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Comparison of two photosensitizers Al(III) phthalocyanine chloride tetrasulfonic acid and *meso*-tetrakis(4-sulfonatophenyl)porphyrin in the photooxidation of *n*-butylparaben

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ABSTRACT

A visible light-sensitized oxidation of endocrine disrupter–*n*-butylparaben (BP) in the presence of Al(III) phthalocyanine chloride tetrasulfonic acid and *meso*-tetrakis(4-sulfonatophenyl)porphyrin photosensitizers was studied. The major role of singlet oxygen in BP degradation was proved by the experiments performed in the presence of hydroxyl radicals scavengers and singlet oxygen quenchers. Direct interactions between BP and triplet state of both were investigated using time resolved technique. The rate constants of singlet oxygen quenching by BP in D_2O buffer (pD 7, 9 and 10.8) for $TPPS_4$ and $AlPcS_4$ were determined. The efficiencies of BP photodegradation applying both photosensitizers were compared under various process parameters i.e. initial photosensitizer concentration, oxygen content and pH of reaction solution.

1. Introduction

Parabens, esters of p-hydroxybenzoic acid have been used as preservatives in foodstuffs, pharmaceuticals, cosmetics and personal care products since the 1920s [1]. These compounds are stable and effective in a wide range of pH and depending on ester group in parabens demonstrate different solubility and various spectrum of antimicrobial activity. The increase of the alkyl chain length in parabens' ester group causes decrease of water solubility and raises oil solubility [1]. The investigated *n*-butylparaben (BP) is listed among the compounds suspected of the endocrine disrupting activity by US National Institute of Environmental Health Science (NIEHS) and World Wildlife Fund (WWF). The application of BP is regulated by the U.S. Environmental Protection Agency (EPA) under the Toxic Substances Control Act. U.S. Food and Drug Administration has also approved the use of BP as synthetic flavoring substance and adjuvant (21 CFR 172.515) in foods at minimum required quantity to produce intended effect, e.g. to beverages in amounts not exceeded 20 ppm (21 CFR 172.515). The estrogenic effects of parabens were extensively investigated [1,2]. Among widely used parabens BP showed the highest estrogenic activity [2]. Despite the widespread usage of BP and potent health impact the literature giving attention of its removal from waters and wastewaters is scarce [3,4]. Advanced oxidation processes often used for degradation of water contaminants at low concentrations, are also employed for endocrine disruptors (EDCs) decomposition [5,6]. An interesting option among the photochemical processes suitable for EDCs removal appears to be the photooxidation by singlet oxygen [3,7,8].

The singlet oxygen $^1O_2$, short-living, highly oxidative species can be generated by photosensitized reaction i.e. by energy transfer from an excited photosensitizer to oxygen molecule (type II, [9]). Energy transfer from the excited triplet state of the photosensitizer (PS) to the ground state (triplet) oxygen is a spin allowed process, coupled with spin inversion of oxygen to singlet oxygen $^1O_2$. Alternatively, the hydrogen or electron transfer between excited triplet photosensitizer and a target compound initiate radical reaction (type I). The photosensitized reactions mainly in a proper solvent containing dissolved oxygen, photosensitizer and a target molecule have reached many applications since after the energy transfer the photosensitizer goes back to ground state and is ready to re-absorb the next photon. This process may occur

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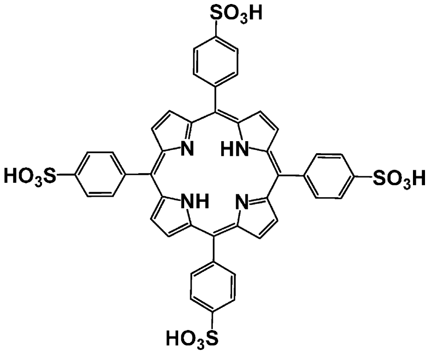
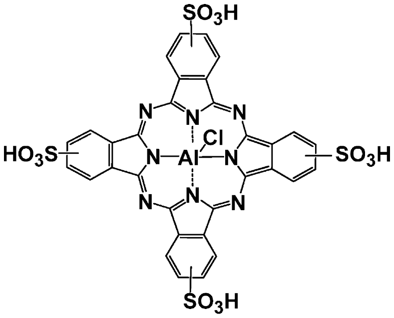
Table 1
Photophysical properties of uses photosensitizers.

