PHOTOLYTIC DEGRADATION OF 4-TERN-OCTYLPHENOL IN AQUEOUS SOLUTION

4-tern-octylphenol (OP), the endocrine disrupting compound, in aqueous solution was degraded by polychromatic UV lamp. It was found that the rate of OP depletion depends on light intensity, pH of the reaction mixture, initial compound concentration and the presence of natural water constituents. Nitrate addition seemed to give the best results in terms of OP decay rate. The time of 50% OP degradation in the presence of NO₃⁻ (2 mg l⁻¹) was about 8 times shorter in comparison to degradation without any additives.

1. INTRODUCTION

A great number of contaminants emitted to the natural environment are responsible for harmful effects on ecosystems. Some of the anthropogenic chemicals have been proven to affect the endocrine systems of vertebrates and invertebrates by mimicking their hormones (LINTERMANN et al. 2003, CAMPBELL et al. 2006). Causing changes, among others, in reproductive systems (feminization effect), endocrine disrupting compound (EDCs) influence not only single organisms but may also cause disturbances at the level of whole populations.

One of the predominant EDCs are alkylphenol ethoxylates (APEs) and their metabolites (nonylphenol and octylphenol). They are widespread in the environment and have been detected worldwide in surface waters, effluents of sewage treatment plants, sediments, soil, air and organism tissues (e.g., YING et al. 2002, OSPAR 2006, QUEDNOW and PUTTMANN 2008). APEs are non-ionic surfactants which have been widely used in a variety of industrial, household and commercial applications for over...
60 years (GADZALA-KOPCIUCH et al. 2008). Moreover 4-tert-octylphenol is used in production of phenol/formaldehyde resins (OSPAR 2006).

The worldwide average production of APEs reach 390,000 Mg/year (LINTERMANN et al. 2003). In the UK alone 16,000–19,000 Mg of APEs are consumed annually, of which 6,500 Mg (37%) are estimated to be released into the aquatic environment (BLACKBURN 1995, NING 2007). In wastewater treatment plants as well as in the environment, APEs are fairly quickly biodegraded by removal of ethoxy groups, producing more persistent products: alkylphenols such as nonylphenol, octylphenol and alkylphenol mono-, di- and triethoxylates. The low solubility of these products as well as the presence of a benzene ring are responsible for their relatively low level of microbial degradation (LINTERMANN et al. 2003, YING et al. 2002, NING et al. 2007). Octylphenols concentrations measured in surface waters had values up to 0.43 μg l⁻¹. In waste waters from industrial and municipal sewage treatments plants octylphenol content was in the range from 0.17 μg l⁻¹ to 9 μg l⁻¹, and occasionally up to 195 μg l⁻¹ (OSPAR 2006). The contaminant was also found in drinking water (0.06 μg l⁻¹) (GIBS et al. 2007).

Research on biodegradation of octylphenol within the water phase revealed that its half-life varies between 7 and 50 days. In anaerobic sediments, however, octylphenol is not biodegradable (JOHNSON et al. 2000). The low solubility of octylphenol and octanol-water partition coefficient (logKOW) value (table 1) leads us to assume that contaminant tends to bind to organic matter in sediments. Measurements showed that sediments can contain up to several hundred times more octylphenol than the corresponding surface water (YING et al. 2002).

From the APEs group of compounds 4-tert-octylphenol has the greatest estrogenic potency. Although 4-tert-octylphenol is about 1500 times less potent than 17β-estradiol (NING et al. 2007a) its tendency to accumulate in sediments and bioaccumulate in the lipids of water organisms (FERREIRA-LEACH and HILL 2001) together with its widespread emission by industry force us to take this compound under consideration as a high risk pollutant.

4-tert-octylphenol is included in the EU list of 66 substances with documented endocrine-disrupting effects. Moreover, with the decision of the UE Council on establishing a list of priority substances in the Water Framework Directive (WFD) in 2001, it is one of 33 priority substances, with the status of ‘priority substances under review’.

