paper presents the comparison of the treatment effectiveness of two UV-based oxidation processes, that is, UV/O_3 and UV/H_2O_2, applied to the retentate stream achieved during the nanofiltration of laundry wastewater. The influence of the UV source type and the O_3 dose, as well as the H_2O_2 dose, was assessed. To identify the possible decomposition by-products of micropollutants, which occur in the treated water stream the GC-MS analysis was applied. In addition, toxicological analyzes of water samples after the chosen oxidation processes were carried out using the Microtox® bioassay.

2. Material and methods

2.1. Retentate samples

The retentate, which was subjected to the oxidation processes, was obtained from the nanofiltration process of pre-treated laundry wastewater from a laundry located in the south part of Poland. The pre-treatment consisted of a classic coagulation process performed at the laundry. The laundry wastewater after the coagulation process was subjected to membrane filtration, which was conducted in a semi-industrial installation TMI 14 by J.A.M INOX Produkt (Poland) in the cross-flow mode with recirculation of the concentrate to the feeding tank to collect 50% of the initial volume of the feed. The nanofiltration process was carried out using a polymeric nanofiltration membrane AFC80 by PCI Membrane System Inc. The total surface area of the membrane was 240 cm^2. The initial volume of the pre-treated filtrated laundry wastewater was 20 dm^3. The process transmembrane pressure was set at 2.0 MPa and the temperature of the feed and the recirculated retentate was kept at 22°C. Details of the process operation parameters and the membrane characteristic were presented in previous studies [16]. The physicochemical characteristic of the highly polluted water stream is given in Table 1.

Table 1
The physicochemical characteristic of the treated retentate

Parameter	Value
pH	10.5
Conductivity, μS/cm	1,891.6
Color, mgPt/dm^3	>500[a]
Turbidity, NTU	133.5
Total organic carbon, mg/dm^3	368.7
Cationic surface active agents (CSAA), mg/dm^3	105.5
Anionic surface active agents (ASAA), mg/dm^3	68.5
Triclosan (TCS), μg/dm^3	4.23

[a]value above the detection limit of the analytical equipment

2.2. Oxidation processes

Both UV/O_3 and UV/H_2O_2 oxidation processes were carried out at laboratory scale by the use of glass batch reactors with a *volume of 0.7 L by* Heraeus (Hanau, Germany). To ensure continuous mixing of the treated water mixture the batch reactors were placed on a magnetic stirrer. The reactors were equipped with a monochromatic UV$_{15}$ lamp with a power of 15 W and a polychromatic UV$_{150}$ lamp of 150 W by Heraeus (Hanau, Germany), respectively. The monochromatic UV$_{15}$ lamp emits radiation with a wavelength λ_{max} = 254 nm, which corresponds to the energy of radiation reaching the reaction mixtures equal to 4.88 eV. The polychromatic UV$_{150}$ lamp has a bride radiation spectrum ranging from 300 to 600 nm. The energy of radiation for the polychromatic UV$_{150}$ lamp is summarized in Table 2. The radiation energy E was calculated based on the multiplication of the Planck's constant with the frequency of light. To prevent the overheating of the water samples during the exposure to the UV$_{150}$ lamp, the light source was placed in a cooling jacket with flowing tap water. The temperature of the oxidized retentate was kept in the range from 20°C to 21°C in both UV-based processes.

The Ozone FM500 generator by WRC Multiozon (Sopot, Poland) was used in the experiments to generate O_3, which was introduced through a ceramic diffuser to the treated water samples occurring in the reactors. The ceramic diffuser was placed about 1 cm above the bottom of the reactor. The UV/O_3 process was carried out at three different O_3 doses: 2, 5, and 10 mg/dm^3. The concentration of O_3 was measured immediately after its introduction to the water matrix in a sample taken from the middle of the reaction mixture by the use of the Spectroquant® Ozone Test by Merck KGaA (Darmstadt, Germany). The dose of H_2O_2 during the UV/H_2O_2 was equal to 3, 9, or 12 mg/dm3 L. The reagent was introduced to the mixtures in the form of a 30% solution purchased from Stanlab Sp z. o. o. (Lublin, Poland). The range of O_3 and H_2O_2 concentration

Table 2
Radiant flux and radiation energy emitted by the applied polychromatic UV_{150} lamp

Wavelength λ, nm	Radiant flux Φ, W[a]	Radiation energy *E*, eV
297	0.1	4.17
302	0.5	4.11
313	2.5	3.96
334	0.4	3.71
366	5.8	3.39
390	0.1	3.18
405–408	2.9	3.06–3.04
436	3.6	2.84
492	0.1	2.52
546	4.6	2.27
578	4.2	2.15

[a] Data achieved from the supplier of Heraeus UV lamp reactors Kendrolab Sp. z o.o.

was selected based on preliminary studies conducted on laundry wastewater (data not shown).

Retentate samples were subjected to the oxidation processes for 10, 30, and 60 min and then imminently analyzed.

2.3. Analytical procedure

The collected post-processed samples were subjected to the following physicochemical analyses:

- Total organic carbon (TOC) measurement,
- Analysis of the concentration of cationic and anionic surfactants,
- Analysis of triclosan (TCS) concentration,
- Turbidity measurement,
- Colour measurement,
- Identification of decomposition intermediates.

The concentration of TOC was estimated by the use of the TOC-L analyzer by Shimadzu Corporation (Kioto, Japan), which analyzes the organic carbon content in water samples based on the combustion catalytic oxidation method and infrared detection. The TOC concentration was calculated as the difference between the total carbon concentration TC and inorganic carbon concentration IC. The analyzes were performed using TC and IC calibration curves with a range from 100 to 1000 mg/dm^3.

The turbidity was measured using the HI-93414-02 EPA Compliant Turbidity and Free & Total Chlorine Meter by HANNA Instruments (Woonsocket, USA). While, the colour of the samples was analyzed by the UV-VIS Spectrophotometer Pharo 300 Spectroquant® by Merck KGaA (Darmstadt, Germany). This equipment together with Surfactants Spectroquant® cell tests was also used for the analysis of the concentration of cationic and anionic surfactants.

