Photo-degradation of butyl parahydroxybenzoate by using TiO₂-supported catalyst

Patrick Atheba, Patrick Drogui, Brahima Seyhi and Didier Robert

ABSTRACT

The present work evaluates the potential of the photocatalysis (PC) process for the degradation of butylparaben (BPB). Relatively high treatment efficiency was achieved by comparison to photochemical process. Prior to photocatalytic degradation, adsorption (AD) of BPB occurred on the titania dioxide (TiO₂)-supported catalyst. AD was described by Langmuir isotherm ($K_L = 0.085 \text{ L g}^{-1}$, $q_m = 4.77 \text{ mg g}^{-1}$). The influence of angle of inclination of the reactor, pH, recirculation flow rate and initial concentration of BPB were investigated. The PC process applied under optimal operating conditions (recirculation flow rate of 0.15 L min⁻¹, angle of inclination of 15°, pH = 7 and 5 mg L⁻¹ of BPB) is able to oxidize 84.9–96.6% of BPB and to ensure around 38.7% of mineralization. The Langmuir–Hinshelwood kinetic model described well the photocatalytic oxidation of BPB ($K = 7.02 \text{ mg L}^{-1} \text{ h}^{-1}$, $K = 0.364 \text{ L mg}^{-1}$).

Key words | adsorption, advanced oxidation process, butylparaben, kinetic, photocatalysis, TiO₂-supported

INTRODUCTION

Parabens are antimicrobial agents, antifungalicidal agents and antioxidants widely used in the cosmetic, pharmaceutical and food industries (Nicoli et al. 2008; Gryglik et al. 2009; Tay et al. 2010). Recent studies have shown the estrogenic effect of parabens; in particular, propylparaben and butylparaben (BPB) adversely affect the secretion of testosterone and the function of the male reproductive system in rats and mice (Terasaka et al. 2006; Nicoli et al. 2008; Bledzka et al. 2009). It has been proved that parabens are able to easily penetrate the skin (Akomeah et al. 2004; Nanayakkara et al. 2005; El Hussein et al. 2007) and to reach unmodified the underlying tissues and the systemic circulation (Soné et al. 2005; Nicoli et al. 2008). Parabens are frequently found in aquatic environments because of their broad application (Radovan et al. 2008; Bledzka et al. 2009). The concentrations of parabens in wastewaters are in the range of ng L⁻¹ to µg L⁻¹ (Terasaki et al. 2012). Recent studies demonstrated that parabens are biodegradable, with half-lives lower than 3 days (Gonzalez-Marino et al. 2011; Fan & Wang 2012). However, it has been shown that conventional wastewater treatment plants release organic pollutants such as parabens into aquatic environments (Gomez et al. 2008; Kasprzyk-Hordern et al. 2008; Bledzka et al. 2009). The parabens are found in wastewater treatment plant effluents and river water samples at a concentration level up to 0.085 µg L⁻¹ (Terasaki et al. 2012).

Many techniques are used such as chemical oxidation, biological oxidation, adsorption (AD), membrane filtration, advanced oxidation processes (AOPs), etc. (Gallard & De Laat 2001; Tahmasseb et al. 2002; Da Pozzo et al. 2005; Esquivel et al. 2009). Chemical oxidation rarely leads to total mineralization of pollutants. Biological oxidation is considered to be very economical. However, it seems to be inappropriate in many cases. Membrane filtration and AD using activated carbon do not destroy the pollutants but rather transfer them from one phase to another (Ozcan et al. 2004; Tahir & Rauf 2006). AOPs including $O_3/H_2O_2$, $UV/O_3$, $UV/H_2O_2$, $H_2O_2/Fe^{2+}$, etc., as well as photocatalysis (PC), have been identified as successful alternatives for the destruction and mineralization of some recalcitrant organic compounds (Naffrechoux et al. 2000; Gallard & De Laat 2001). PC combines semiconductors acting as photocatalysts, and UV irradiation. Under UV irradiation, a multi-step process occurs involving the generation of hydroxyl radical species ($OH$), holes ($h^+$) able to oxidize and mineralize many organic pollutants. The most
extensively used photocatalyst is titanium dioxide (TiO₂) due to its optical and electronic properties, low cost, abundance, chemical stability and non-toxicity. However, in suspension form, the separation step to recover TiO₂ particles becomes a laborious process after the reaction (Phanikrishna et al. 2008). This is due to the small size and the formation of stable hydrocolloid. Such problems have motivated the development of supported photocatalysts, wherein TiO₂ is immobilized on materials that facilitate electron transfer processes (Phanikrishna et al. 2008; Plantard et al. 2011). The materials (zeolites, cellulosic fibres, etc.) provide dispersion of TiO₂ on the surface along with high AD capacity that helps in pooling the pollutants to the vicinity of the TiO₂ surface (Plantard et al. 2011). In the present study, experiments were carried out to evaluate the performance of a PC process using TiO₂-supported catalyst and UV irradiations (350 ± 20 nm) for the efficient treatment of synthetic solution contaminated by BPB. The influence of experimental parameters (such as angle of inclination of the photocatalytic reactor, recirculation flow rate, pH and pollutant concentration) was investigated. The present work also investigated the kinetic of BPB degradation.