Analyses regarding mitigation strategies of octylphenols impact on ecosystems are required. As the main route of wildlife exposure to these chemicals is through water (YING et al. 2002) methods of 4-tert-octylphenol removal from water solutions need to be investigated and developed. Conventional processes in municipal wastewater treatment plants seem to be inefficient for octylphenol removal (NING et al. 2007b). Water treatment processes such as absorption or membrane processes allow only for the separation of contaminants from the flow, which leaves the problem of waste dis-
Photolytic degradation of 4-tert-octylphenol

As an alternative method of octylphenol removal from water and effluents, photolysis and advanced oxidation processes (AOPs) appear to have positive effects.

### Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Information</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C_{14}H_{22}O</td>
<td>–</td>
</tr>
<tr>
<td>Chemical structure</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>–</td>
</tr>
<tr>
<td>Molecular weight (g mol(^{-1}))</td>
<td>206.33</td>
<td>–</td>
</tr>
<tr>
<td>Physical State</td>
<td>white crystal powder</td>
<td>–</td>
</tr>
<tr>
<td>Water Solubility</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.34×10(^{-5}) M at 25 °C</td>
<td>Bergfeld &amp; Co, 2005</td>
</tr>
<tr>
<td></td>
<td>6.11×10(^{-5}) M at 20 °C</td>
<td>Ahel and Giger, 1993a</td>
</tr>
<tr>
<td></td>
<td>4.8×10(^{-5}) M at room temp.</td>
<td>Brand et al., 2000</td>
</tr>
<tr>
<td></td>
<td>2.7×10(^{-5}) M at room temp.</td>
<td>Mazellier and Leverd, 2003</td>
</tr>
<tr>
<td>Acid dissociation constant (pK(_a))</td>
<td>10.33</td>
<td>UNEP, 1995</td>
</tr>
<tr>
<td></td>
<td>10.39</td>
<td>This work</td>
</tr>
<tr>
<td>Octanol-water partition coefficient (log K(_{OW}))</td>
<td>5.28</td>
<td>Bergfeld &amp; Co, 2005</td>
</tr>
<tr>
<td></td>
<td>4.12</td>
<td>Ahel and Giger, 1993b</td>
</tr>
<tr>
<td>Absorption coefficient (ε)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>at 222 nm: ε = 7700 l mol(^{-1}) cm(^{-1})</td>
<td>Brand et al., 2000</td>
</tr>
<tr>
<td></td>
<td>at 277 nm: ε = 1700 l mol(^{-1}) cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>at 222 nm: ε = 7180 l mol(^{-1}) cm(^{-1})</td>
<td>Mazellier and Leverd, 2003</td>
</tr>
<tr>
<td></td>
<td>at 277 nm: ε = 1560 l mol(^{-1}) cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>at 254 nm: ε = 480 l mol(^{-1}) cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>at 222 nm: ε = 7820 l mol(^{-1}) cm(^{-1})</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>at 277 nm: ε = 1760 l mol(^{-1}) cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>at 254 nm: ε = 675 l mol(^{-1}) cm(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

In the available literature we can find examples of 4-tert-octylphenol degradation by simulated sunlight radiation (POPA et al. 2007), UV irradiation at 253.7 nm and by an H\(_2\)O\(_2\)/UV process (MAZELLIER and LEVERD 2003), oxidation reactions photoinduced by Fe(III) (BRAND et al. 2000), photocatalytic degradation on TiO\(_2\) (YAMAZAKI et al. 2008) and decay by ozone in direct and indirect reaction (NING et al. 2007a, NING et al. 2007b). Nevertheless, the degradation of 4-tert-octylphenol in aqueous solution by direct photolysis has not so far been fully investigated. Although the efficiency of direct photolysis in comparison to AOPs is relatively low, it still provides a background for most advanced oxidation processes. Moreover, direct photolysis is important in terms of drinking water treatment because the process does not require any
additives to be introduced into the water. Photochemical technology is simple and clean, cost-effective in many applications, and often gives the dual benefits of both environmental contaminant treatment and disinfection.

The purpose of our research was to study photolytic degradation of 4-tert-octylphenol in aqueous solution when exposed to UV irradiation. The influence of different reaction parameters such as pH of the reaction solution, initial concentration of substrate and the photon flux on the decay rate was investigated. Additionally, the degradation rates in the presence of additives (humic acids or nitrate) occurring in natural waters were studied.