The TCS concentration in the retentate before and after the implementation of selected oxidation processes, as well as the identification of newly formed decomposition intermediates, was estimated by the use of the GC-MS analysis performed by 7890B gas chromatograph by Agilent Technologies (Santa Clara, United States) equipped with a capillary column SLB™ – 5 ms (30 m × 0.25 mm of 0.25 μm film thickness) by Sigma-Aldrich (Poznań, Poland). The analytes present in the water samples were firstly extracted by solid phase extraction (SPE). To ensure the correct extraction process of the analytes the pH of each sample was adjusted to 7.0 by the use of 0.1 mol/dm^3 HCl (purity grade >99.8%) from Avantor Performance Materials Poland S.A. (Gliwice, Poland). The procedure of the extraction was described by the study of Kudlek [17,18]. Recovery of TCS after the implemented SPE conditions exceeded 98%. Helium 5.0 acts as the carrier gas for chromatographic analysis. The samples were injected automatically with a speed of 3,000 mm^3/min. The injector temperature was equal to 250°C. The oven temperature program was as follows: 80°C (6 min), 5°C/min up to 260°C, 20°C/min up to 300°C (2 min). The ion trap temperature was set at 150°C, and the ion source operated at 230°C. The quantitative analysis of TCS concentrations was operated in the selected ion monitoring (SIM) mode, during which the 218, 288, and 290 m/z ions were monitored. The percentage of TCS removal after the UV-based oxidation processes was calculated by determining the initial C_i concentrations of the compound in the retentate before the treatment process and post-processed C_p micropollutant concentrations (mg/dm^3) according to Eq. (1):

$$\text{Removal}\left(\%\right)=\frac{C_i-C_p}{C_i}\cdot 100 \tag{1}$$

The identification of new compounds in the post-processed samples was made based on their mass spectra obtained after GC-MS analysis carried out in the total ion current (TIC) mode ranging from 50 to 400 m/z. The mass spectra were compared with the United States National Institute of Standards and Technology NIST v17 Mass Spectral Library using the MassHunter software.

The results presented in all figures are the arithmetic average of three replicates of each experiment. The standard deviation was used for the calculation of the error bars, which did not exceed 4%.

2.4. Toxicity tests

The toxicity of the untreated retentate and the retentate after chosen oxidation processes was estimated by the Microtox® bioassay, which measures the changes in the intensity of light emitted by bioluminescent saltwater bacteria *Aliivibrio fischeri* exposed to the tested samples. The toxicity examination was carried out using the Microtox analyzer model 500 by Modern Water (London, United Kingdom). The samples were analyzed according to the assumptions of the Screening Test procedure of MicrotoxOmni software after 5 min of exposure. The obtained results were presented in a percentage value of the caused toxicity effect and interpreted based on a four-class toxicity classification summarized in Table 3 [19,20].

Table 3
Toxicity classification system of water samples [19,20]

Effect (%)	Description	Toxicity class
<25.00	Non-toxic	I
25.00–50.00	Low-toxic	II
50.01–75.00	Toxic	III
75.01–100	Highly-toxic	IV

3. Results and discussion

3.1. Effectiveness of UV/H_2O_2 and UV/O_3 oxidation process

The pollutants occurring in the treated retentate were decomposed during different co-occurring reactions. Firstly the compounds can undergo direct photolysis as a result of various sources of UV radiation [21]. The irradiation of solutions containing dissolved organic matter can also lead to the generation of photogenerated reactive oxygen species, which leads to the indirect photolysis of compounds [22]. The introduction of the second type of oxidant in the form of H_2O_2 or O_3 improves the particular compound decomposition. The irradiation of H_2O_2 with UV light leads to the formation of $HO^\bullet$ radicals [23], which have a nonselective character and the second strongest oxidation potential after fluoride. $HO^\bullet$ radicals were also generated during the self-decomposition of O_3 in the presence of H_2O [24].

The analysis of the changes in the cationic surface active agents (CSAA) (Figs. 1 and 2) and ASAA (Figs. 3 and 4) concentrations during the implemented oxidation processes indicated that those compounds were more efficiently decomposed during processes conducted by the use of the UV_{150} lamp. The polychromatic light source affects CSAA and ASAA compounds with higher total energy than the UV_{15} lamp and breaks the bonds between the atoms of these compounds leading to their decomposition. For example, the removal rate of CSAA and ASAA after 60 min of UV_{150}/O_3 process by the O_3 dose equal to 5 mg/dm^3 and 10 mg/dm^3 exceed 100%. Whereas the removal of CSAA and ASAA after 60 min of UV_{15}/O_3 process (O_3 dose equal

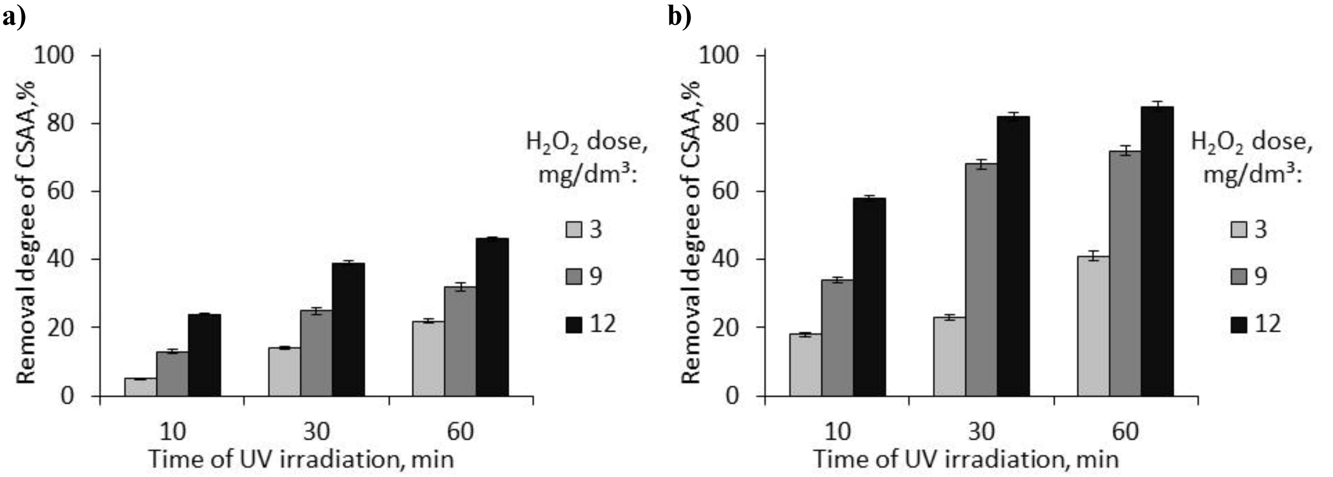

Fig. 1. Removal of CSAA after the (a) UV_{15}/H_2O_2 and (b) UV_{150}/H_2O_2 process.