MATERIALS AND METHODS

Chemicals and TiO₂ photocatalyst

BPB was an analytical grade reagent (purity >99%, Sigma Aldrich). BPB stock solution was prepared in deionized water at 100 mg L⁻¹ and kept at 4 °C. Supported TiO₂ catalyst (Millennium PC500, 317 m² g⁻¹) was provided by Ahlström Inc. (France). TiO₂ was coated on a perforated non-woven textile comprised of cellulosic fibres and zeolites. The surface morphology of the TiO₂ photocatalytic coating was examined by scanning electron microscopy (SEM) observations (Figure 1). It can be seen that TiO₂ coating (white colour) is not uniform in thickness and forms a very rough and non-continuous interface with the underlying substrate (the cellulosic fibre). The surface area of the textile and the quantity of TiO₂ deposited were 200 cm² and 25.5 g m⁻², respectively. Initial pH of the BPB solution was adjusted by NaOH and HCl supplied by Fisher Scientific (Canada).

Experimental unit

The photocatalytic reactor (20 cm × 10 cm × 8 cm) was made of Pyrex glass material (Figure 2). It was equipped with TiO₂-supported catalyst located at the bottom and was illuminated by three UVA lamps (8.0 W, Hitachi Light Ltd, Japan) installed horizontally above. Irradiation wavelength was around 350 ± 20 nm. The reactor was designed to have different angles of inclination (0–45 degrees), and it was operated at room temperature (20 ± 2 °C).

Experimental procedure

Experiments were conducted in batch mode. The photocatalytic reactor was fed by using a peristaltic pump (Masterflex L/S, Cole Parmer). Preliminary investigation was conducted to compare the removal efficiencies of BPB using direct photolysis (DP), AD and PC processes. The DP process consists of exposing the BPB solution to UV irradiation (350 ± 20 nm) in the absence of catalyst. The AD process was carried out in the presence of TiO₂ catalyst without UV irradiation. The PC process combined UV irradiation and TiO₂ catalyst. Experiments were carried out over 6 h. Operating parameters were investigated,
such as angle of inclination of the reactor (0, 15, 30 and 45°), recirculation flow rate (0.05–0.15 L min⁻¹), initial pH (3–11) and initial BPB concentration (5.0–25 mg L⁻¹). The lifetime of the catalyst was evaluated by experiments using the same TiO₂ catalyst and BPB solution at 5.0 mg L⁻¹. The reactor and the catalyst were rinsed several times with tap water before each experiment.

Measurement of BPB concentrations

BPB removal was monitored by the measurements of absorbance using a UV-Visible spectrophotometer (Carry 50, Varian Canada Inc.) (Zaviska et al. 2009). The maximum absorption of BPB in samples has been made at 256 nm in an optical quartz cell (1.0 cm).