$TPPS_4$	$AlPcS_4$
	
$C_{44}H_{30}N_4O_{12}S_4$	$C_{32}H_{16}AlClN_8O_{12}S_4$
934.99 $\mathrm{g\,mol^{-1}}$	895.19 $\mathrm{g\,mol^{-1}}$
$\phi_\Delta = 0.62$[a] [10]	$\phi_\Delta = 0.34$[a] [12]
$\phi_T = 0.78$[a] [11]	$\phi_T = 0.44–0.28$[b] [13]
$\varepsilon_{413\,\mathrm{nm}} = 359{,}000\ \mathrm{M^{-1}\,cm^{-1}}$[a]	$\varepsilon_{351\,\mathrm{nm}} = 52{,}166\ \mathrm{M^{-1}\,cm^{-1}}$[a]
$\varepsilon_{515\,\mathrm{nm}} = 13{,}500\ \mathrm{M^{-1}\,cm^{-1}}$[a]	$\varepsilon_{677\,\mathrm{nm}} = 125{,}500\ \mathrm{M^{-1}\,cm^{-1}}$[a]

[a] Determined in water.
[b] Determined in various solvents.

periodically until the photosensitizer undergoes photobleaching. Usually photosensitizer, before being degraded by $^1O_2$ or other processes, can produce 10^3–10^5 molecules of singlet oxygen [9].

There are several groups of UV–vis absorbing molecules (natural or synthetic) showing ability to produce singlet oxygen. The photosensitizer should exhibit the following properties: (i) long lifetimes of the sensitizer triplet state (more than 1 μs [9]); (ii) high quantum yield of the triplet state formation ($S_1 \rightarrow T_1$), it has to be greater than the other channels of excited singlet state PS deactivation (florescence, internal conversion); (iii) energy of the triplet state of the photosensitizer should be higher than the energy of the singlet oxygen ($E_T > 95\ \mathrm{kJ\,mol^{-1}}$); (iv) high absorption coefficient and high photostability.

The compounds of porphyrin and phthalocyanine moiety are widely used as photosensitizers in photodynamic therapy [14–16]. $TPPS_4$ and $AlPcS_4$ have been reported to be powerful photosensitizers used in the photodegradation of toxic substances in aqueous solutions [17,18]. The photosensitizing properties of $TPPS_4$ and $AlPcS_4$ are collected in Table 1. The aim of the study was to compare the effectiveness of chosen two photosensitizers in photodegradation of BP.

2. Experimental

2.1. Photoreactor

Experiments were conducted in a semibatch mode in two reactors presented schematically in Fig. 1. The experiments with $AlPcS_4$ were performed in a glass tank reactor of the capacity of 1.2 $\mathrm{dm^3}$ (1). In the centre of the reactor a glass well was placed for immersion of xenon lamp (100 W, XBO OFR, Osram). Reactor and the well were equipped with cooling jacket to maintain constant