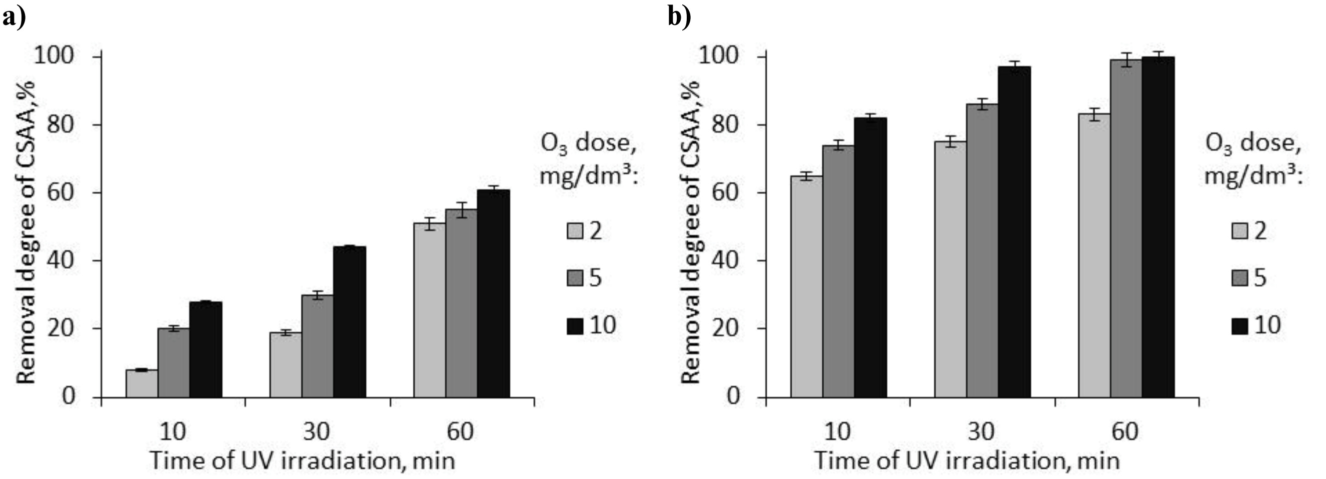

Fig. 2. Removal of CSAA after the (a) UV_{15}/O_3 and (b) UV_{150}/O_3 process.

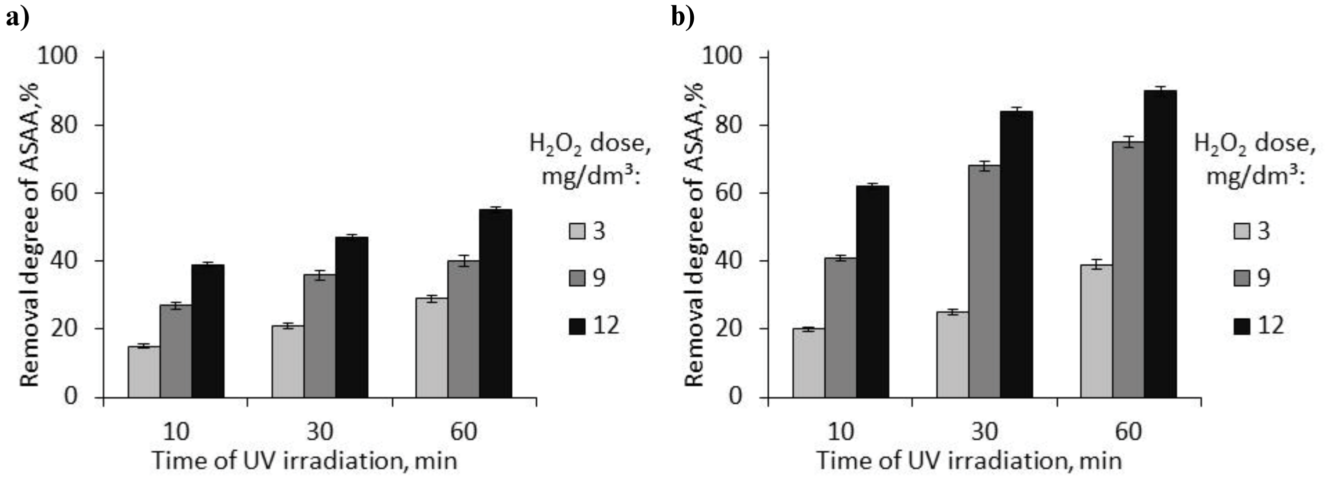

Fig. 3. Removal of ASAA after the (a) UV_{15}/H_2O_2 and (b) UV_{150}/H_2O_2 process.