RESULTS AND DISCUSSION

Preliminary investigation

The removal of BPB recorded using the DP process was 15–18% over 6 h of treatment time. By comparison, when UV irradiations were combined with TiO₂-supported catalyst, BPB concentrations decreased from 22.9–24.7 to 5.8–9.0 mg L⁻¹. The UV-Vis spectra variations are presented in Figure 3. The removal of BPB ranged from 61.9 to 73.9%. In fact, under UV irradiation, the electrons (e⁻) were ejected from the valence band to the conduction band of the TiO₂ semi-conductor, thereby creating an ‘h⁺’ hole in the valence band. These charge carriers (e⁻/h⁺) can migrate to the surface of the catalyst, where they are then available to undergo redox reactions with pollutants. Electrons ejected to the conduction band can either react with electron acceptors such as adsorbed oxygen (O₂) to form superoxide radicals or react with adsorbed water molecules to form oxidative species such as hydroxyl radicals (Robert & Malato 2002). AD tests showed that around 53.7% of BPB was adsorbed on the material used to support TiO₂. Langmuir isotherm described well the AD process over the entire concentration range studied (5–38.5 mg L⁻¹). Langmuir constants were: \( K_L = 0.085 \text{ L g}^{-1} \) and \( b = 0.018 \text{ L mg}^{-1} \), with higher correlation coefficient \( R^2 = 0.98 \). The maximum BPB concentration \( (q_m) \) capable of being adsorbed on the supported catalyst was estimated to be 4.77 mg g⁻¹. AD of BPB on the cellulosic material facilitated the photocatalytic degradation.

Effect of angle of inclination

Different angles of inclination (0°, 15°, 30°, 45°) have been tested. Initial BPB concentration ranged from 23.5 to 24.7 mg L⁻¹ and the recirculation flow rate was 0.10 L min⁻¹. From 0 to 15°, removal of BPB increased from 45.9 to 71.5% over 6 h of treatment time. Beyond 15°, removal slightly decreased to 61.9% (for 30°) and to 63.3% (for 45°). For the inclination angle of 0°, a formation of a thick layer of water was observed on the surface of the catalyst. Thus, there was not a sufficient contact between the pollutant and the catalyst for photocatalytic oxidation of BPB. However, when the angle of inclination increased from 0 to 15°, the surface run-off velocity slightly increased (from \( 8.3 \times 10^{-5} \) to \( 8.5 \times 10^{-5} \text{ m s}^{-1} \)) and a relatively thin layer of water was observed on the surface of the catalyst. In these conditions, the photocatalytic oxidation rate of BPB increased to 71.5%. When the angle of inclination increased to 30° (or to 45°), the rate of BPB removal decreased to about 62–63%, whereas the surface run-off velocities were quite similar (around \( 8.6 \times 10^{-5} \) and \( 8.7 \times 10^{-5} \text{ m s}^{-1} \), respectively). It is believed that (in our experimental conditions), from a certain level of inclination, the flow rate inside the reactor was relatively high, so that the rate of BPB removal decreased. However, in view of better understanding of the photocatalytic process for BPB removal, the thickness of water flowing on the surface of the catalyst combined with the surface run-off velocity needs to be rigorously studied.
Effect of the recirculation flow rate

The performance and behaviour of photocatalytic oxidation were investigated for different recirculation flow rates (0.05, 0.10 and 0.15 L min\(^{-1}\)). Angle of inclination of the reactor and initial BPB concentration were fixed at 15\(^\circ\) and 25 mg L\(^{-1}\), respectively. The influence of the recirculation flow rate is presented in Figure 4. BPB removal increased from 55.3 to 82%, as the recirculation flow rate increased from 0.05 to 0.15 L min\(^{-1}\). The recirculation flow rate affects the photocatalytic degradation of BPB by changing mass transfer and diffusion between BPB and catalyst. Yu et al. (2007) observed a similar effect. The authors reported that the photocatalytic degradation of formaldehyde using TiO\(_2\) catalyst was affected by the flow rate, when it was increased from 0 to 0.0001 m s\(^{-1}\).

