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PHOTODEGRADATION OF *n*-BUTYLPARABEN IN NATURAL WATER FROM SULEJOW RESERVOIR

FOTODEGRADACJA KSENOBIOTYKU *n*-BUTYLOPARABENU W WODZIE Z ZALEWU SULEJOWSKIEGO

Abstract: Removal of *n*-butylparaben (BP) - a compound which disrupts the endocrine system - from pure water and natural water taken from Sulejow Reservoir was investigated. Target compound degradation was performed using photochemical methods: direct photolysis by UVC irradiation, advanced oxidation in an H_2O_2/UV system and photosensitized oxidation employing a xenon arc lamp as a solar radiation simulator with two sensitizers. In the course of direct photolysis by UVC light (λ = 254 nm) and degradation in the H_2O_2/UV system, no or slight influence of the natural water matrix was observed, respectively. In the case of photosensitized oxidation, the decrease of BP concentration was 15% higher in natural water in comparison to pure water.

Keywords: EDCs, *n*-butylparaben, natural water, H_2O_2/UV system, photosensitized oxidation

The Sulejow Reservoir, from which natural water sample was taken, is a shallow (average depth: 3.3 m), lowland dam reservoir, covering 23 km^2 at full capacity. The reservoir is an important freshwater resource for the city of Lodz [1]. As with most artificial reservoirs, Sulejow Reservoir faces several problems like cyanobacterial blooms, which results in water quality deterioration [2]. To assure proper functioning of the water ecosystem and effective use of the natural potential for self-purification, maintenance of its homeostasis is crucial. The presence of *endocrine disrupting compounds* (EDCs) in industrial effluents and, as a result, in freshwater and drinking water supplies, poses serious environmental concern. Among others, EDCs are responsible for male fish feminization, disruption of sex structure of a population, reduced sperm counts, hermaphroditism, changes in nuptial behavior and vertebrate infertility [3, 4]. An exposure to EDCs affects not only at the individual organism scale, but can influence whole populations. It can lead to a domino effect, causing changes in the trophic network and disturbing the normal functioning of the ecosystem.

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Butylparaben (BP) is a substance widely used as a preservative, mainly in cosmetics, and has been regarded as harmless for a long time. However, a number of reports confirming BP estrogenic activity is rising [5-7]. EDCs can cause harmful effects on wildlife even at very low concentrations [8]. Yamamoto et al [9] reported that the maximum no-effect concentration determined by male medaka VTG assay for *n*-butylparaben was 40 µg dm^{-3} ($2\cdot10^{-7}$ mol dm^{-3}) and the predicted no-effect concentration determined on the basis of conventional acute/chronic tests was 8.0 µg dm^{-3}. Therefore, there is a need for an effective method for BP removal from water to be found.

In natural water bodies BP undergo slow biodegradation with half-live times ranging from 9.5 to 16 h (temperature range 20÷28°C) [10]. The chlorination of *n*-butylparaben solution by addition of 2.0 mg dm^{-3} chlorine as sodium hypochlorite (NaClO) for 15 min caused a decrease in BP initial concentration (C_0 = $5.15\cdot10^{-7}$ M) by 67% [9]. Still, the formation of halogenated by products of parabens in chlorinated water was found [11]. The batch sunlight photolysis of *n*-butylparaben conducted by Yamamoto et al [10] revealed the low efficiency of the process: the post-treatment aqueous concentration remained as high as 90% of the initial concentration ($C_0 = 5.15\cdot10^{-7}$ M) after 50 h exposure. Photolysis by UVC irradiation (254 nm) also was found to be inefficient, with a quantum yield equal to only 0.003 [12]. Far better results were obtained applying advanced oxidation processes. The rate constant for reaction of hydroxyl radicals with BP has a value on the order of $4.8\cdot10^{9}$ dm^3 mol^{-1} s^{-1} [13]. BP reaction with singlet oxygen generated during photosensitized oxidation also leads to the target compound decay [14].

Further investigation concerning BP decay methods is required. The main stress should be placed on compound degradation from natural waters. The main goal of our study was the investigation of how natural water influences BP degradation by UVC irradiation, H_2O_2/UV and photosensitized oxidation.