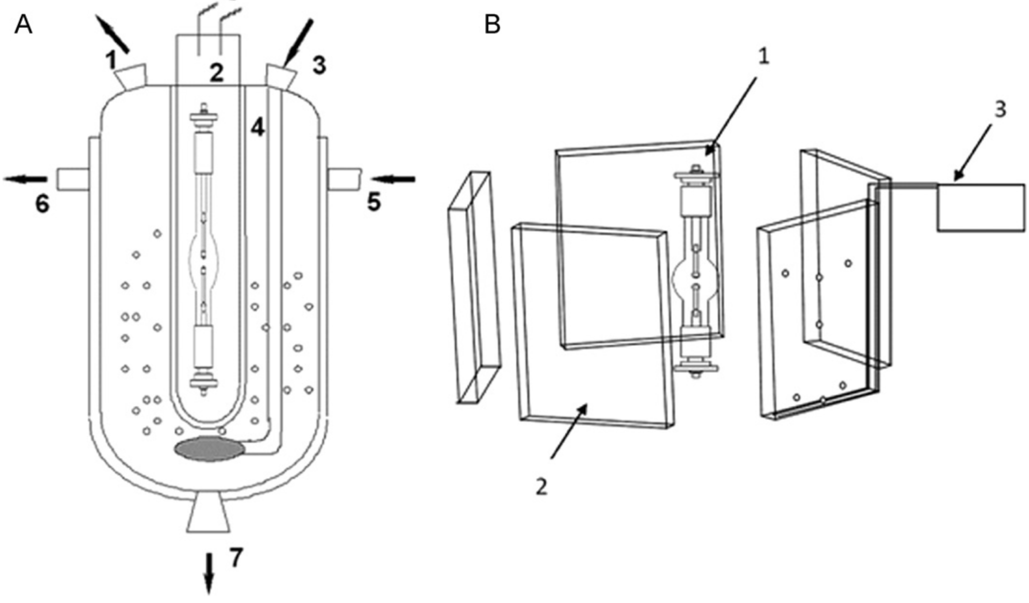


Fig. 1. (A) Scheme of tank photoreactor: 1, sampling port; 2, xenon lamp; 3, gas inlet; 4, glass well; 5, cooling water inlet; 6, cooling water outlet; 7, valve outlet; (B) scheme of plate photoreactors: 1, xenon lamp; 2, plate reactor; 3, peristaltic pump.

temperature 20 °C. The distance between the well and the inner reactor wall was 3 cm.

Experiments with $TPPS_4$ were performed in the series of five flat plate reactors made from optical glass symmetrically positioned around the lamp (2). The distance between the inner walls of the plate reactor was 0.3 cm and the capacity of the reactor amounts to $0.01\,dm^3$.

The photon flux entering the reaction space was measured using Reinecke's actinometer for wavelengths ranging from 310 to 770 nm [19]. The calculations gave the fluence rate E_0 equal to 3.91×10^{19} quanta $s^{-1}\,dm^{-3}$ and 1.95×10^{20} quanta $s^{-1}\,dm^{-3}$ for reactors (1) and (2), respectively.

2.2. Chemicals and analytical methods

Meso-tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$, Fluka), Al(III) phthalocyanine chloride tetrasulfonic acid (a mixture of regioisomers, $AlPcS_4$, Frontier Scientific), and *n*-butylparaben (>99%, BP, Fluka) were used as received.

The experiments were carried out in phosphate buffer solutions (NaH_2PO_4–K_2HPO_4; p.a. POCH, Poland) for pH 5–8 and in carbonate buffer (Na_2CO_3–$NaHCO_3$, p.a. POCH, Poland) for pH 9–10.8. The BP stock solution (10^{-2} M) was prepared in methanol (p.a. POCH, Poland). The reaction solution was prepared from proper amount of stock solution, evaporating methanol and adding buffer and photosensitizer. All solutions were prepared in distilled water additionally treated in Millipore Milli-Q Plus system. The reaction solution was aerated by gas bubbling (air, oxygen or nitrogen). The samples for analysis were taken regularly in time. When reaction underwent at pH above 8, the samples were acidified with 0.5 M sulfuric acid (p.a. POCH Gliwice). The BP decay was monitored by HPLC apparatus (Waters) with a UV diode array detector. The chromatograph was equipped with a Nova-Pak 150/C18 column. A mixture MeOH–acidified water (0.1% H_3PO_4) was used as a mobile phase. For the first 12 min of the analysis the mobile phase consisted of water, over the next 8 min eluent was changed to MeOH/water in the ratio 70:30 (v/v) and this composition of eluent was maintained for the last 10 min of the analysis. Detection wavelength was 257 nm. The eluent flow rate was constant and equal to $1\,cm^3\,min^{-1}$. The absorption spectra were measured in a 1 cm quartz cell on UNICAM spectrophotometer. The initial reaction rates were calculated by differentiating exponential curve that fitted experimental points (C, t) at the correlation factor higher than 0.97.

2.3. Time-resolved measurements

The samples were excited by a FL 3002 dye laser ($\lambda_{exc} = 425$ nm for $TPPS_4$, $\lambda_{exc} = 672$ nm for $AlPcS_4$, output energy 0.1–3 mJ/pulse, pulse width ~28 ns) pumped by a COMPEX102 XeCl excimer laser (both Lambda Physik). The time profiles of the triplet states of sensitizers were probed using their absorption at 460 nm ($TPPS_4$) and 490 nm ($AlPcS_4$) with a 150 W Xe lamp with pulse unit on LKS20 laser kinetic spectrometer (Applied Photophysics). The formation of singlet oxygen $^1O_2$ was followed using time-resolved near-infrared phosphorescence at 1270 nm. The time-resolved phosphorescence was monitored with a Ge diode (Judson J16-8SP-R05M-HS) after passing by a 1270 nm band-pass filter (Laser Components, Olching, Germany). The signal from the detector was collected in a 600 MHz oscilloscope (Agilent Infiniium) and transferred to a computer for further analysis. Individual traces were accumulated 200 times to improve the signal-to-noise statistics. The samples were saturated by air or by oxygen, where appropriate, and oxygen was removed from the solution by argon purging.