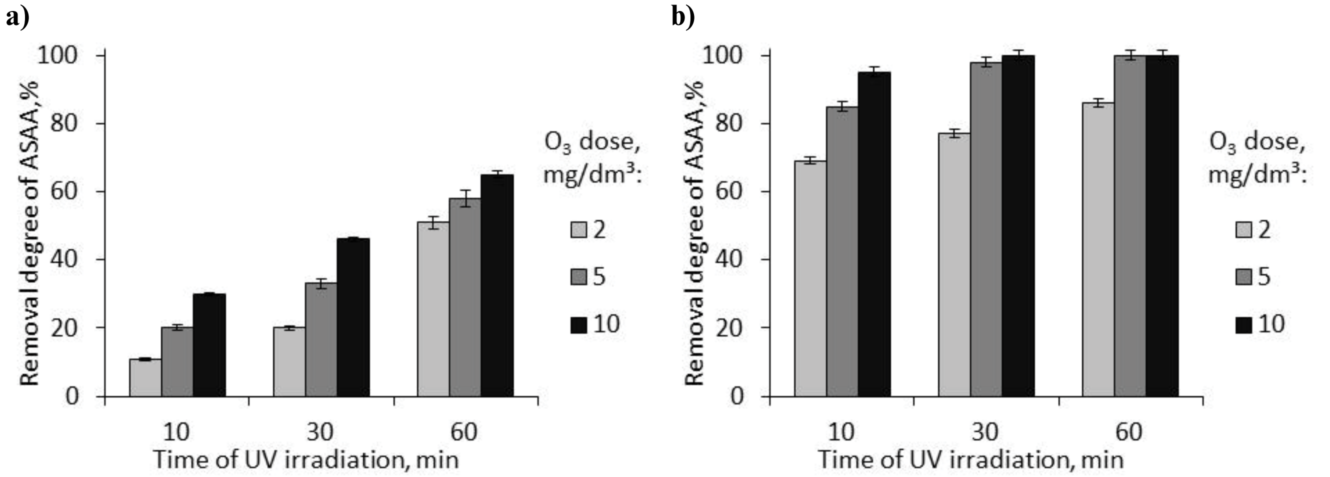

Fig. 4. Removal of ASAA after the (a) UV_{15}/O_3 and (b) UV_{150}/O_3 process.

to 10 mg/dm^3) reached only 61% and 65%, respectively. Also, the UV/H_2O_2 process performed using the UV_{150} lamp result in a higher CSAA and ASAA removal effectiveness than the process conducted using the UV_{15} lamp. For example, the removal of CSAA during the UV_{15}/H_2O_2 process implemented for 60 min in the presence of 3, 9, and 12 mg/dm^3 of H_2O_2 did not exceed 22%, 32%, and 46%, respectively. While the removal degrees of CSAA after 60 min of UV_{150}/H_2O_2 process carried out at an H_2O_2 dose equal to 3, 9, and 12 mg/dm^3 reached 41%, 72%, and 85%, respectively.

It should be noted that both CSAA and anionic surface active agents (ASAA) achieved higher removal degrees during the UV-based processes carried out in the presence of O_3. This can be explained by the fact that O_3 has a stronger oxidation potential than H_2O_2. Eqs. (2) and (3) present the reduction reaction of O_3 and H_2O_2.

$$O_3 + H^+ + 2e^- \rightarrow O_2 + H_2O \quad 2.08\text{ eV} \tag{2}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad 1.76\text{ eV} \tag{3}$$

Figs. 5 and 6 present the obtained TCS removal degrees, which also increase with the increase of the UV irradiation time and the increase of the dose of the used oxidants. It should be mentioned, that the TCS removal degrees noted for both UV_{15} and UV_{150} processes in the presence of 9 and 12 mg/dm^3 of H_2O_2 took similar values, which was especially visible after 60 min of process duration. For example, the TCS removal after 60 min of the UV_{15}/H_2O_2 was 91% for both doses of 9 and 12 mg/dm^3 of H_2O_2. The same dependence was noted for the processes supported by the action of O_3. For example, the removal of TCS after 30 min of the UV_{150}/O_3 process was equal to 100% (for the O_3 dose 5 and 10 mg/dm^3).

The highest TCS removal was noted for the UV_{150}/O_3 process, during which the micropollutant concentration was lowered by over 98% after 10 min of UV irradiation assisted by the O_3 dose equal to 5 and 10 mg/dm^3. Also the O_3 dose of 2 mg/dm^3 lead to an over 97% removal of TCS after 60 min of this process. On the other hand, the lowest decrease in the TCS concentration was noted during the UV_{15}/O_3 process. Therefore it can be concluded that the simultaneous action of H_2O_2 and both, mono-and

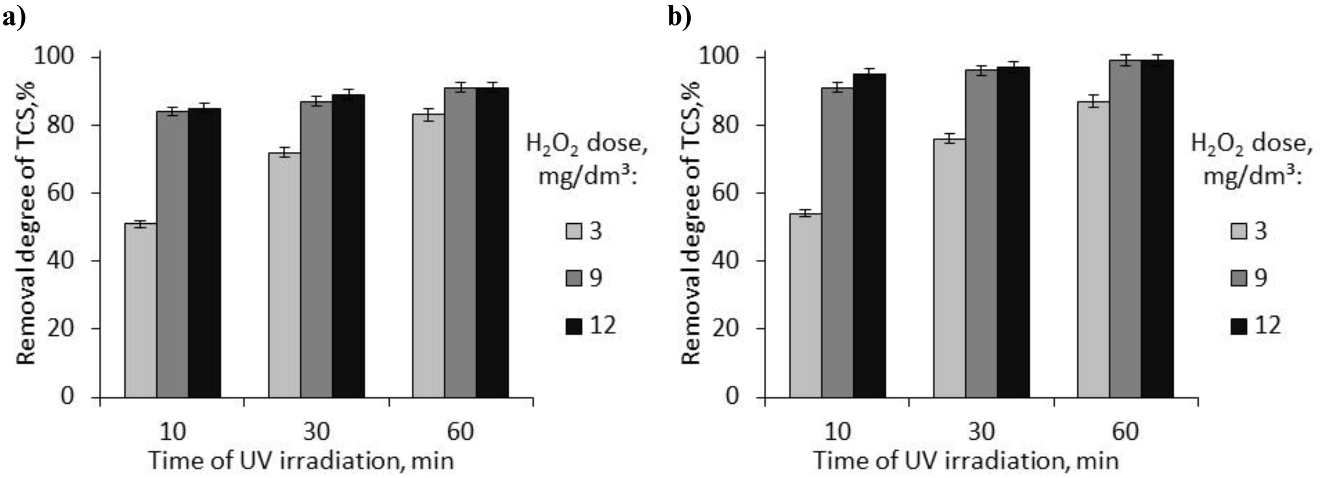

Fig. 5. Removal of TCS micropollutant after the (a) UV_{15}/H_2O_2 and (b) UV_{150}/H_2O_2 process.

