Decomposition of xenobiotics during visible light irradiation in the presence of immobilised photosensitisers: kinetics study

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ABSTRACT

The objective of this work was to study the photosensitised oxidation of the xenobiotics benzylparaben (BeP) and 2,4dichlorophenol (2,4DCP) in aqueous solutions using photosensitisers immobilised into chitosan carrier particles and visible light radiation. Zn(II) phthalocyanine tetrasulfonate tetrasodium salt and Al(III) phthalocyanine chloride tetrasulfonic acid were used as photosensitisers. The major role of the singlet oxygen during photodegradation was proven by using scavengers of reactive oxygen species. The influence of initial xenobiotic concentration and temperature on degradation rate was examined. The investigations were focused on kinetics (Langmuir–Hinshelwood model) as well as activation energy determination. Moreover, the adsorption isotherms of BeP and 2,4DCP into chitosan carrier were determined using the Brunauer–Emmett–Teller model.

Key words | adsorption isotherms, immobilised photosensitisers, Langmuir–Hinshelwood model, photosensitised oxidation, singlet oxygen, xenobiotics

INTRODUCTION

Aquatic wildlife is exposed to xenobiotics including natural and synthetic endocrine-disrupting compounds, which cause adverse effects in living organisms. The subjects of this study were compounds with proven hormonal activity, such as 2,4dichlorophenol (2,4DCP) and benzylparaben (BeP). 2,4DCP is used as a pesticide and as a substrate in the production of other compounds, e.g. triclosan, a commonly used antibacterial and antifungal agent (Czaplicka 2006). BeP is used as a preservative in cosmetics, pharmaceuticals and industrial products. Generally, it is used in mixtures with other parabens, which leads to an extended preservative spectrum (Cashman & Warshaw 2005).

In the literature, many reports on the degradation of endocrine-disrupting compounds (Esplugas et al. 2007; Bledzka et al. 2010; Qiang et al. 2013) can be found. In recent years, special attention has been paid to methods applying visible light or natural sunlight (Daskalaki et al. 2011; Prieto-Rodríguez et al. 2013; Chang et al. 2013). Among them, photosensitised oxidation can be distinguished (Pajares et al. 2011; Gmurek et al. 2012; Gmurek et al. 2015). The main reactant formed during this process is the very reactive species singlet oxygen. Photosensitised oxidation requires only molecular oxygen (\(\text{O}_2\)), light of an appropriate wavelength, and a photosensitiser capable of absorbing light and using that energy to excite oxygen to its singlet state. Photosensitised oxidation may occur in homogeneous and heterogeneous systems. The immobilisation of photosensitisers and their application (heterogeneous system) allows them to be easily removed from the reaction system and reused. Zanjanchi et al. (2010) investigated the photodegradation of 2,4DCP using anion sulpho-cobalt phthalocyanine immobilised onto Mobil Composition of Matter No. 41 (MCM-41) in the presence of \(\text{H}_2\text{O}_2\). The application for this process of visible light within 3 h resulted in about a 60% reduction of initial 2,4DCP concentration (Zanjanchi et al. 2010). Meso-tetraphenylporphyrin immobilised onto polyurethane polymer nanofibre is capable of degrading parabens in the presence of visible light and molecular oxygen (Gmurek et al. 2015). One very interesting solution is the immobilisation of photosensitisers into natural carriers like chitosan (Ferrari et al. 2014). Rose bengal immobilised by irreversible covalent bonding to the polymer chitosan was successfully employed in the photodegradation of trihydroxybenzene derivatives in an acidic aqueous solution (Ferrari et al. 2014).

This paper presents a study of the decomposition of xenobiotics (2,4DCP and BeP) during visible light
irradiation in the presence of immobilised photosensitisers. Zn(II) phthalocyanine tetrasulfonate tetrasodium salt (ZnPcS4) and Al(III) phthalocyanine chloride tetrasulfonic acid (AlPcS4) immobilised into chitosan beads were used as photosensitisers. The influence of initial xenobiotic concentration, temperature and the presence of reactive oxygen species scavengers on the degradation rate was examined. The obtained results allowed us to determine the kinetics parameters and activation energy. Moreover, the adsorption isotherms of BeP and 2,4DCP into chitosan carrier were determined using a Brunauer–Emmett–Teller (BET) model.

METHODS

ZnPcS4 and AlPcS4 (a mixture of regioisomers) were purchased from Frontier Scientific. BeP (≥99%), sodium azide (≥99%) (NaN3) and tert-butanol (≥99.7%) (t-BuOH) were purchased from Fluka and 2,4DCP (≥99%) and superoxide dismutase (SOD) were from Aldrich. Chitosan from crab shells (deacetylation degree ≥75%) used for carrier preparation was purchased from Sigma.

The pH of the BeP reaction solution was adjusted by a phosphate buffer to 9 (H3PO4, KH2PO4, Na2HPO4, NaOH, all of p.a. quality; POCh, Poland). All reaction solutions were prepared in distilled water treated additionally in a Millipore Milli-Q Plus System (18.2 MΩ). When necessary, samples for analysis were acidified with 0.5 M phosphoric(V) acid (p.a. POCH, Poland). The 2,4DCP reaction solution was prepared in Milli-Q water (pH = 5.8) and was not buffered.