Materials and methods

Chemicals

Butylparaben (> 99%) (BP), humic acid, *tert*-butanol and sodium azide (99%) were purchased from Fluka, hydrogen peroxide (30%) from POCH, Poland, aluminium *phthalocyanine chloride* tetrasulfonic acid (mixture of regioisomers, PC) from Frontier Scientific and *Meso-tetra(4-sulphonatophenyl)porphin* (TPPS) from Sigma-Aldrich, and used as received. Water was purified using a Millipore Milli-Q Plus System (> 18.2 MΩ).

Sample preparations

Two basic matrices for preparation of BP solutions were used: Milli-Q water and *natural water* (NW). The acidity of the Milli-Q water solution was adjusted by adding phosphate buffer: Na_2HPO_4 - KH_2PO_4 (p.a. POCH, Poland). For more details, see [12, 14]. Natural water samples were collected in June 2009 from the Sulejow Reservoir, situated in central Poland in the middle course of the Pilica River. Water for chemical analyses was filtered through Whatman GF/F (0.45 µm) filters and stored at 4°C before use. The characteristics of NW are shown in Table 1.

Table 1

Characteristic data of natural water (Sulejow Reservoir)

Parameter		**Value**
pH		8.11
DOC [mg dm^{-3}]		6.85
Cations [mg dm^{-3}]	Li^+	0.003
	Na^+	6.509
	NH_4^+	0.044
	K^+	9.795
	Mg^{2+}	0.969
	Ca^{2+}	34.024
Anions [mg dm^{-3}]	F^-	0.112
	Cl^-	12.343
	NO_2^-	0.025
	NO_3^-	0.46
	Br^-	0.007
	PO_4^{3-}	0.003
	SO_4^{2-}	21.727

Irradiation experiments

Two experimental setups were used, with UVC or xenon arc lamps as a source of light. For UVC direct photolysis and the H_2O_2/UV system, low pressure (LP) lamps (Luzchem) emitting mainly at the wavelength $\lambda = 254$ nm were employed. The tested solutions were irradiated in a merry-go-round device with quartz test tubes (10 cm^{-3}), placed between two exposure panels, each of them consisting of three 7.2 W lamps. Calculated on the basis of actinometric experiments with uranyl oxalate [15], the photon flux rate entering the reaction space equaled $1\cdot10^{-5}$ einstein dm^{-3} s^{-1}.

For photosensitizing oxidation experiments an immersion xenon arc lamp (XBO, 100 W, Osram) located in a quartz well with cooling jacket was used. The lamp was surrounded by five plate reactors ($V = 0.1$ dm^3), each placed 11 cm from the light source. A single reactor consisted of two glass plates (10 cm × 6 cm) bound with silicone seal in such a way that the distance between the inner surfaces of the plates was 0.3 cm. The tested solutions were aerated and agitated by gas bubbling.

BP solutions at a concentration of $8\cdot10^{-5}$ mol dm^{-3} in distilled water (buffered in order to obtain pH 8) and in natural water were used. For BP degradation analysis in the H_2O_2/UV system an experimentally determined optimal amount of hydrogen peroxide equal to 0.01 mol dm^{-3} [12] was added to the reaction solution. TPPS and PC at their optimal concentration ($C_0 = 2\cdot10^{-5}$ M) [14] were used as a sensitizers.

Analytical methods

BP decay in reaction solution was monitored by HPLC-UV using a Waters apparatus. Analysis was performed with a Waters Nova-Pak C_{18} column (3.9 mm × 150 mm) using mobile phase consisting of a degassed mixture of methanol and water acidified with 0.01% orthophosphoric acid at a constant flow 1 cm^3 min^{-1}. The details of HPLC analysis for BP are reported elsewhere [12, 14]. UV spectra were recorded on a Unicam UV 300 spectrophotometer. The *dissolved organic carbon* (DOC) measurements were performed on a HACH IL 550TOC-TN apparatus. The ion concentrations were determined by an ion chromatograph (Dionex model ICS) on an IonPac CS18 (for cations) and an IonPac AS18 (for anions).

Results and discussion

For studies on photochemical degradation, the absorption spectrum of the target compound and lamp emission spectra are important factors. Figure 1 presents BP and NW absorption spectra at pH equal to about 8, overlayed against emission spectra of arc xenon and UVC lamps. Both BP and natural water constituents absorb light in the lamps' emission ranges, what is necessary for photolysis to take place. In alkaline solution BP absorbs at two wavelengths, corresponding to undissociated particles with maxima at λ = 256 nm and to the BP anionic form at λ = 297 nm.