Effect of initial pH

The pH affects the capacity of AD and dissociation of target compounds, the distribution of charge on the surface of the photocatalyst and the oxidation potential of the valence band (Fernández et al. 2004). To study the impact of pH on the oxidation of pollutants, the point of zero charge (PZC) of the photocatalyst TiO\(_2\) has been used (Di Paola et al. 2004). For TiO\(_2\), PZC has pH value of 6 (pHPZC). Effect of pH on the photocatalytic degradation of BPB was investigated at 15\(^\circ\) of inclination of the reactor and 0.15 L min\(^{-1}\) of recirculation flow rate. Different pH were tested: 3.1, 4.5, 7.0, 8.0 and 11.0 (Figure 5). The maximum photocatalytic degradation of BPB (82%) was recorded at pH = 7.0. The changes in BPB degradation rate as a function of pH variation can be attributed to the acid/base properties of the TiO\(_2\) surface. For pH values lower than PZC of TiO\(_2\), the surface becomes positively charged (TiOH\(_2^+\)) and an electrostatic repulsion toward cationic compounds dominates, whereas when pH is higher than PZC of TiO\(_2\), the surface becomes negatively charged (TiO\(^-\)) and an electrostatic repulsion toward anionic compounds dominates (Di Paola et al. 2004). Likewise, according to pK\(_a\) value, the anionic form of BPB is dominant at pH higher than 8–8.5 (Equation (1)). Thus, repulsion phenomena between negatively charged BPB and the negatively charged TiO\(_2\) surface could explain the decrease of photocatalytic degradation at pH higher than 7.

\[
\text{C}_4\text{H}_9\text{C}_6\text{H}_4(\text{OH})\text{COO}^- + \text{H}_2\text{O} \leftrightarrow \text{C}_4\text{H}_9\text{C}_6\text{H}_4(\text{O}^-)\text{COO}^- + \text{H}_3\text{O}^+ \quad (1)
\]

Under low pH, the highest production of chloride ions, which adsorbed on the positively charged catalyst surface and reduced BPB AD, as well photon absorption (Muruganandham & Swaminathan 2004). In BPB molecule, C=O linkage and aromatic ring are particularly susceptible to electrophilic attack by hydroxyl radical species. However, at low pH the concentration of H\(^+\) is in excess and H\(^+\) ions interact with C=O linkage, which decreases the electron densities at the C=O group. Consequently, the reactivity of hydroxyl radical species by the electrophilic mechanism decreases.

Effect of BPB concentration

The effect of concentrations of BPB (4.0–24.7 mg L\(^{-1}\)) on the photocatalytic degradation has been investigated. The Langmuir–Hinshelwood (L–H) equation fitted the
experimental kinetic data. According to L–H model, kinetic of disappearance of BPB is given as follows (Equations (2)–(3)):

\[
\frac{dC}{dt} = k\theta = \frac{kKC}{1 + KC} \tag{2}
\]

\[
\theta = \frac{KC}{1 + KC} \tag{3}
\]

where \( C \) is BPB concentration at time \( t \), \( k \) is the true kinetic rate constant and \( K \) (L mg\(^{-1}\)) represents Langmuir AD constant. The kinetic parameters are summarized in Table 1. L–H parameters are found to be \( k = 7.02 \text{ mg L}^{-1} \text{ h}^{-1} \) and \( K = 0.364 \text{ L mg}^{-1} \). Removal of BPB decreases when initial concentration increases. When initial concentration was close to 4 mg BPB L\(^{-1}\), removal reached 85.7% over 6 h of treatment time. Removal decreased to 66.3% when the concentration was increased to 24.7 mgBPB L\(^{-1}\) (Table 1). At low concentrations, kinetic of degradation follows apparent first order reaction. Equation (2) is simplified as follows:

\[
\ln\left(\frac{C_0}{C}\right) = k_d t \tag{4}
\]