The experiments were carried out in a heterogeneous system. The chitosan carrier was prepared in the form of beads by the phase inversion method from an aqueous solution of chitosan in acetic acid. The chitosan solution was dropped by needle into NaOH, where coagulation took place. Immobilisation of the photosensitiser (ZnPcS4 for BeP photodegradation and AlPcS4 for 2,4DCP photodegradation) by adsorption was performed.

The experiments were performed in a semi-bath mode in a 0.5 dm³ glass reactor with a cooling jacket, equipped with a porous plate to deliver gas into the reaction solution and external sources of light. Simulated sunlight was used to excite the photosensitisers. To avoid UV light, a high pressure sodium lamp (Lumatek, 600 W, 404.5 ± 0.12 W/cm², 1.48 × 10¹⁷ photons/(cm²·s)) was used as a light source. The experiments were performed in buffered water solutions (BeP) as well as Milli-Q water (2,4DCP) in the temperature range from 4–50 °C. When chitosan carrier was placed into the reactor, the reaction solution was added. The reaction mixture was aerated and mixed by oxygen (99.995%) bubbling.

The reactions progress was monitored by determination of BeP as well as 2,4DCP concentration using a Waters high-performance liquid chromatograph with diode array detector at the wavelengths of 255 nm and 294 nm respectively. Separation was carried out on a Waters Nova-Pak C18 column (3.9 mm × 150 mm) with the mobile phase of methanol–water (70:30, v/v), at a flow-rate of 0.7 cm³/min.

Data analysis was performed using Origin (Microlab Software Inc., USA). The initial reaction rates (r0) were calculated by differentiating the exponential curve that fitted the experimental points (C, t) at a correlation coefficient higher than 0.97.

RESULTS AND DISCUSSION

Preliminary study

At first, the effect of temperature and scavengers of reactive oxygen species on the photosensitised oxidation rate was examined. Figure 1 shows the changes of BeP and 2,4DCP relative concentration versus irradiation time at different temperatures of reaction mixture. The increase of temperature resulted in an increase of degradation rate, and, in the case of the reaction performed at 50 °C, the degradation degree of BeP and 2,4DCP was close to 100% after 5 h.
and 2 h (Figure 1), respectively. It is well known that oxygen solubility in water decreases with increasing temperature, which should result in a decrease of singlet oxygen concentration, as well as a decrease of degradation rate. It should be noted that the lifetime of singlet oxygen in water (3.3, 3.5 and 3.6 μs at 50, 20 and 5 °C, respectively) (Jensen et al. 2010) depends negligibly on temperature. In the case of a heterogeneous system, the temperature effect is much more complex, because besides changes of the physico-chemical properties of the aqueous solution, the change of polymer material properties should be taken into account. The increase of temperature causes an increase of the diffusion coefficient of oxygen in polymer materials (Poulsen et al. 2003), which may influence the better access of oxygen to immobilised photosensitisers, and the acceleration of photosensitised oxidation.

The next series of experiments was performed in the presence of reactive oxygen species scavengers. In order to establish photodegradation pathways, NaN₃ (physical quencher of singlet oxygen (Larkin et al. 2003), t-BuOH (hydroxyl radicals scavenger (Staehelin & Hoigne 1985)) and SOD (superoxide anion radicals scavenger (Afanas’ev 1989)) were used. As seen in Figure 2, the addition of NaN₃ to the reaction solution resulted in the strong inhibition of degradation rate, which proved the major role of the singlet oxygen in the photodegradation. In the case of BeP, the process was slowed down to the adsorption level (Figure 2(a)) and for 2,4 DCP (Figure 2(b)) to the sum of photolysis and adsorption levels. The experiments carried out in the presence of SOD did not cause any changes in the reaction run both for BeP and 2,4DCP, which excluded the participation of superoxide anion radicals in these processes. The use of t-BuOH did not influence the 2,4 DCP decay rate (Figure 2(b)), whereas for BeP, photodegradation was slightly slowed down (Figure 2(a)), which may indicate the participation of hydroxyl radicals in the BeP degradation. However, confirmation of this hypothesis requires further research.

**Activation energy determination**

The temperature dependence of the reaction rate constant can be described by the Arrhenius equation:

\[
\ln (k_\text{z}) = \ln (A) - \frac{E_\text{a}}{R} \left(\frac{1}{T}\right)
\]  

where \(k_\text{z}\) is the pseudo-first-order reaction rate constant dependent on the singlet oxygen concentration, \(A\) is the frequency factor for the reaction, \(R\) is the universal gas constant, and \(T\) is the temperature.

