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Mariusz DUDZIAK[1]

CHANGE OF TOXICITY OF WATER CONTAINING BISPHENOL A DURING ITS TREATMENT BY COMPLEX OXIDATION PROCESS

ZMIANY TOKSYCZNOŚCI WODY ZAWIERAJĄCEJ BISFENOL A W TRAKCIE JEJ UZDATNIANIA W ZŁOŻONYM PROCESIE UTLENIAJĄCYM

Abstract: Water containing bisphenol A was UV irradiated (medium pressure immersion lamp with the electric power of 150 W) with and without the addition of H_2O_2 (6–12 mg/dm^3 dose). To control of the water quality Microtox® biotest was used. Bioluminescent bacteria *Vibrio fisheri* was involved. Decomposition of bisphenol A was depended on the UV irradiation time and dose of the H_2O_2. The observations connected with the bioluminescence value in the examined solutions were surprised. Decomposition of the compound did not cause of decrement the bioluminescence inhibition value characterizing solution indicating the formation of toxic intermediates products. However, the combined use of H_2O_2 with UV radiation improves the rate of decomposition of bisphenol A, but also causes an increase in bioluminescence inhibition of the solutions. For this reason selection of the most favorable conditions for the oxidative process have to be proceed based on both agents: effectiveness of the compounds decomposition and the toxicity of the solution after process.

Keywords: bisphenol A, water treatment, toxicity, Microtox® biotest

Modern technologies of water and waste water treatment are increasingly using various chemical oxidation processes. Oxidation in the water treatment may be used for different purposes, mostly for the oxidation of Fe(II), Mn(II) and other reduced inorganic substances, oxidation of organic substances of natural and anthropogenic origin and for disinfection [1]. Chemical oxidants may be added to the treated water at different stages of the treatment system, thus preliminary, intermediate and final steps of disinfection can be distinguished. In the case of waste water treatment oxidation is used as a key step, for example, in industrial waste water treatment [2], or as a treatment method for the waste water containing biologically active organic compounds [3–6]. Apart from oxygen the oxidants used in water and waste water treatment include

[1] Institute of Water and Wastewater Engineering, Silesian University of Technology, ul. Konarskiego 18, 44–100 Gliwice, Poland, phone: +48 32 237 16 98, fax: +48 32 237 10 47, email: mariusz.dudziak@polsl.pl

chlorine, chlorine dioxide, ozone, potassium permanganate and hydrogen peroxide [1–2]. Moreover, the oxidation processes in which the generated hydroxyl radical is used (or another peroxide radical) belong to the group of advanced oxidation process (AOPs).

AOPs more and more frequently employ synergistic combination of different oxidants (ozone, hydrogen peroxide and others) and UV radiation, which increases the efficiency and rate of organic compounds degradation [2, 7–11]. The authors of [7] compared the effectiveness of single oxidation processes, this is, photolysis (UV) and ozonation (O_3) with a coupled system combining both of these processes, in terms of the elimination of selected antibiotics from aqueous stream. Based on the obtained results it was determined that the process of photolysis proved to be completely ineffective for the elimination of the tested antibiotics. On the other hand, the efficiency of the ozonation process depended on the contact time of ozone with the treated solution. Satisfactory results of antibiotics degradation were observed only after 30 minutes of ozonation. In contrast, when both UV and O_3 were used the removal efficiency of antibiotics was over 87 % after 10 minutes. On the other hand, according to other authors [8–10] the use of UV and H_2O_2 significantly increases the removal efficiency of micropollutants, compared to the use of the UV process itself. UV radiation causes direct photolysis of hydrogen peroxide molecules and as a result hydroxyl radicals are generated. In the case of the research conducted by Esplugass et al [11] the addition of a solution of 10 mg/dm^3 H_2O_2 caused an increase of the removal efficiency of psychotropic drug carbamazepine, which is practically non-UV-degradable, to a level of 99 %. These studies confirmed that a combination of both of these processes causes a synergistic effect.