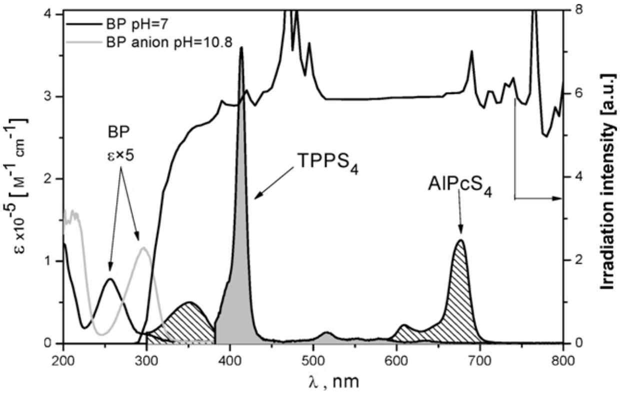


Fig. 2. Emission spectrum of xenon lamp outside the cooling well and absorption spectra of $TPPS_4$, $AlPcS_4$ at pH = 7 and BP at pH = 7 and pH = 10.8.

3. Results and discussion

Porphyrins are characterized by a strong absorption band around 410 nm (Soret band) and weak bands in the range of 510–650 nm (Q-bands). Phthalocyanines showed strong absorption bands around 350 nm (Soret band) and in the range of 600–700 nm (Q-bands). Fig. 2 presents absorption spectra of used photosensitizers with overlapped emission spectra of used xenon lamp. The fluence rate absorbed by photosensitizers solutions at a concentration of 2×10^{-5} M, used in experiments was 3.92×10^{-5} einstein $s^{-1}\,dm^{-3}$ and 5.1×10^{-5} einstein $s^{-1}\,dm^{-3}$ for $TPPS_4$ and $AlPcS_4$, respectively.

The comparison of the emission spectrum of the used lamp and absorption spectrum of BP and BP anion (Fig. 2) indicate the possibility of direct BP phototransformation. It is especially important in alkaline solution (BP $pK_a = 8.24$ [3]) where absorbed photon flux in plate reactor in the range 288–365 nm amounted to 5.93×10^{-8} einstein $s^{-1}\,dm^{-3}$ ($[BP] = 8 \times 10^{-5}$ M) and was higher than the absorbed photon flux for undissociated BP (2.5×10^{-7} einstein $s^{-1}\,dm^{-3}$). For tank reactor calculated photon flux were equal 1.66×10^{-7} and 6.29×10^{-7} einstein $s^{-1}\,dm^{-3}$ in pH 7 and pH 10.8, respectively. In each case these values represent less than 1% of the total number of photon entering the reaction space. However the direct irradiation of BP anion solution did not lead practically to any degradation whereas at pH 7 the BP concentration decreased by about 5% after 1 h irradiation, what was found out in our earlier studies [3].

The increase of $TPPS_4$ and $AlPcS_4$ concentrations resulted in higher initial rate of BP decay, attaining the highest rate at the concentration of about 2×10^{-5} M. Therefore, all next experiments were performed at this concentration. Further increase of photosensitizers concentrations leads to diminishing of BP decay rate probably due to aggregation of photosensitizer, decrease of the efficiency of singlet oxygen formation and consequently BP decomposition rate [11].

The photostability of studied photosensitizers was tested by monitoring the absorption spectra during the time of irradiation. The obtained results indicate a good photostability of $AlPcS_4$ (Fig. 3A). In contrary, the $TPPS_4$ is less photostable probably due to higher quantum yield of singlet oxygen formation responsible for photosensitizers photobleaching. The efficiencies of both photosensitizers in BP degradation were studied in acidic, neutral and alkaline solutions (Fig. 3B). The use of $AlPcS_4$ contributed to complete BP disappearance in alkaline reaction mixture within 2 h. $TPPS_4$ in the same conditions gave 91% reduction of BP initial concentration. In turn, reaction carried out in solution at pH 5 caused decline of BP concentration by about 6% and 27% for $AlPcS_4$ and $TPPS_4$, respectively. In neutral solutions the achieved reduction