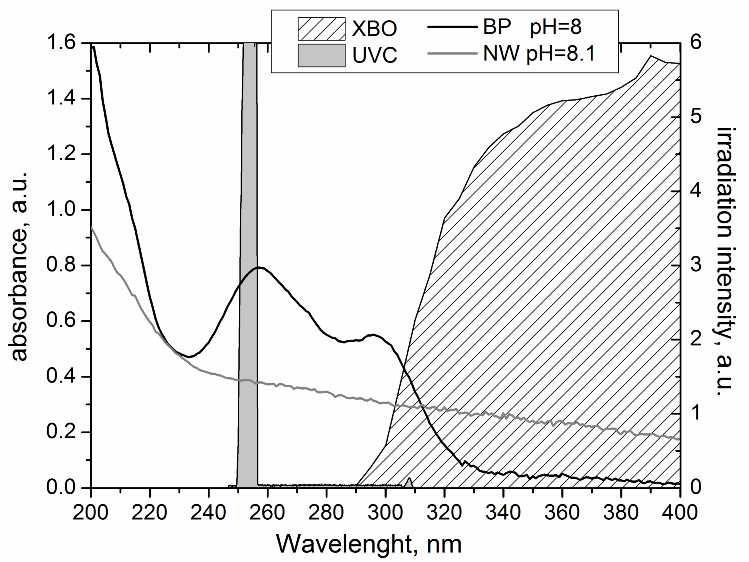

Fig. 1. Absorption spectra of BP (pH = 8, $C_{BP} = 8 \cdot 10^{-5}$ M) and natural water overlayed against emission spectra of xenon (XBO) and UVC lamps used in experiments

Experiments with low pressure lamp

Figure 2 shows the relative changes of BP concentration during photolysis (Fig. 2A) and in the H_2O_2/UV system (Fig. 2B). The influence of dissolved organic matter on direct photolysis of BP was negligible. Moreover, the additional amounts of humic acids (4.4 mg dm^{-3}) or nitrate(V) (4 mg dm^{-3}), did not influence BP degradation rate (Fig. 2A).

Many aquatic constituents, such as humic acids (HA) and NO_3^- can have an influence on compound degradation course. Dual effect of HA and Cl^- presence in water solution was observed - they may as well promote as inhibit reaction course [16]. In the presence of dissolved organic matter and NO_3^- in water, the generation of additional $^{\bullet}OH$ under light conditions can take place [17]. However, the photolysis of solutions containing nitrates in the presence of the hydroxyl radical scavenger (*tert*-butanol) indicated that species capable of increasing the reaction rate are not generated. It can be explained by the low radiation absorption, at λ = 254 nm, of NO_3^- [18]. Moreover, Gloslan et al [19] found that UVC photolysis do not lead to organic matter degradation.

BP degradation in H_2O_2/UV system (Fig. 2B) can take place through direct photolysis or reaction with hydroxyl radicals generated during hydrogen peroxide photolysis. A slight increase of reaction rate under natural water conditions in comparison with decay in pure water was observed. Degradation in water from Sulejow Reservoir can be slightly accelerated by species generated as a result of dissolved organic carbon photolysis or its reaction with H_2O_2.