However, as shown by previous studies, none of the chemical oxidants that are available and used in practice are neutral towards the quality of purified water or waste water [1–2]. All the strong oxidizing agents cause, to a various extent, the formation of oxidation by-products, which are often of unknown biological activity. This problem also applies to AOPs, however, in this case the information available in the literature is limited.

The above-mentioned issues were taken into account in the present study, which assessed the toxicity changes in water containing bisphenol A (as a selected xenobiotic) during the treatment using a combined oxidation process UV-H_2O_2.

Materials and methods

Bisphenol A, which was selected for the study, is an organic compound belonging to a group of phenols used, among others, for the production of plastics [12]. The subject of the study was model solutions prepared using deionized water and an analytical standard of the studied xenobiotic at a concentration of 0.5 to 5.0 mg/dm^3. The analytical standard of bisphenol A was purchased from Sigma-Aldrich (Poznan, Poland). The pH of the solution was adjusted to pH 7 with 0.1 mol/dm^3 HCl solution or 0.2 mol/dm^3 NaOH. The compound was determined by solid phase extraction (SPE) method and liquid chromatography analysis (HPLC). Supelclean^{TM} ENVI-18 cartridges

(volume 6 cm^3, 1.0 g solid phase) from Supelco (Poznan, Poland) were used for the extraction. The filling of the cartridges prior to the extraction was conditioned with methanol (5 cm^3) and acetonitrile (5 cm^3), and then washed with deionized water (5 cm^3). The analyte was eluted with a 1 cm^3 mixture of acetonitrile and methanol (60:40, v/v). The qualitative and quantitative analysis of the xenobiotic in the eluent was performed using HPLC with a UV detector (λ = 218 nm) from Varian (Warsaw, Poland). The eluents were previously concentrated in a gentle stream of nitrogen. The chromatographic column used for the analysis was Microsorb 100 C18 with a length of 25 cm, a diameter of 4.6 mm and a pore size of 5 μm. A mixture of acetonitrile and water (85:15, v/v) was used as the mobile phase. Organic solvents of analytical grade purchased from the Avantor Performance Materials International Company(Gliwice, Poland) were used in this study.

The applied analytical procedure allows the determination of bisphenol A in water at low concentrations, this is, 0.3 $\mu g/dm^3$. The extraction yield exceeded 61 % for the concentration of the compound in deionized water equal to 0.5 mg/dm^3 and 74 % for the concentration of 5 mg/dm^3. The obtained analysis results did not differ by more than 10 %.

At the preliminary stage of the study, the bioluminescence inhibition was assessed in the model solutions with varying bisphenol A concentrations (Fig. 1). The analysis was carried out using the MICROTOX® bioassay system in the Microtox Model 500 analyser from Tigret Ltd. (Warszawa, Poland) in accordance with the *Screening Test* procedure of the MicrotoxOmni system. This analyser serves both as an incubator and a photometer. Percent bioluminescence inhibition against the control sample (bacteria not treated with the potential toxicant) was measured after 5 minutes of exposure.

It was observed that the increasing concentration of xenobiotic in water was accompanied by simultaneous increase of the bioluminescence inhibition. The presented

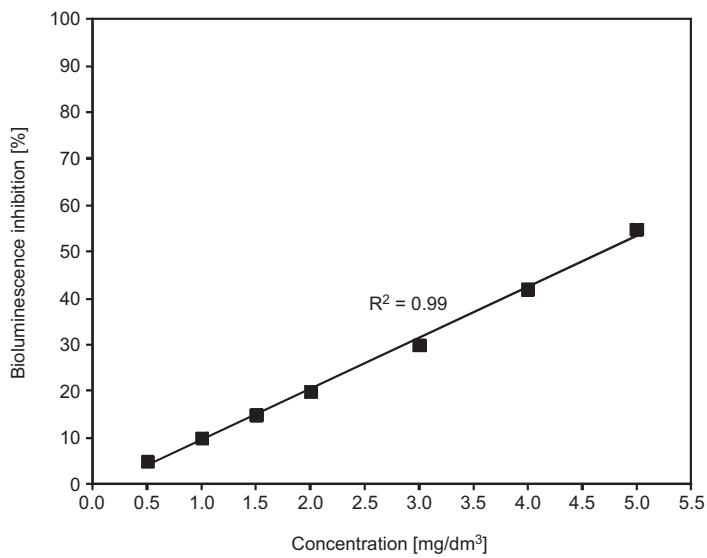

Fig. 1. Impact of bisphenol A concentration on the bioluminescence inhibition value