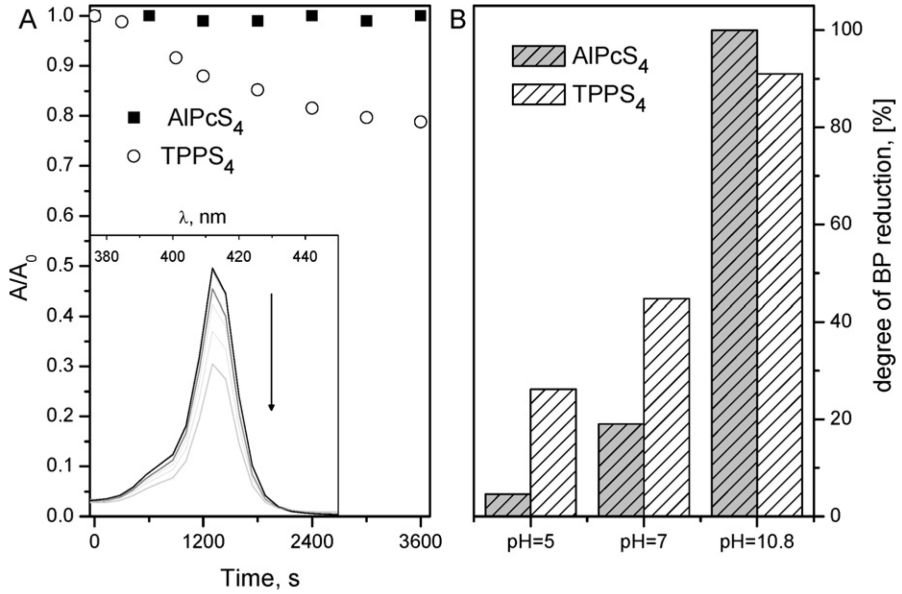


Fig. 3. (A) Changes in the $TPPS_4$ and $AlPcS_4$ relative absorption during irradiation by a xenon arc lamp. ($[AlPcS_4] = [TPPS_4] = 2 \times 10^{-5}$ M), *inset*: variation of the absorption spectra during $TPPS_4$ irradiation at concentration 4×10^{-6} M; (B) comparison of BP concentration reduction for both PS at various pH of the reaction solution ($t = 2$ h; $[AlPcS_4] = [TPPS_4] = 2 \times 10^{-5}$ M; $[BP]_0 = 8 \times 10^{-5}$ M).

level amounts to 20% and 45% for $AlPcS_4$ and $TPPS_4$, respectively. Therefore, in natural waters (pH = 5–9) the use of $TPPS_4$ seems to be more effective than $AlPcS_4$.The rate of photosensitized oxidation upon various BP initial concentration was investigated over BP concentrations in the range of 8×10^{-6}–1.5×10^{-4} M. The results are presented in Fig. 4. The rates of BP decay at pH 10.8 were similar for both PS, despite of the significant difference in quantum yields of singlet oxygen formation by both photosensitizers (Table 1). More pronounced difference in BP disappearance was noticed in the neutral solution (Fig. 4). These observations may indicate on stronger interaction of excited $AlPcS_4$ with BP than with BP anion.The next series of experiments were performed with the goal to explain this observation. The total singlet oxygen quenching rate constant (physical + chemical) by BP was determined. These constants, k_t, were calculated for both photosensitizers measuring the lifetime of singlet oxygen $^1O_2$ luminescence in the absence (τ_0) and presence (τ) of BP according to Stern–Volmer equation:

$$\tau^{-1} = \tau_0^{-1} + k_t[\mathrm{BP}] \quad (1)$$

Experiments were carried out in D_2O at different pD values: 7, 9 and 10.8 (Fig. 5). The application of heavy water enabled to perform easier measurements and to transfer observed dependences into aqueous solutions. The intercept of these plots corresponds to the singlet oxygen lifetime in the D_2O equal to 52 ± 3 μs. The k_t