The degradation rate of target compounds can be described by the pseudo-first-order equation:

\[
\frac{dC}{dt} = -k_\text{z}C
\]  

Plots of the integrated form of Equation (2) for different temperatures are presented in Figure 3(a) and 3(b), and the slope of these lines corresponds to \(k_\text{z}\). The results of the pseudo-first-order reaction rate constants were plotted in an Arrhenius diagram (Figure 3(c)). The determined values of the apparent activation energy are equal to 28.22 ± 3.35 kJ/mol and 11.36 ± 1.11 kJ/mol for BeP and 2,4DCP, respectively. These values are rather low but are typical for photochemical reactions (Miller & Olejnik 2001; Błędzka et al. 2012).

**Kinetic study**

Photosensitised oxidation of BeP and 2,4 DCP was carried out in the heterogeneous system by using photosensitisers immobilised into chitosan carrier. Therefore, at the beginning of the kinetic determination, the amount of adsorbed xenobiotics in chitosan was examined. The adsorption isotherms of BeP and 2,4DCP adsorption into the chitosan...
carrier were determined using the BET equation in the linearised form Equation (3). The values of the BET parameters for BeP and 2,4 DCP are presented in Table 1.

\[
\frac{1}{qe(1 - X)} = \frac{1}{q_{\text{max}}} + \left(\frac{1}{q_{\text{max}}K_{\text{RET}}}\right)\left(\frac{1}{X}\right)
\]

where \(X = C^* / C^0\), \(q_{\text{max}}\) is the amount of adsorbed xenobiotic that takes place in a complete monolayer (mol/g), \(q_e\) is the amount of xenobiotic adsorbed into chitosan particles at equilibrium (mol/g), \(C^*\) is the saturated solubility of xenobiotic in water, and \(C^0\) is xenobiotic equilibrium liquid-phase concentration. \(K_{\text{RET}}\) is the equilibrium constant that characterises the interaction energy of the adsorbate with the surface of the adsorbent.

Figure 4(a) and 4(b) show the influence of the initial concentration of the target compound on photosensitised oxidation: the increase of this process parameter resulted in an increase of initial reaction rate, both for BeP and 2,4 DCP.

The kinetics of the photosensitised oxidation in the heterogeneous system can be described by the Langmuir–Hinshelwood (L–H) model, which assumes that the reactions take place at the carrier surface and the reaction rate is proportional to the fraction of the surface covered by the reactant. This model has been successfully adopted to describe BeP photosensitised oxidation in a heterogeneous system using meso-tetraphenylporphyrin immobilised in a polyurethane nanofibre material (Gmurek et al. 2015), as well as for the description of 4-chlorophenol degradation in an aqueous solution using an electrospun polystyrene fibre incorporating zinc phthalocyanine (Zugle et al. 2012).

The simplified L–H model (Equation (4)) can be used to explain the relation between the initial reaction rates and the xenobiotics concentration after adsorption equilibrium has been achieved.

\[
r_0 = \frac{dC_0}{dt} = \frac{k_{\text{LH}}KC_0}{1 + KC_0}
\]

where \(k_{\text{LH}}\) is the apparent reaction rate constant, and \(K\) is the dynamic equilibrium constant of xenobiotics adsorption into chitosan particles.

The L–H kinetic constants (\(k_{\text{LH}}, K\)) can be determined using a linearised form of the L–H model:

\[
\frac{1}{r_0} = \frac{1}{k_{\text{LH}}} + \frac{1}{Kk_{\text{LH}}}\left(\frac{1}{C_0}\right)
\]
The L–H model describes the experimental data fairly well (Figure 4(a) and 4(b)), and can be used for prediction of process performance. The orders of magnitude of the determined apparent reaction rate constants ($k_{LH}$) are comparable to literature data (Zugle et al. 2012; Gmurek et al. 2015). The value of $k_{LH}$ for BeP and 4-chlorophenol photosensitized oxidation in a heterogeneous system using different immobilised photosensitisers is equal to $1.077 \pm 0.043 \times 10^{-8}$ M/s (Gmurek et al. 2015) and $5.5 \times 10^{-9}$ M/s (Zugle et al. 2012), respectively. The dynamic equilibrium constant of xenobiotics adsorption into specified carriers ($K$) is strongly linked to the carrier material, and is equal to $14,552 \pm 582$ 1/M (Gmurek et al. 2015) and $2,480$ 1/M (Zugle et al. 2012) for BeP and 4-chlorophenol, respectively.

**CONCLUSIONS**

Photosensitised oxidation using immobilised photosensitisers and visible light radiation is an efficient method for BeP and 2,4 DCP degradation. Singlet oxygen plays a major role in the degradation of the investigated compounds. The initial reaction rate increases with increasing temperature and initial xenobiotics concentration. The most important parameter seems to be temperature, proving that the process can occur in winter as well as high summer.

The determined values of activation energy are low but typical for photochemical reactions. The L–H model describes the experimental data well, and can be used to predict the photo-process performance.

**ACKNOWLEDGEMENTS**

This work was supported by the National Science Centre (NCN) in Poland within research project no. 2012/07/B/ST8/03787. Marta Gmurek acknowledges support from the Foundation for Polish Science within the START scholarship.

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First received 26 July 2016; accepted in revised form 4 October 2016. Available online 19 October 2016.