graphical relationship between the concentration of xenobiotic and the bioluminescence inhibition shows linear correlation between the two parameters (R^2 = 0.99), confirming that the toxicity of water depends on the concentration of the xenobiotic. Based on this observation, it can be hypothesized that the effective elimination of the xenobiotic from water using a variety of physical and chemical processes should be accompanied with a reduction of the toxic effect. Any exception to this rule may prove the occurrence of other dangerous phenomena accompanying the implementation of these processes.

The UV irradiation of the model solutions was performed at 20 ^{o}C in a reactor from the Heraeus Company (Warsaw, Poland) with a medium-pressure immersion lamp with the power of 150 W for 45 min (Fig. 2). The irradiation was carried out with and without the addition of hydrogen peroxide (H_2O_2) for comparison. The analysed H_2O_2 doses were in the range of 6 to 12 mg/dm^3. Analytical grade 30 % hydrogen peroxide purchased from the Stanlab Company (Gliwice, Poland) was used in this study. It was diluted by 10-fold prior to its use. The samples for the analysis were collected at different times of the process, this is 5, 10, 15, 20, 30 and 45 min. The degree of decomposition of the xenobiotic was assessed by the chromatographic analysis, and the bioluminescence inhibition was assessed by the Microtox® bioassay, which allowed determination of the toxicity of the solution.

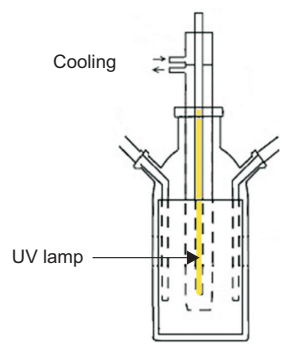

Fig. 2. The scheme of the laboratory UV reactor Heraeus

Results and discussion

The degree of decomposition of the xenobiotic and the change of the bioluminescence inhibition occurring in the solutions during the UV irradiation with and without the addition of hydrogen peroxide H_2O_2 (dose of 9 mg/dm^3) depending on the duration of the process is shown in Figure 3. During the irradiation of water with UV the studied xenobiotic was undergoing decomposition (Fig. 3a). The effectiveness of decomposition of bisphenol A in water increased with time of exposure to UV radiation. For example, after 5 minutes of the process the decomposition of bisphenol A was approx. 38 %, and after 45 minutes approx. 72 %. The observations related to the bioluminescence inhibition in the test solutions were somewhat surprising. The decomposition of bisphenol A did not cause reduction of the bioluminescence inhibition of the solution.

Regardless of the UV irradiation time the bioluminescence inhibition in the test solutions was greater than that specified in the solution before the process. The value of the bioluminescence inhibition depended clearly on the duration of the process. The highest value of this parameter was observed in the sample taken after 45 minutes of the ongoing process (approx. 66 %), in which, paradoxically, the decomposition of