where \( C_0 \) is initial BPB concentration, \( C \) is BPB concentration at time \( t \), and \( k_d \) (h\(^{-1}\)) is the apparent kinetic rate constant. \( k_d \) values varied from 0.186 to 0.314 h\(^{-1}\) and the linear regression coefficient ranged from 0.98 to 0.99. The rate of photocatalytic reaction increases with increasing initial concentration of BPB. Many authors used L–H model to analyse heterogeneous photocatalytic reactions successfully (Yu et al. 2007; Bledzka et al. 2010; Barka et al. 2011; Plantard et al. 2011). Lin et al. (2009) indicated that the methylparaben photodegradation by using TiO\(_2\) (powder, P25) is well described by L–H model. The authors found an apparent kinetic constant \( k_d = 1.0854 \text{ h}^{-1} \) higher than the value obtained in our study. A first reason can be TiO\(_2\) loading, with positive effect of the increased number of TiO\(_2\) active sites. Generally, the photocatalytic degradation rate increases when TiO\(_2\) loading increases. In our study, TiO\(_2\) loading was 0.51 g L\(^{-1}\), which was lower than the 2.5 g L\(^{-1}\) used by Lin et al. (2009). A second reason can be the analytical method used. Lin et al. (2009) analysed BPB by gas chromatography–mass spectrometry (GC–MS), while in our study a UV-Vis absorption spectrophotometer was used (an indirect analytical method). The presence of interfering substances such as by-products can influence the absorption spectrum and consequently modify the results.

**Effectiveness of the photocatalytic degradation in the optimal experimental conditions**

Experiments were conducted using optimal values of the operating parameters studied above. Recirculation flow rate was maintained at 0.15 L min\(^{-1}\), angle of inclination of the reactor was 15°, and pH was 7.0. Initial BPB concentration was around 3.66–4 mg L\(^{-1}\). After 6 h of treatment time, BPB concentration decreased to 0.15–0.57 mg L\(^{-1}\), corresponding to 84.9–96.6% of removal. Total organic carbon (TOC) was measured. Firstly, experiments were carried out with only deionized water (without BPB). The results showed that some organic matter was released from the celluliosic material used to fix the catalyst. Then, the supported catalyst was washed many times before each experiment, allowing decreasing TOC release from the support (from 4.4 to 0.10 mg L\(^{-1}\)). Total disappearance of TOC was not possible. Over 6 h of experimental time, around 58.7% of TOC mineralization was observed. The majority of BPB transformed into by-products. Under the optimal conditions, energy consumption was 8.64 kWh m\(^{-3}\).

**CONCLUSION**

The results demonstrated that the AD of BPB on TiO\(_2\)-supported catalyst occurred prior to photocatalytic

<table>
<thead>
<tr>
<th>Initial concentration (mg L(^{-1}))</th>
<th>Final concentration (mg L(^{-1}))</th>
<th>Removal (%)</th>
<th>( r_d ) (mg L(^{-1}) h(^{-1}))</th>
<th>( k_d ) (h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.6</td>
<td>85.7</td>
<td>1.57</td>
<td>0.314</td>
</tr>
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<td>9.2</td>
<td>2.3</td>
<td>75.4</td>
<td>2.30</td>
<td>0.230</td>
</tr>
<tr>
<td>15.5</td>
<td>4.5</td>
<td>70.8</td>
<td>2.97</td>
<td>0.198</td>
</tr>
<tr>
<td>21.2</td>
<td>6.5</td>
<td>69.3</td>
<td>3.90</td>
<td>0.195</td>
</tr>
<tr>
<td>24.7</td>
<td>8.3</td>
<td>66.3</td>
<td>4.65</td>
<td>0.186</td>
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</tbody>
</table>

\( k = 7.02 \text{ mg L}^{-1} \text{ h}^{-1} \).

\( K = 0.364 \text{ L mg}^{-1} \).
degradation. Langmuir isotherm described well AD of BPB. The angle of inclination of the photocatalytic reactor, initial pH, and recirculation flow affect the process. Under optimal operation conditions (recirculation flow rate of 0.15 L min⁻¹, pH = 7, angle of inclination of 15° and 5 mg L⁻¹ initial concentration of BPB) it is possible to oxidize 84.9–96.6% of BPB and to ensure partial mineralization (38.7%). Kinetic study shows that the L–H kinetic model describes well photocatalytic degradation of BPB. However, in view of better understanding of the photocatalytic process for BPB removal, the thickness of water flowing on the surface of the catalyst combined with the surface run-off velocity need to be rigorously studied.

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REFERENCES


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