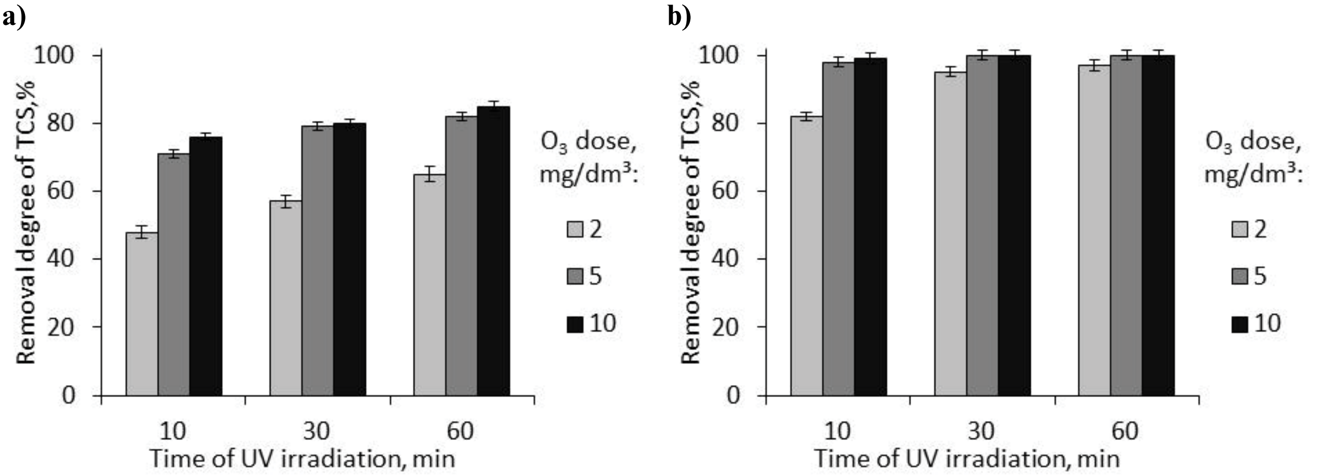

Fig. 6. Removal of TCS micropollutant after the (a) UV_{15}/O_3 and (b) UV_{150}/O_3 process.

polychromatic UV light on the TCS molecule leads to his faster decomposition than the action of O_3 together with the monochromatic UV_{15} lamp.

The decomposition of TCS as well as, the decomposition of ASAA and CSAA depends not only on the used type of UV light source and the occurrence of H_2O_2 or O_3 but also on the presence and concentration of $HO^•$ radicals. In alkaline solutions, like the treated retentate, there is a possibility of recombination of the generated $HO^•$ radicals and the production of H_2O_2 according to reaction (3) [25], which leads to a reduction in the efficiency of decomposition of organic compounds. The possibility of TCS adsorption on the surface of high molecular weight compounds should also be taken into account. Furthermore, when optimizing the process of decomposition of micropollutants, surfactants, and other compounds present in the retentate, it is necessary to take into account the correction of the pH of the solution, which may contribute to increasing the process efficiency.

$$OH^• + OH^• \rightarrow H_2O_2 \quad (4)$$

Figs. 7 and 8 present the removal of all types of organic compounds measured as TOC after the implementation of both monochromatic and polychromatic UV-based oxidation processes assisted by the action of H_2O_2 or O_3, respectively. It was noted that the concentration of TOC decreases with the increase of the O_3 or H_2O_2 dose and the increase of the process time. For example, the TOC decreased after 10 min of the UV_{15}/O_3 by 1% for the H_2O_2 dose equal to 3 mg/dm³, 6% for the H_2O_2 dose equal to 9 mg/dm³, whereas 12 mg/dm³ of H_2O_2 lead to an over 11% decrease in TOC concentration. Extending the process time to 60 min increased the organic compound removal, and the TOC concentration decreased for the mentioned H_2O_2 doses by over 10%, 18%, and 29%, respectively. A similar relation was observed for the UV-based processes supported by the action of O_3. The application of the O_3 dose equal to 2 mg/dm³ allowed for an 11% decrease of the measured TOC value after 10 min of the UV_{150}/O_3 process, while 10 mg/dm³ of O_3 resulted in an over 21% decrease in the TOC concentration.

The lowest TOC removal degrees were noted during the UV_{150}/H_2O_2. The TOC concentration decreased only by 20%

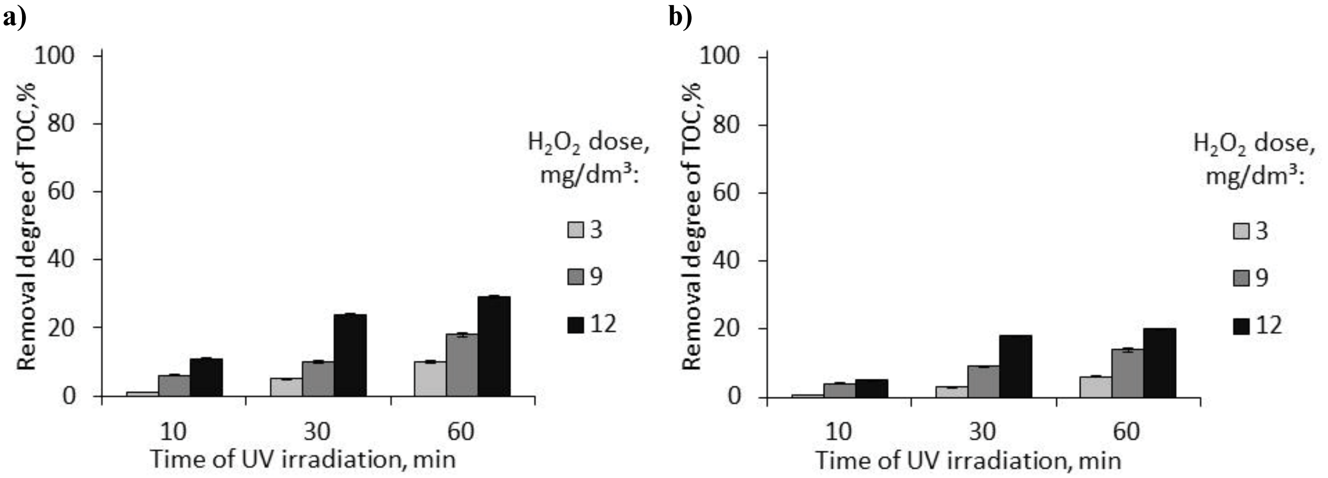

Fig. 7. Changes in the TOC concentration after the (a) UV_{15}/H_2O_2 and (b) UV_{150}/H_2O_2 process.