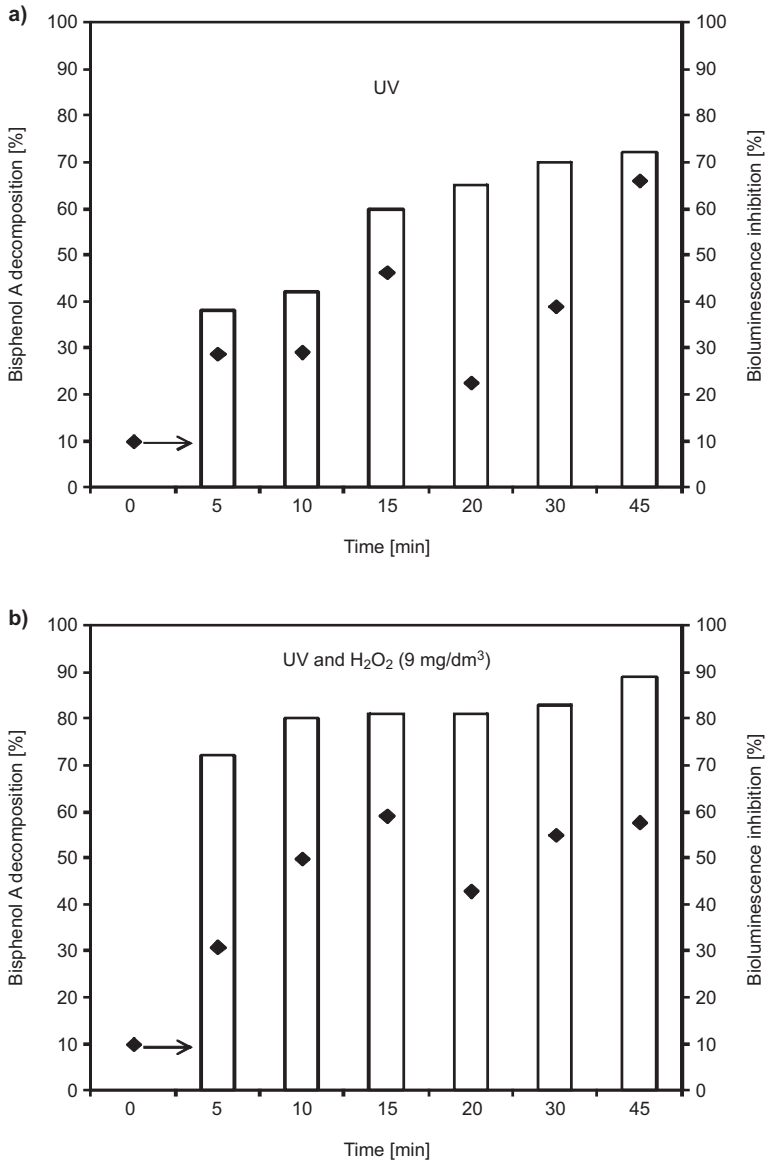

Fig. 3. Decomposition of bisphenol A and change of the inhibition of bioluminescence in solutions irradiated with and without the addition of H_2O_2

bisphenol A was the highest. The difference between the values of the bioluminescence inhibition of the solutions containing the studied compound was already observed in the initial studies (Fig. 1). In contrast, the use of hydrogen peroxide along with UV radiation significantly improved the degree of degradation of the studied xenobiotic, but also resulted in a significant increase in the bioluminescence inhibition of the solutions (Fig. 3b). The increased intensity of xenobiotic degradation was probably the result of the formation of a larger amount of hydroxyl radicals (OH) in the presence of the oxidant. The observed increase in the bioluminescence inhibition during the UV irradiation with and without the addition of hydrogen peroxide H_2O_2 implies the formation of toxic intermediate products of decomposition of the compound, whereas the intensity of this phenomenon was greater when the complex oxidation process with UV and H_2O_2 was applied.

In their earlier work in this field [13] the authors of this paper were testing the feasibility of removing bisphenol A from water using the UV and UV/O_3 process. In this case it was also shown that the decomposition of bisphenol A was greater in the process of coupling irradiation of water and ozonation (ozone dose was 3 mg/dm^3), but the toxicity of the water after the addition of ozone significantly increased. Moreover, in [14] the treated water was containing zearalenone (mycotoxin of estrogenic properties produced by certain *Fusarium* fungi). The paper presented comparatively water ozonation (ozone dose of 1 mg/dm^3, contact time 1 min) and photocatalysis (dose 100 mgTiO_2 catalyst/dm^3, time 5 min). It was shown that both ozonation and photocatalysis allow efficient decomposition of zearalenone in water, but both processes induce formation of by-products during the oxidation of the studied mycotoxin, which was evaluated using GC-MS technique. In terms of the amount of oxidation by-products