2. MATERIALS AND METHODS

4-tert-octylphenol (OP) was purchased from Fluka (purity $\geq$ 90%) and used after recrystallization. The main characteristics of OP are presented in table 1. Stock solutions of the compound were prepared by dissolving OP in methanol. Aqueous solutions of OP were made by introducing a proper volume of stock, evaporating alcohol and dissolving compound in Milli-Q water (18.2 M$\Omega$ cm at 25 °C) or buffer. The solution was treated in an ultrasonic bath in order to speed up dissolution. Afterwards the aqueous solutions of OP were placed in quartz tubes and irradiated in a merry-go-round device (figure 1).
Experiments were carried out using the medium-pressure lamp TQ 150 (150 W, Heraeus, Hanau) placed in a quartz well with cooling jacket. Actinometry experiments were conducted using uranyl oxalate (MUROV et al. 1993). The calculated photon flux ranged from \(4.05 \times 10^{-5}\) einstein l\(^{-1}\) s\(^{-1}\) to \(2.02 \times 10^{-4}\) einstein l\(^{-1}\) s\(^{-1}\).

The OP concentrations were determined by HPLC with a UV detector (Waters). Analysis were performed on a Waters Nova-Pak C\(_18\) column (3.9 mm\(\times\)150 mm) using mobile phase consisting of a degassed mixture of acetonitrile and water (65/35%, v/v) acidified with H\(_3\)PO\(_4\) (0.01%). All separations were carried out at ambient temperature (25 °C). The flow rate was maintained at 1 ml min\(^{-1}\). Spectrophotometric diode array detector was used and analyses were done at a wavelength of 225 nm. Absorption spectra of OP were determined using a UNICAM UV 300 spectrophotometer.

Reagents used during analysis were: phosphate buffer, range: 6-12 (Na\(_2\)HPO\(_4\), KH\(_2\)PO\(_4\), NaOH; POCH, Poland), humic acid (Fluka) and nitrate (KNO\(_3\), POCH). The solutions of humus and nitrate were prepared according to OECD standards (OECD, 2000).

3. RESULTS AND DISCUSSION

4-\textit{tert}\-octylphenol is weakly soluble in aqueous solution. The water solubility of OP was determined to be about \(4.5 \times 10^{-5}\) mol dm\(^{-3}\) under our experimental conditions at room temperature, which is consistent with published data (table 1). Determined on the basis of absorption spectra of OP at various pH an acid dissociation constant \(pK_a\) had value 10.39.

![Absorption spectra of OP in buffer solution (\([\text{OP}]_0 = 2.4 \times 10^{-5}\text{M}\)) overlayed against the medium-pressure lamp emission spectra in near ultraviolet](image-url)
For UV degradation experiments the absorption spectrum of the target compound is an important factor. Direct photolysis can take place when the emission spectrum of the light source overlaps the target substance absorption spectrum. Figure 2 presents an extinction coefficient ($\varepsilon$) of OP in neutral (pH = 7) and alkaline (pH = 12) solution overlayed against the medium-pressure lamp emission spectra. At neutral and acid pH the compound absorbs in the ultraviolet region in two bands, with maxima at 222 nm ($\varepsilon = 7817 \text{ l mol}^{-1} \text{cm}^{-1}$) and 277 nm ($\varepsilon = 1757 \text{ l mol}^{-1} \text{cm}^{-1}$). The values are similar to those obtained by BRAND et al. (2000) and MAZELLIER and LEVERD (2003) (table 1). For alkaline pH the absorption spectra of OP is shifted toward longer wavelength and magnified. The absorption maxima in this spectra are at 238 nm ($\varepsilon = 11400 \text{ l mol}^{-1} \text{cm}^{-1}$) and 293 nm ($\varepsilon = 2700 \text{ l mol}^{-1} \text{cm}^{-1}$).

3.1. THE INFLUENCE OF THE UV IRRADIATION INTENSITY

The reaction rates of photolytic degradation resulting from different irradiation intensities were investigated. Variations in light intensity were obtained by changing the distance between the lamp and the merry-go-round device. As the intensity of light increases the particles absorb more energy. Thus their kinetic energy increases, and there are more productive collisions. Due to this the rate of reaction increases (figure 3). The rates of OP degradation were calculated from the slope of the disappearance curves. Under our experimental conditions the dependence of the initial reaction rate of OP degradation versus irradiation intensity has a rectilinear character.