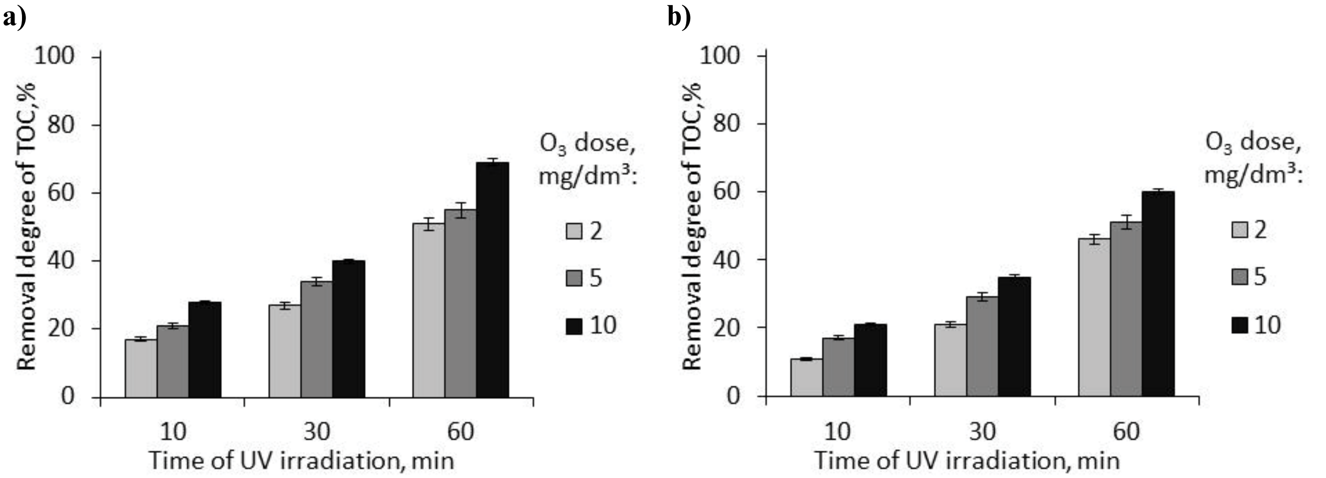

Fig. 8. Changes in the TOC concentration after the (a) UV_{15}/O_3 and (b) UV_{150}/O_3 process.

after 60 min of UV_{150} irradiation assisted by the action of 12 mg/dm^3 of H_2O_2. In general higher removal of TOC was noted during the processes carried out using the monochromatic UV_{15} lamp than during the implementation of processes based on the action of the polychromatic UV_{150} lamp. For example, during the UV_{15}/O_3 process carried out by the O_3 dose equal to 5 mg/dm^3 the TOC decreased after 30 min by over 34%, while after 30 min of the UV_{150}/O_3 process the value of TOC decreased only by 29%. The measurement of the TOC indicated that the mineralization of compounds is more effective in the case of the treatment carried out in the presence of the UV_{15} light source compared to the UV_{150}, which is opposite to the decomposition of TCS and ASAA and ACAA compounds. The TOC concentration value give the information not only about the concentration of TCS and CSAA and ASAA in the treated solution but also about the presence of other organic contaminants like dyes, pharmaceutical residues, fragrances, industrial additives etc. [26] and their decomposition by-products along with high molecular weight compounds. Some of them can be more effectively decomposed by the action of a single wavelength with a high energy polychromatic UV lamp. On the other hand those different types of compounds can resist the action of the implemented processes and can still occur in the treated retentate causing high TOC concentration values.

The implemented oxidation processes lead also to the reduction of the turbidity and the colour of the treated retentate. Table 4 summarizes the measured turbidity and colour values achieved after 60 min of each oxidation process. The elimination of the colour of the treated solution also gives an indirect answer to the question of whether a given process effectively eliminates the contaminants contained in the treated solution. Because the removal of colour is related to the decomposition of colour-causing compounds, which can have both an organic and inorganic nature. Laundry wastewater can exhibit in its composition various types of dyes rinsed out of the cleaned textiles [27] and inorganic mordants [28], which were responsible for the occurrence of colour in the wastewater. The decrease of the colour observed during the implemented treatment processes corresponds to the decrease in the TOC concentration. For example, the lowest decolorization was noted

Table 4
Turbidity and colour of post-processed samples after 60 min of chosen oxidation process

Parameter	Process											
	UV_{15}/H_2O_2			UV_{150}/H_2O_2			UV_{15}/O_3			UV_{150}/O_3		
	Reagent concentration, mg/dm³											
	3	9	12	3	9	12	2	5	10	2	5	10
Turbidity, NTU	127.5	98.9	74.6	55.1	39.2	25.7	15.2	6.9	6.7	5.5	2.4	1.0
Colour, mgPt/dm³	>500	>500	356	>500	471	302	408	314	128	138	15	2

for samples subjected to the UV_{15}/H_2O_2 and UV_{150}/H_2O_2 processes, in which also the lowest decrease of the TOC concentration was observed. However, it should be noted that the decolorization of the solutions exposed to the UV_{150}/O_3 was more effective than the removal of the TOC during this process. This fact could indicate that the colour-causing compounds decompose to low-molecular-weight contaminants, which still have an organic nature. The lowest reduction in turbidity was noted for processes carried out in the presence of H_2O_2. The most beneficial influence of the decrease of the solution turbidity was observed for O_3. The implementation of the UV_{150}/O_3 allowed for the decrease of the turbidity from 133.5 NTU in the untreated retentate to 5.5 NTU for solutions exposed to the action of UV_{150} light in the presence of 2 mg/dm³ of O_3. Whereas the O_3 dose equal to 10 mg/dm³ lead to the decrease of the turbidity value to 1 NTU. Also, the colour of the post-processed solution treated by O_3 at a dose of 10 mg/dm³ in combination with UV_{150} irradiation was reduced to 2 mgPt/dm³. Turbidity, as well as the color of the treated water solution, can be caused by the occurrence of organic matter and inorganic contaminants. The implementation of treatment processes can lead to an arise in turbidity [29]. This phenomenon is related to the possibility of dissolved substances precipitation from the water phase. This fact was not observed during the preformed treatment processes. The decrease of turbidity after the action of UV light supported by O_3 or H_2O_2 was related to the decomposition of the organic compounds.