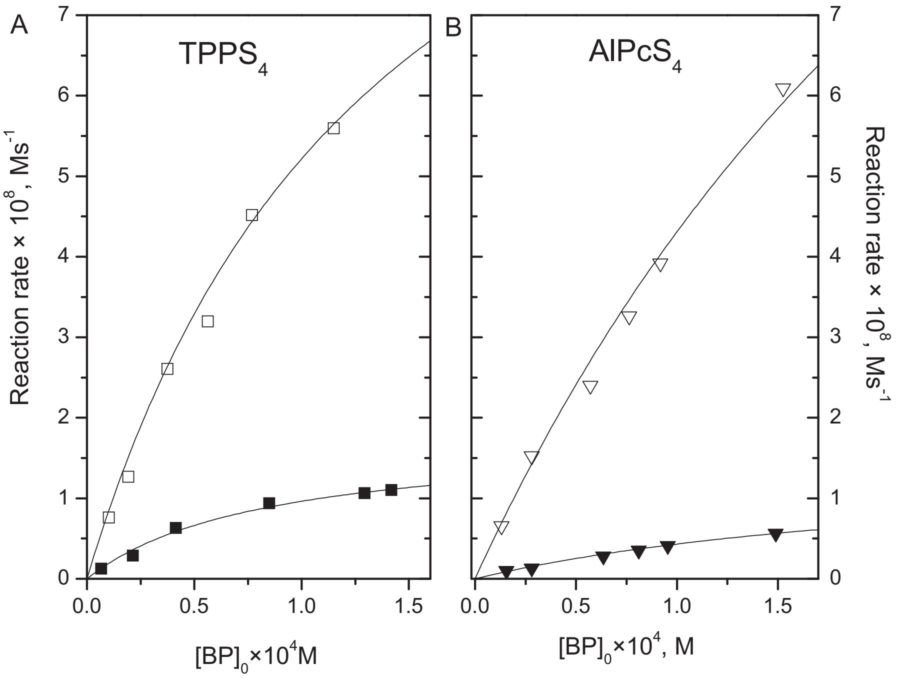


Fig. 4. Dependence of reaction rate on initial BP concentration at pH 7 (filled symbols) and at pH 10.8 (empty symbols) for two photosensitizers: (A) $TPPS_4$ and (B) $AlPcS_4$ ($[AlPcS_4] = [TPPS_4] = 2 \times 10^{-5}$ M).

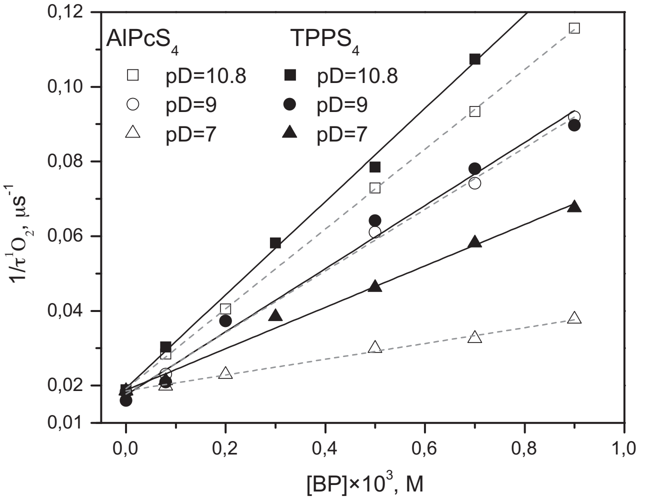


Fig. 5. Stern–Volmer plot of total quenching of singlet oxygen by BP in D_2O buffer (TPPS$_4$ λ_{ex} = 425 nm, AlPcS$_4$ λ_{ex} = 672 nm).

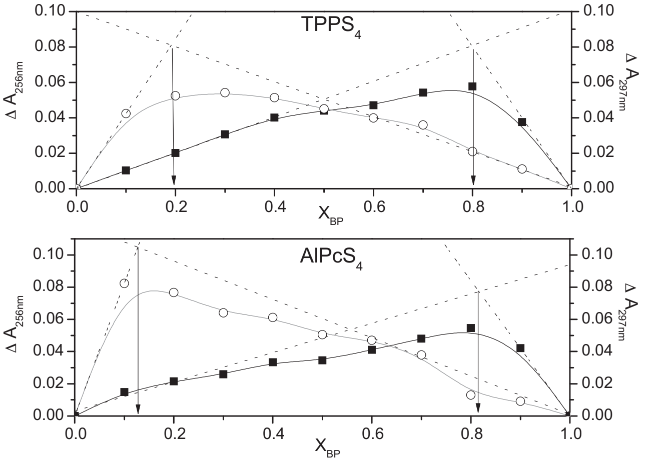


Fig. 6. Job's plots for BP–TPPS$_4$ complexes (top) and BP–AlPcS$_4$ complexes (bottom) at pH 7 (empty symbols) and pH 10.8 (filled symbols).