![Fig. 3. Evolution of relative OP concentration as a function of irradiation time. Inset: Dependence of initial reaction rate of OP degradation versus irradiation intensity ([OP]$_0$ = 2.4 × 10$^{-5}$M; pH = 7)](image-url)
3.2. THE INFLUENCE OF pH

The rate of photolytic reactions is often affected by the pH of the solution. The rate of OP decay was investigated in buffer solutions at pH 6, 7 and 12. Figure 4 presents the changes in normalized OP concentration during the reaction for various pH values. The slowest reaction rate was observed at pH 7. 45 minutes of irradiation under experimental conditions results in approximately 95% OP concentration reduction at pH 6 and 12 whereas at pH 7 depletion reached only 70%. The increase of the reaction rate in alkaline media can be explained by increased extinction coefficient ($\varepsilon$) value of OP anion ($pK_a = 10.39$). Additionally, at pH 12 the OP absorption spectra better overlap the UV source emission spectra (compare figure 2). A better understanding of OP degradation kinetics at different pH requires further experimentation.

![Fig. 4. Changes of relative OP concentration versus irradiation time for various pH values of reaction solution ($[\text{OP}]_0 = 2.4 \times 10^{-5}$ M; $I_0 = 1.28 \times 10^{-4}$ einstein l$^{-1}$ s$^{-1}$)](image)

3.3. THE INFLUENCE OF OP INITIAL CONCENTRATION

Figure 5 shows the variation in relative OP concentration upon different initial OP concentrations. A typical relationship between OP amount and initial reaction rate was observed – reaction rate value increases along with an increase of the target substance concentration. The observed reaction rate increases in direct photolysis can be explained by higher light absorption followed by a higher reactant concentration. Similar events are reported by MILLER and OLEJNIK (2001).
3.4. THE INFLUENCE OF COMMON WATER CONSTITUENTS

The substances commonly occurring in natural waters as nitrate ions and humic acids can influence the photolytic reactions. Figure 6 shows the effect of these additives on photodegradation of ocyphenol.

The presence of humus in the reaction solution caused a decrease in the OP decomposition rate. Humic acids absorb light in the near ultraviolet range and in consequence acts as an inner filter for the UV light.

Although nitrate also absorbs UV light, the photolysis of the constituent in the 200–400 nm region results in the OH\(^*\) radical formation, as shown below (MACK & BOLTON (1999), NEAMTU and FRIMMEL (2006) (eqs. (1)–(5)):

\[
\begin{align*}
\text{NO}_3^- \xrightarrow{hv} & \text{NO}_2^- + \text{O}^* \quad (1) \\
\text{NO}_3^- \xrightarrow{hv} & \text{O}^{**} + \text{NO}_2^- \quad (2) \\
2\text{NO}_2^* + \text{H}_2\text{O} & \xrightarrow{} \text{NO}_2^- + \text{NO}_3^- + 2\text{H}^+ \quad (3) \\
\text{O} + \text{H}_2\text{O} & \xrightarrow{} 2\text{OH}^* \quad (4)
\end{align*}
\]

Fig. 5. Changes of relative OP concentration versus irradiation time for its various initial concentrations. Inset: Dependence of initial reaction rate of OP degradation versus its initial concentration 
\((I_0 = 1.28 \times 10^{-4} \text{ einstein l}^{-1} \text{ s}^{-1}; \text{pH} = 7)\)
Photolytic degradation of 4-tert-octylphenol

\[ \text{O}^* + \text{H}_2\text{O} \rightarrow \text{OH}^* + \text{HO}^- \]  \hspace{1cm} (5)

Occurrence of hydroxyl radicals in the reaction solution leads to an increase of OP degradation rate.