It can be assumed, that polychromatic UV_{150} irradiation assisted by the action of O_3 can effectively decompose high concentrated organic matter, surfactants, and the TCS micropollutant. But on the other hand the decomposition of those compounds not always means their complete mineralization and there is a legitimate risk of producing intermediates with strong toxic potential.

3.2. Identification of decomposition intermediates

The GC-MS analysis of samples after the oxidation in both UV/O_3 and UV/H_2O_2 processes indicated the presence of newly formed micropollutants, which did not occur in the untreated retentate. The mass spectra of each potential micropollutant decomposition by-product noted on the chromatograms were compared to the NIST Standard Reference Database v17. Only compounds with a matching similarity of over 70% were taken into account as potential by-products. Tables 5 and 6 summarize all compounds matched in samples collected from the conducted oxidation processes by the use of the monochromatic and polychromatic UV lamp respectively. Those micropollutants could be among others direct decomposition by-products of triclosan, like for example 2,8-dichlorodibenzo-p-dioxin, 2,3-dichlorophenol, and 4-chlorophenol, which were also detected in other studies [30]. The intermediates could be also by-products of the decomposition of other phenolic compounds occurring in the treated retentate.

The obtained results indicated that intermediates were formed more favourable during processes assisted by the action of the polychromatic UV_{150} lamp. This is also confirmed by the previously described higher removal degrees of the

Table 5
Micropollutant decomposition by-products detected in post-processed samples irradiated with the monochromatic UV_{15} lamp

Identified compound	Molecular weight, g/mol	Process					
		UV_{15}/O_3			UV_{15}/H_2O_2		
		10 min	30 min	60 min	10 min	30 min	60 min
2,8-Dichlorodibenzo-p-dioxin	253.08	–	+	+	–	–	–
2,3-Dichlorophenol	163.00	–	+	+	–	+	+
4-Chlorophenol	128.56	–	–	+	–	–	–
3,5-Dichlorocatechol	179.00	–	–	–	–	–	–
4-Chlorocatechol	144.55	–	–	+	–	–	–
Catechol	110.11	–	–	+	–	–	+
Phenol	94.11	+	+	+	+	+	+

+ compound identified in the sample; – compound not identified in the sample

Table 6
Micropollutant decomposition by-products detected in post-processed samples irradiated with the polychromatic UV_{150} lamp

Identified compound	Molecular weight, g/mol	Process					
		UV_{150}/O_3			UV_{150}/H_2O_2		
		10 min	30 min	60 min	10 min	30 min	60 min
2,8-Dichlorodibenzo-p-dioxin	253.08	–	+	–	–	–	–
2,3-Dichlorophenol	163.00	+	+	–	–	+	+
4-Chlorophenol	128.56	+	–	–	–	+	–
3,5-Dichlorocatechol	179.00	+	+	–	+	+	–
4-Chlorocatechol	144.55	+	+	–	+	+	–
Catechol	110.11	–	+	+	–	+	+
Phenol	94.11	+	+	+	+	+	+

+ compound identified in the sample; – compound not identified in the sample

tested TCS micropollutant, which faster decompose during the irradiation with the polychromatic UV lamp, than during the exposure to monochromatic UV_{15} radiation. It should be noted that the newly occurring compounds were generated after 10 min of the monochromatic UV-based processes implementation, and their concentration, estimated from the area of the chromatogram peaks, increased with the process elongation. For example, the phenol concentration increase during the UV_{15}/O_3 was about 20% higher after 60 min of process duration than after 10 min. An inverse relation was observed for solutions subjected to the radiation emitted by the polychromatic UV_{150} lamp. The intermediates occur more often and in higher concentration in samples subjected to 10 min of process elongation. This was especially noted during the UV_{150}/O_3 process, during which the concentration of 2,3-dichlorophenol, 4-chlorophenol, 3,5-dichlorocatechol, 4-chlorocatechol, and phenol decreased linearly between the 10th min and 30th min of process implementation. Also, the catechol and 2,8-dichlorodibenzo-p-dioxin concentration were higher in samples after 30 min of UV_{150}/O_3 process than after 60 min, where the 2,8-dichlorodibenzo-p-dioxin concentration was under the detection limit of the used analytical equipment. The largest number of six decomposition by-products during the UV_{150}/H_2O_2 process was noted after 30 min of process duration and gradually lowered to only 3 intermediates after 60 min of this process.

3.3. Toxicity analysis of post-processed retentate samples

The appearance of intermediates during the conducted oxidation processes of compounds occurring in the treated retentate requires the implementation of toxicological tests to assess the possible negative impact of the newly formed compounds on the quality of the treated solution. The results of the toxicological assessment are presented in Figs. 9 and 10. The Microtox® test, which is considered to be one of the fastest and most sensitive topological tests of aqueous solutions [31] indicated that an increase in the toxicity of the treated solution was only noted in samples after 30 min of the UV_{150}/O_3 process. This increase can be directly related to the generation of toxic intermediates. In the case of other oxidation processes, a gradual decrease of the toxic character of the samples was observed (Figs. 5 and 6a).

The toxicological analysis showed a significant decrease in the toxicity of solutions subjected to the UV_{150}/H_2O_2 process at the H_2O_2 equal to 12 mg/dm^3 from highly toxic to low toxic (Table 3) solutions after 60 min of process duration (Fig. 5b). While 60 min of the UV_{15}/H_2O_2 process allowed, in case of all tested H_2O_2 doses, only for a decrease of the toxicity from highly toxic to the toxic class (Fig. 5a).

On the other hand, the UV_{150}/O_3 process carried out for 60 min at the O_3 dose equal to 10 mg/dm^3 allowed to reduce the toxicity of the solutions to the non-toxic class. Whereas the samples collected after 60 min of the simultaneous action of the polychromatic UV lamp and O_3 at a concentration of 2 and 5 mg/dm^3 took values close to the under border of the low toxicity range. The decrease of the toxicity is related to the decrease of both types of surfactants occurring in the treated retentate and to some extent it can be linked to the decrease of the TOC concentration, which also can be a potential indicator about the amount of potentially toxic compounds of organic nature. It should be noted that the TOC concentration refers to all types of organic contaminants, to those which are toxic but also to a large group of neutral or even beneficial to the development of organisms. Moreover, the decrease of turbidity also has a positive impact on the behaviour of the test organisms.