values were calculated from Eq. (1). The total quenching constants were found to be pD dependent (Table 2). The highest k_t values were obtained at alkaline pD and were lower at neutral pD. At pD 9 singlet oxygen was quenched at the same rate constants for both photosensitizers. But in other cases the $^1O_2$ generated by AlPcS$_4$ causes slower quenching with BP than in the case of TPPS$_4$. The different k_t values in neutral solutions for both photosensitizers can partly explain the different rates of BP decay.

The quenching rate constants of excited photosensitizer with BP and with molecular oxygen were estimated in the next series of experiments. The decay of the triplet states of photosensitizers was monitored directly from the time evolution of the triplet–triplet absorption signals observed at appropriate wavelength 460 nm. The quenching of the triplet state of the TPPS$_4$ by BP took place only in neutral solution giving the value $k_Q^{BP} = (1.2 \pm 0.5) \times 10^6\ M^{-1}\,s^{-1}$. There was no quenching of the AlPcS$_4$ triplet states by BP in both neutral and alkaline solution. The diffusion-controlled quenching rate constants of triplet states of TPPS$_4$ and AlPcS$_4$ by molecular oxygen were determined as $k_Q^{O_2} = (1.77 \pm 0.05) \times 10^9\ M^{-1}\,s^{-1}$, $k_Q^{O_2} = (1.87 \pm 0.01) \times 10^9\ M^{-1}\,s^{-1}$ what is in good agreement with other values found in literature [20,21].

The verification of the possibility of complex formation between a photosensitizer and BP was the subject of the following studies. The stoichiometric ratio of both components in BP–photosensitizer complexes were determined by the Job's method of continuous variation [22]. The method is widely used for elucidating the composition of complexes and is based on the variation of both reagents concentrations (BP and PS) at constant global molar concentration (2×10^{-5} M). The absorbance of series of solutions was measured at the optimum wavelength i.e. 256 nm for neutral solutions and 297 nm for alkaline solutions for both PS. The plots of absorbance against the mole fraction of the BP in the mixture showed maxima at the composition of BP-PS complex (Fig. 6). In neutral solution the maximum of absorbance was observed at a molar ratio of $X_{BP} = 0.2$ and $X_{BP} = 0.1$ for TPPS$_4$ and AlPcS$_4$, respectively. In alkaline solution Job's plot gave a maximum at $X_{BP} = 0.8$ for both photosensitizers. The complex formation constant, K_f, was calculated from the following equation [23,24]:

$$K_f = \frac{A/A_m}{\left[1-(A/A_m)\right]^{n+2}[BP](n)^n} \tag{2}$$

where A and A_m are observed maximum absorbance and the absorbance obtained from the extrapolation of the two tangents to the curve (see Fig. 6), n is the stoichiometry which BP associates with photosensitizer, [BP] is the molar concentration of BP at the maximum absorbance.

Table 2
Comparison of rate constant of singlet oxygen quenching by BP using AlPcS$_4$ and TPPS$_4$.

Photosensitizer	Reaction rate constant, k_t ($M^{-1}\,s^{-1}$)		
	pD = 7	pD = 9	pD = 10.8
TPPS$_4$	$(5.06 \pm 0.2) \times 10^7$	$(8.45 \pm 0.5) \times 10^7$	$(1.15 \pm 0.04) \times 10^8$
AlPcS$_4$	$(2.11 \pm 0.07) \times 10^7$	$(8.36 \pm 0.1) \times 10^7$	$(1.07 \pm 0.01) \times 10^8$

The log K_f value for BP–TPPS$_4$ complexes were found to be 6.96 and 5.49 at pH 7 and 10.8, respectively. For BP–AlPcS$_4$ complexes the log K_f were 7.62 and 5.42 at pH 7 and 10.8, respectively. The results indicated on comparable stability of BP–PS in alkaline solution but in neutral solution the complex of BP with AlPcS$_4$ was more stable than the BP–TPPS$_4$ complex. As can be expected, at pH 7 the higher stability of complex BP–AlPcS4 causes energy dissipating and restricts the access of oxygen. It can probably result in reduction of singlet oxygen generation and can explain slower BP degradation.