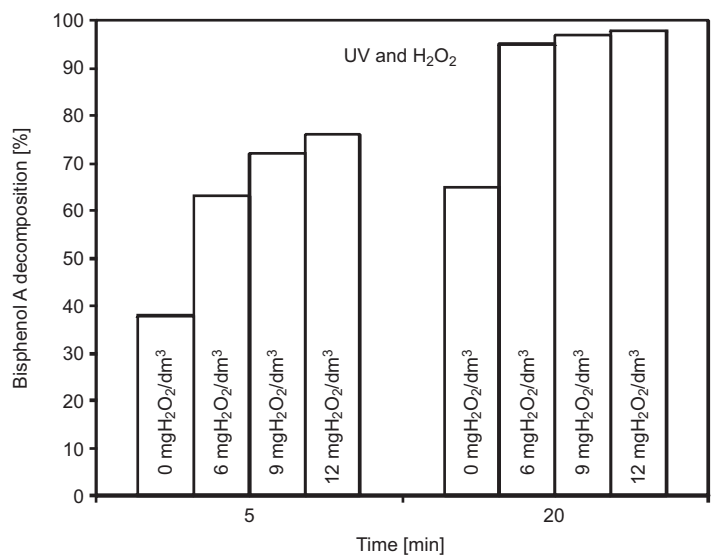

Fig. 4. The dependence of decomposition of bisphenol A in the UV irradiation process of the solution in the function of a dose of H_2O_2 (process time of 5 and 20 min)

water ozonation proved to be more disadvantageous than photocatalysis. However, regardless of the oxidation process and the intensity of the formation of oxidation by-products, the treated water showed no toxic effect.

The observations from previous studies and the results shown in the present study indicate a significant impact of both the oxidation process itself (or a combination of different processes) as well as the type of the removed contaminant on the water toxicity.

Further steps of the present study focussed on assessing the effect of hydrogen peroxide doses on the decomposition of bisphenol A (Fig. 4) and the value of the bioluminescence inhibition of the solutions (Fig. 5a), which was studied at two UV irradiation times, this is 5 and 20 min. Additionally, a toxicity class of the solutions was determined (Fig. 5b).

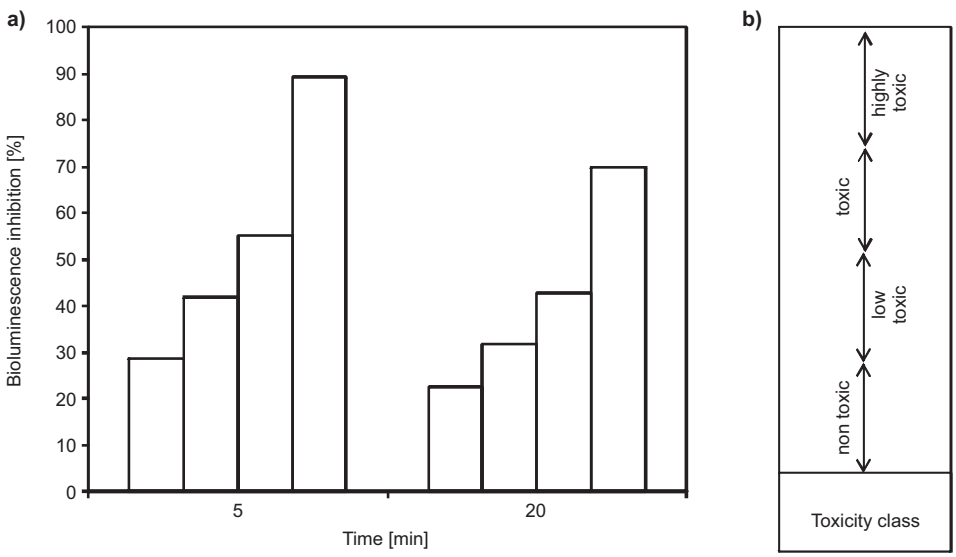

Fig. 5. Changing of the bioluminescence inhibition of the solutions containing bisphenol A in the UV irradiated water in the function of the H_2O_2 dose (a) and their toxicity class (b): time of the process equal to 5 min and 20 min