4. Conclusions

The results obtained during the conducted studies indicated that UV-based advanced oxidation processes can be a part of a promising retentate treatment technology. The simultaneous action of UV irradiation and H_2O_2 or O_3 leads to a decrease of the TOC, CSAA, ASAA, and TCS concentrations. The value of all tested parameters decreased with the increase of the process time and the increase of the H_2O_2 or O_3 dose. The highest removal of TOC which exceeds 69% was noted during the processes carried out by the use of the monochromatic UV_{15} lamp and the O_3 dose equal to 10 mg/dm^3. The use of the polychromatic UV_{150} lamp allowed for a higher removal of CSAA, ASAA, and TCS in both UV_{150}/H_2O_2 and UV_{150}/O_3 processes. It should be noted that the TCS, CSAA and ASAA removal degrees are dedicated to a specified group of compounds. While the TOC concentration decrease indicated the reduction of the

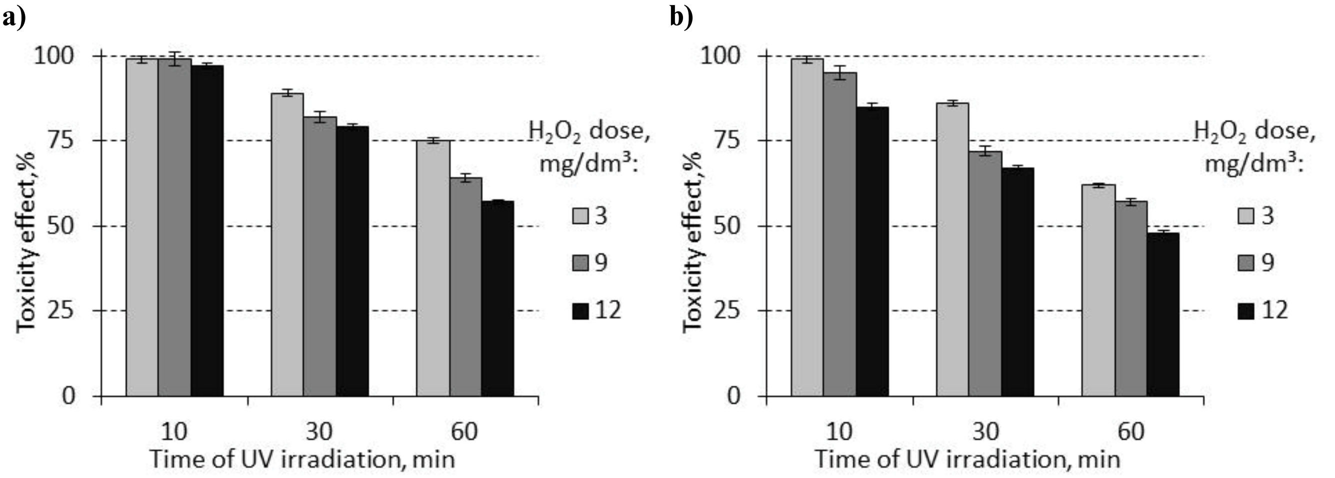

Fig. 9. Changes in toxicity of samples after (a) UV_{15}/H_2O_2 and (b) UV_{150}/H_2O_2 process.

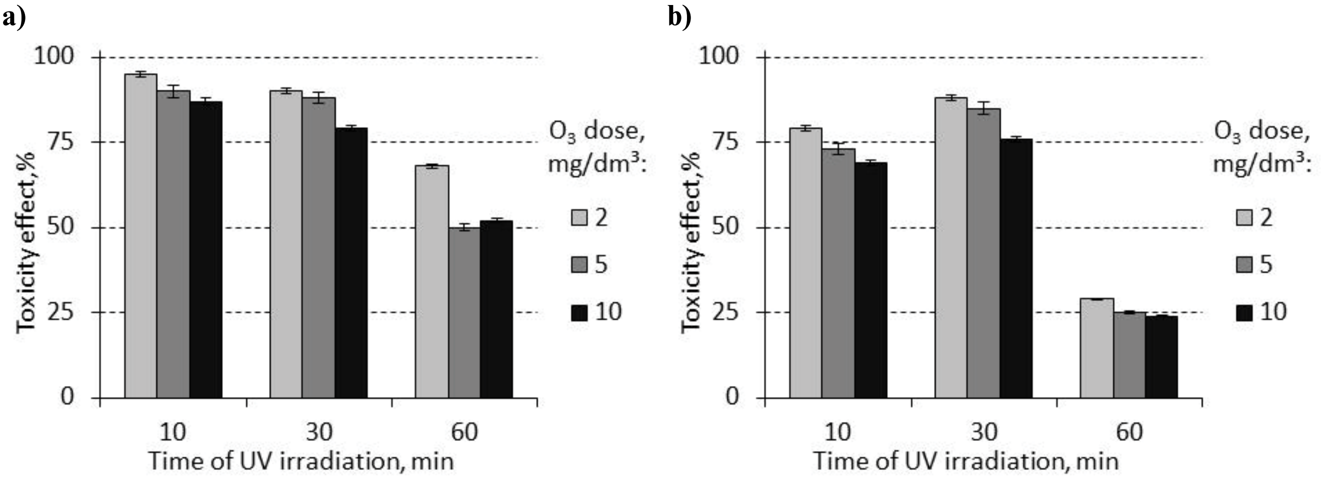

Fig. 10. Changes in toxicity of samples after (a) UV_{15}/O_3 and (b) UV_{150}/O_3 process.

concentration of both, TCS, CSAA, ASAA and other organic compounds. Those unspecified compounds can be more easily photodecomposed by the operation of a monochromatic UV lamp supported by the action of other oxidizing species. Also, the turbidity and the colour of the retentate were removed most efficiently during the UV_{150}/O_3 at an O_3 dose equal to 10 mg/dm³. The implementation of all tested oxidation processes leads to the formation of seven decomposition intermediates, whose concentrations varied during the process. The conducted toxicological analysis confirmed the reduction of the CSAA, ASAA, and TCS concentration and indicated the decrease of the toxic nature of the retentate after the oxidation processes.

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