The influence of oxygen content in reaction mixture on BP degradation rate was also studied. The reaction solution was purged with oxygen, air and nitrogen. The decrease of oxygen concentration resulted in the decrease of BP decomposition rate and the lack of oxygen stopped the reaction course.

Finally we performed some experiments confirming the dominating role of singlet oxygen in BP photodegradation. The presence in the reaction mixture of azide ion – known water soluble physical quencher of singlet oxygen [25] caused almost complete inhibition of BP degradation (Fig. 7). It was observed at pH 7, 9.2 and 10.8 of the reaction solution what means that reaction with $^1O_2$ was equally important in the decay of BP and its anion. When sodium azide was added in sufficiently high concentration the reaction of BP with $^1O_2$ was completely stopped. In this case the experimental points overlapped the points collected in the BP photolysis experiments. The reaction occurring in the presence of hydroxyl radicals scavengers (*t*-BuOH, isopropanol [26]) did not produce any changes in the reaction run (Fig. 7). The degradation of BP in the presence of superoxide dismutase (SOD), specifically reacted with superoxide anion ($O_2^{\bullet-}$) [27] also does not changed the rate of BP decay. The observed influence of the additives on the BP decay rate indicated on major role of singlet oxygen in this process.

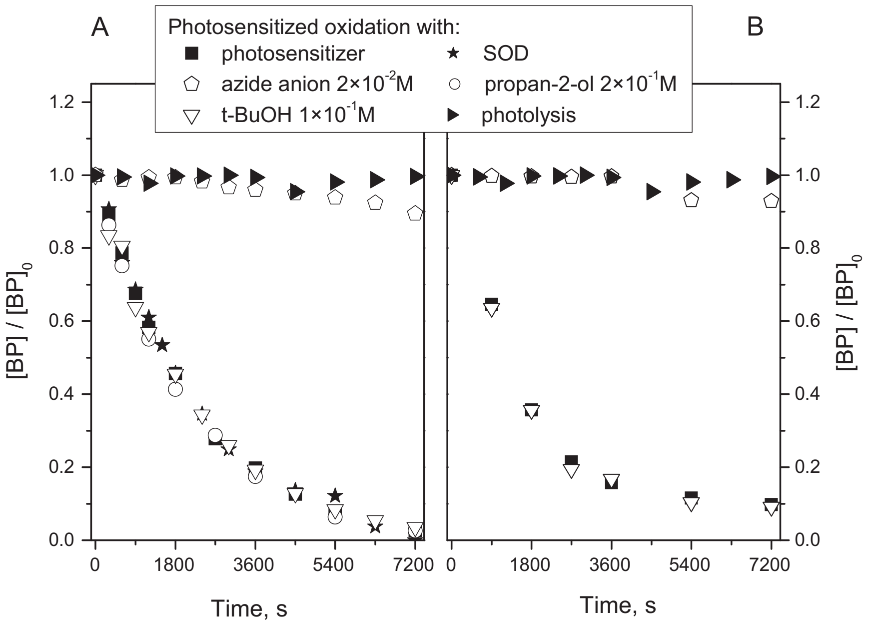


Fig. 7. Decay of BP concentration during photolysis and sensitized oxidation alone using (A) $AlPcS_4$ and (B) $TPPS_4$, and in the presence of additives: sodium azide, *t*-BuOH, propan-2-ol and SOD at pH = 10.8 ($[BP]_0 = 8 \times 10^{-5}$ M, $[AlPcS_4] = [TPPS_4] = 2 \times 10^{-5}$ M).

4. Conclusions

The photosensitized oxidation using $TPPS_4$, and $AlPcS_4$ as a sensitizer can be applied for photodegradation of BP in water solutions. Analysis of experimental results allowed us to come to the following conclusions:

The study showed that each of the photosensitizers was able to generate singlet oxygen that dominating role in the photodegradation of BP was confirmed. The efficiency of BP photodegradation is strongly depended on the initial photosensitizers concentration as well as pH of reaction mixture. The quenching rate constants of excited triplet photosensitizers and singlet oxygen by BP were determined. The formation of a supramolecular complexes of BP and used photosensitizers were found. The higher stability of BP–$AlPcS_4$ complexes in neutral solution is probably responsible in some extent for the lower efficiency of BP degradation in comparison with the photooxidation using $TPPS_4$.

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