The increase of the dose of H_2O_2 caused an increase of both the degree of degradation of bisphenol A and the bioluminescence inhibition of the solutions (Fig. 4, Fig. 5a). Comparing the values of the studied parameters for two selected process durations, this is, 5 and 20 min, it can be seen that a longer duration causes the reduction of the toxicity of the solutions (Fig. 5b). However, regardless of the dose of hydrogen peroxide the solutions subjected to the irradiation showed inhibition of vital functions of the bacteria *Vibrio fischeri* at a level of higher than 25 %, even at the longer duration of the process, which classifies them outside the class of non-toxic solutions. Only the solution subjected to the UV irradiation without H_2O_2 for 20 min was found to be non-toxic. Taking the above-mentioned observation into account, it can

be concluded that the selection of the process conditions should be based not only on its effectiveness, but also on the possibility of the occurrence of adverse phenomena.

The applied Microtox® bioassay using the bioluminescent bacteria *Vibrio fisheri* was successfully used for toxicological evaluation of the quality of water containing bisphenol A during the treatment with the coupled oxidation process UV-H_2O_2. Currently, an increasing use of the Microtox® bioassay can be observed in the studies regarding elimination of toxic organic substances from water or waste water [15–18]. Its popularity can be attributed, amongst others, to the fact that this bioassay can be carried out in a very short time. It is a considerable advantage compared to other toxicological bioassays currently used in environmental research.

Conclusions

Based on the results of the present study the following specific conclusions regarding the assessment of the quality of water containing bisphenol A during the UV irradiation with and without the addition of H_2O_2 can be drawn:

– the degree of decomposition of the xenobiotic depended on the time of the UV irradiation,

– the decomposition of the compound did not reduce the bioluminescence inhibition of a given solution, indicating the formation of toxic by-products,

– the combined use of hydrogen peroxide and UV radiation increased the decomposition efficiency of the xenobiotic, but also caused an increase in the bioluminescence inhibition of the solutions,

– the selection of the most favorable conditions for the oxidation process cannot be merely based on the effectiveness of the decomposition of the compound but should also consider the toxicity of the resulting solution.

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ZMIANY TOKSYCZNOŚCI WODY ZAWIERAJĄCEJ BISFENOL A W TRAKCIE JEJ UZDATNIANIA W ZŁOŻONYM PROCESIE UTLENIAJĄCYM

Instytut Inżynierii Wody i Ścieków
Politechnika Śląska w Gliwicach

Abstrakt: Wodę zawierającą bisfenol A poddano napromieniowaniu UV (zanurzeniowa lampa średniociśnieniowa o mocy elektrycznej 150 W) bez i z dodatkiem H_2O_2 (dawka 6–12 mg/dm^3). Do kontroli jakości wody zastosowano biotest Microtox® wykorzystujący bakterie bioluminescencyjne *Vibrio fisheri*. Określono, że rozkład bisfenolu A zależał od czasu napromieniowania UV jak i dawki H_2O_2. Zaskakujące z kolei były obserwacje związane z wartością inhibicji bioluminescencji w badanych roztworach. Rozkład związku nie powodował obniżenia wartości inhibicji bioluminescencji charakteryzującej roztwór, co wskazuje na powstawanie toksycznych produktów pośrednich. Z kolei łączne zastosowanie nadtlenku wodoru z promieniowaniem UV poprawia stopień rozkładu bisfenolu A, ale jednocześnie powoduje wzrost wartości inhibicji bioluminescencji roztworów. Z tego względu w doborze najkorzystniejszych warunków prowadzenia procesu utleniającego nie można opierać się wyłącznie na skuteczności rozkładu związków, lecz należy również rozważyć toksyczność roztworu poprocesowego.

Słowa kluczowe: bisfenol A, uzdatnianie wody, toksyczność, biotest Microtox®