![Graph showing the influence of additives (humic acids, nitrate) on OP degradation versus irradiation time](image)

Fig. 6. Influence of additives (humic acids, nitrate) on OP degradation versus irradiation time ([OP]₀ = 2.4 \times 10^{-5} \text{ M}; I₀ = 1.28 \times 10^{-4} \text{ einstein l}^{-1} \text{ s}^{-1})

3.5. PHOTOPRODUCT FORMATION

HPLC analysis allowed us to follow formation of one OP degradation product. Other authors found that during the OP degradation processes 4-tert-octylcatechol was one of the main degradation products (Mazallier and Leverd 2003, Brand et al. 2000) and the only product detected in HPLC method (Mazallier and Leverd 2003). Moreover 4-tert-octylcatechol was identified as a metabolite of OP decay in the fish tissue (Ferreira-Leach & Hill (2001)) and rat liver (Nomura et al. 2008). Kinetics of OP photolytic degradation corresponding to product formation under our experimental conditions are shown in Figure 7. The photoproduct was more polar than the compound of interest and its UV-VIS spectrum obtained from the diode array detector showed two maxima around 222 nm and 282 nm, which is similar to Mazallier and Leverd (2003) observations made for the product recognize as 4-tert-octylcatechol. Still confirmation that in our reaction matrix main photoproduct is 4-tert-octylcatechol and determination of other products demands more accurate analytical methods.
3.6. KINETICS

In direct photolysis of organic compounds reaction progression is caused by light absorption by the target substance. In order to undergo photochemical transformation, light energy should be adsorbed by the compound to produce an electronically excited state molecule. Moreover chemical transformations of the excited state should be competitive with deactivation processes (equations (6)–(8). The resultant excited state molecule reacts to form new species. The concentrations of the products obtained during this reaction depend on the concentration of the reactants and the UV dose.

\[
\begin{align*}
OP + h\nu & \rightarrow OP^* \quad r_1 = k_1 I_a \\
OP^* & \rightarrow OP \quad r_2 = k_2 C^* \\
OP^* & \rightarrow \text{products} \quad r_3 = k_3 C^*
\end{align*}
\]

Considering reactions (6)–(8) for OP degradation we obtain the following equation:

\[
\frac{dC}{dt} = k_1 I_a - k_2 C^*
\]

where:
$r$ – the initial reaction rate $[\text{M s}^{-1}]$,  
$\varphi$ – the quantum yield of OP decay,  
$I_a$ – the intensity of absorbed irradiation $[\text{einstein l}^{-1} \text{s}^{-1}]$,  
$C$ – the compound concentration $[\text{M}]$,  
$k$ = reaction rate constant.

Applying the pseudo-stationary assumption for the excited OP molecules concentration we obtain:

$$k_1 I_a = k_2 C^* + k_3 C^*$$  \hspace{1cm} (10)

After combination and rearrangement of the equation (9) and (10) we obtain:

$$r = -\frac{dC}{dt} = \frac{k_1 k_2 I_a}{k_2 + k_3} = \varphi I_a$$  \hspace{1cm} (11)

where

$$\varphi = \frac{k_1 k_2}{k_2 + k_3}$$  \hspace{1cm} (12)

As OP-related products in fact absorb in lamp emission spectra, ignoring this effect allows us to obtain the so called apparent quantum yield. Estimated from our experimental conditions, the average apparent quantum yield had a value of $0.020 \pm 0.003$. The order of magnitude of the calculated quantum yield value is consistent with the literature (Mazallier and Leverd 2003, Brand et al. 2000).

4. CONCLUSION

The 4-tert-octylphenol degradation was observed under medium-pressure lamp irradiation. The evaluated quantum yield of direct photolysis ($\text{pH} = 7; I_0 = 1.28 \times 10^{-4}$ einstein $1^{-1} \text{s}^{-1}$) for the degradation of OP in aqueous solution by polychromatic UV light (range 250–600 nm) had a value of $0.020 \pm 0.006$. The rectilinear dependence of reaction rate vs. irradiation intensity and reaction rate vs. initial OP concentration was observed. Addition of humic substances into the experimental solution was found to slow down the degradation, while the presence of another common water constituent – nitrate ion – effectively accelerated the reaction rate. Explanation of the OP degradation mechanism under polychromatic irradiation requires further investigation.

ACKNOWLEDGEMENTS

This work was sponsored by Polish Ministry of Science and Higher Education from resources for science in 2006–2009 as the research project No. N207 032 31/1438.
REFERENCES

[7] FERREIRA-LEACH A.M.R., HILL E.M., Bioconcentration and distribution of 4-tert-octylphenol residues in tissues of the rainbow trout (Oncorhynchus mykiss), Marine Environmental Research, 2001, 51, 75–89.