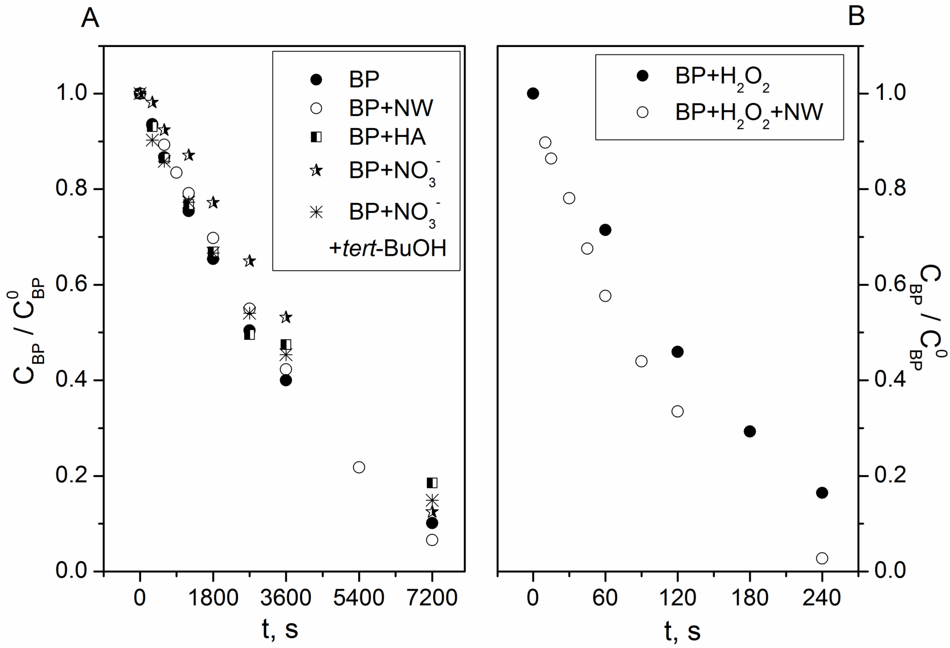

Fig. 2. Changes of relative BP concentration during degradation in natural water (NW) solution and in pure water without and with the additives: humic acid (HA, 4.4 mg dm^{-3}), nitrate(V) ions (NO_3^-, 4 mg dm^{-3}), NO_3^- and *tert*-butanol (0.1 mol dm^{-3}) and in natural water (NW) solution under UVC lamp irradiation (A). Evolution of relative BP concentration in H_2O_2/UV system as a function of irradiation time under buffer or natural water conditions (B). $C_{BP}^0 = 8\cdot10^{-5}$ M; $E_0 = 1\cdot10^{-5}$ einstein dm^{-3} s^{-1}, pH = 8

Experiments with xenon arc lamp

For BP photosensitized oxidation two sensitizers: TPPS and PC with different durability but similar quantum yield of singlet oxygen generation were used [20]. Absorption of UV radiation by sensitizer results in excited state, which initiates organic compounds degradation. Excited sensitizer can react either with oxygen, which leads to singlet oxygen or superoxide radical anion generation or directly with target compound.

An increase of photosensitized oxidation in natural water from Sulejow Reservoir in comparison with buffered pure water solution (pH = 8) was observed (Fig. 3). As shown in Figure 3A, after two hours of irradiation in the presence of TPPS 77% conversion in pure water and 93% of BP initial concentration reduction under natural water conditions was achieved. Also in photosensitized oxidation with PC as a sensitizer, increase of BP depletion in natural water (80%) in comparison with pure water solution (66%) was observed (Fig. 3B).

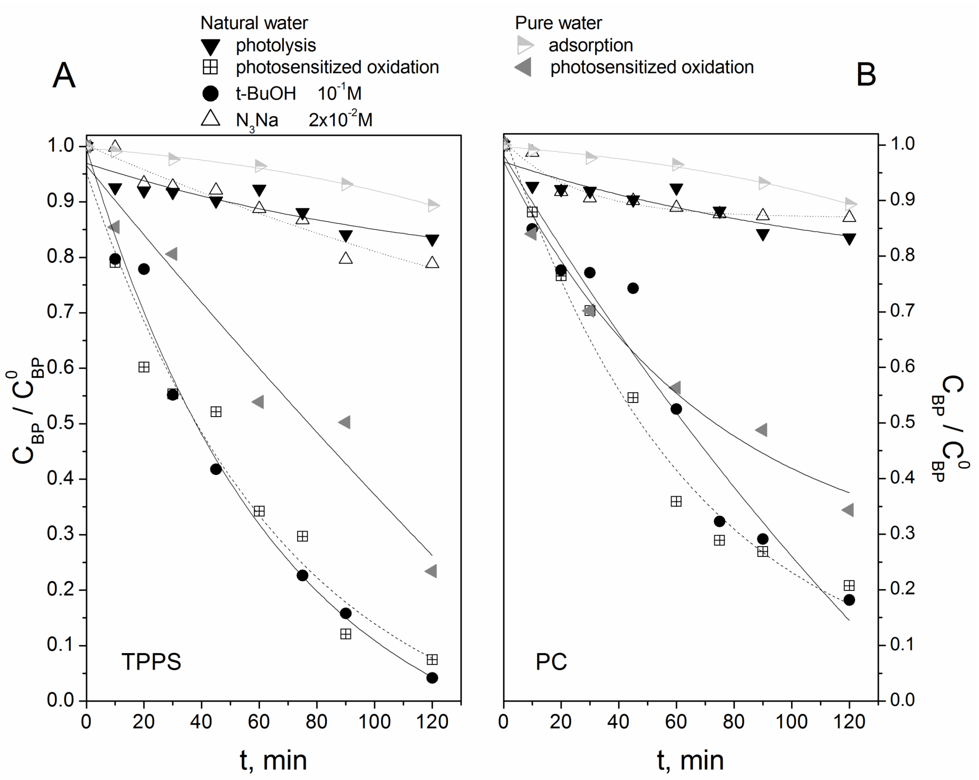

Fig. 3. Changes of the BP relative concentration during photosensitized oxidation in natural water (pH = 8.1) and buffer pure water (pH = 8) solution in presence of TPPS ($C^0 = 2 \cdot 10^{-5}$ mol dm^{-3}) (A) and PC ($C^0 = 2 \cdot 10^{-5}$ mol dm^{-3}) sensitizers. $C_{BP}^0 = 8 \cdot 10^{-5}$ M; $E_a = 1.30 \cdot 10^{-6}$ einstein dm^{-3} s^{-1}

An important factor which needs to be taken into consideration in the case of our photosensitized oxidation experiments was reactors construction, where the adsorption of BP on silicone seal can occur. Preliminary studies showed that BP concentration decrease caused by its adsorption on silicone seal equal about 10% after 2 hours (Fig. 3). Moreover, BP anionic forms undergo direct photolysis under xenon arc lamp irradiation (Fig. 1).

Therefore, during photosensitized oxidation the reduction of BP concentration in pure and natural water should be diminished by 15÷18%.

The difference in the degree of BP degradation during photosensitized oxidation (about 15%) was probably caused by substances present in natural water, which increase BP decay. It is known that absorption of ultraviolet and visible radiation by dissolved organic matter (DOM) in aerated solution leads to a *reactive oxygen species* (ROS) such as singlet oxygen (${}^1O_2$), superoxide radical anion (${}^{\bullet}O_2^-$) hydroxyl radicals (${}^{\bullet}OH$) and peroxyl radicals ($ROO^{\bullet}$) generation [21, 22]. These species participate in the BP degradation causing an increase of the reaction rate.

Experiments conducted during photosensitized oxidation in the presence of hydroxyl radical scavenger - *tert*-butanol permitted to exclude the participation of hydroxyl radicals. However, experiments with addition of sodium azide - physical quencher of singlet molecular oxygen indicated that singlet oxygen plays a dominant role in BP degradation (Fig. 3).

DOM, in particular humic acids, are known as a natural sensitizer and plays a key role in the intensification of BP degradation. Nevertheless, it was estimated that only from 1 to 3% of the absorbed by humic substances solar radiation energy is used for singlet oxygen generation [23]. Therefore, we can assume that also other constituents present in Sulejow Reservoir water could accelerate BP degradation.

Conclusions

Analysis of experimental results allowed us to come to the following conclusions:

1. The most efficient BP degradation method was the reaction in the H_2O_2/UV system.
2. The presence of natural constituents in water taken from Sulejow Reservoir did not influence on direct photolysis by UVC and slightly increase BP depletion rate in H_2O_2/UV system.
3. The course of BP photosensitized oxidation was accelerated under natural water conditions.
4. BP degradation during photosensitized oxidation, both in pure water and in natural water from Sulejow Reservoir, is a result of reaction with singlet oxygen.

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FOTODEGRADACJA KSENOBIOTYKU *n*-BUTYLOPARABENU W WODZIE Z ZALEWU SULEJOWSKIEGO

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Abstrakt: W pracy przedstawiono badania degradacji *n*-butyloparabenu, ksenobiotyku zakłócającego pracę gruczołów wydzielania wewnętrznego w roztworach wody destylowanej i w wodzie naturalnej, pochodzącej z Zalewu Sulejowskiego. Reakcję rozkładu prowadzono metodami fotochemicznymi na drodze fotolizy promieniowaniem lampy UVC, bez i w obecności nadtlenku wodoru oraz poprzez fotosensybilizowane utlenianie z użyciem dwóch sensybilizatorów i lampy ksenonowej imitującej promieniowanie słoneczne. Przebieg fotolizy oraz utleniania w układzie H_2O_2/UV prowadzony w buforowanej wodzie destylowanej i w wodzie naturalnej praktycznie się nie różni. Natomiast proces fotosensybilizowanego utleniania w wodzie naturalnej przebiega ze zwiększoną szybkością, pozwalając uzyskać w tym samym czasie reakcji o około 15% wyższą redukcję zanieczyszczenia.

Słowa kluczowe: ksenobiotyki, butyloparaben, fotoliza, układ H_2O_2/UV, fotosensybilizowane utlenianie, woda naturalna