Removal of Bisphenol-A using Rotating Photocatalytic Oxidation Drum Reactor (RPODR)

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Abstract

This study evaluated the photocatalytic oxidation of BPA using the RPOD reactor under various conditions. This study found that the RPOD was effective for BPA degradation. It could reduce 1 mg/L of BPA by half within 5 min under the optimum conditions. According to the study results, TiO2 coating was important for the BPA oxidation. As the coating thickness increased, the removal efficiency improved. The light source, the light intensity and the drum rotating speed were important for the oxidation. The UV light was more effective for the BPA degradation than the visible light. The removal efficiency improved with increasing intensity. As the drum speed increased, the removal efficiency improved. The maximum speed was 240 rpm in this study. Addition of air and nitrogen was not beneficial for the BPA degradation in this study probably due to enough oxygen in the water.

Keywords: Photocatalytic oxidation, Bisphenol-A, UV/TiO2, Kinetic constant, Half-time

1. Introduction

Endocrine disrupting chemical (EDC) has become an issue of worldwide concern because of concern for its health hazard at very low concentration. Of these, bisphenol-A (BPA) is the most commonly found EDC. BPA is a monomer used in manufacture of numerous chemical products such as epoxy resin and polycarbonate. Since epoxy resin finds its applications in many products such as inner coating of food cans, dental composites, and drug delivery systems,1,2) BPA has exhibited estrogenic activity and alters metabolism kinetics, induces DNA damages, and results in telomeric associations together with chromosomal aberrations.3)

The degradation of organic compounds using a photocatalyst such as titanium dioxide (TiO2) in solution has attracted much attention as a promising method in water purification due to its easy handling and effectiveness.4,5) The purification with TiO2 as a photocatalyst in the presence of UV radiation has been known to have several advantages; effective removal of organic compounds dissolved or dispersed in water and inexpensive cost.6) The well-known principle of photooxidation is that UV illumination onto photocatalyst excites to produce electron and hole pair (e-/h+) with high-energy state, which migrate to the particle surface and initiate a wide range of chemical reactions.7) The valence band potential is positive enough to generate hydroxyl radicals at the surface and the conduction band potential is negative to reduce molecular oxygen. The hydroxyl radical is used as a powerful oxidizing agent to convert organic pollutants into CO2, H2O, and less toxic byproducts of a low molecular weight.

There have been some reports on the photodegradation of BPA by using TiO2 in the solution. Ohko et al.8) reported that the photocatalytic degradation of BPA was performed in aqueous suspension of TiO2 particles under a UV radiation of 10 mW/cm2 for 20 h, where BPA concentration decreased from 175 to 0.04 μM in 10 h.

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Many other studies related to the photodegradation with TiO2 particles in solutions have been performed.9-12) However, they have several problems to be solved. In case of suspended TiO2 particles, there are problems such as exponential decrease of the available light with distance from a light source due to the absorbance of UV light by particles themselves and recycle of TiO2.
Photocatalysts may also be attached to or immobilized on various substrate, including glass tubing, sand, thin oxide covered glass, and stainless steel plate. By comparison with suspended catalysts, supported catalysts have less surface area and may suffer from mass transfer limitations during the photocatalytic reactions. Consequently, immobilized catalysts are more likely to be used in practical applications, since they eliminate the need for filtration or replenishment. However, one of the disadvantages of a reactor using supported catalysts is its low reaction rate.

Therefore, this study employed TiO2 coated drum type reactor together with the UV irradiation for the degradation of BPA. This technique was evaluated in a special reactor called, “rotating photocatalytic oxidation drum reactor (RPODrum)”.

2. Materials and Methods

2.1. Materials

BPA (Sigma-Aldrich Chemical Co., U.S.A.) was diluted to 1 mg/L before experiments. Dichloromethane (pesticide grade, Merck, Germany) was used for extraction and 98% of Titanium isopropoxide (TTIP, Junsei Chemical Co., Japan) was used for TiO2 coating.

Drum was manufactured using stainless steel (SUS-304). Its diameter was 15 cm, and length was 28 cm. Two UV lamps were used. One was 10 W-germicidal lamp (254 nm : Sankyo Denki, Japan) and the other was 10 W-blacklight lamp (360 nm : Phillips, Netherlands). 10 W-vita-lite lamp (Duro-Test, U.S.A.) was also used to evaluate an effect of a light source. Dissolved oxygen was maintained at 8.0±0.2 mg/L through aeration for 20 min in an incubator at 25°C. Its pH was maintained at 7.0.

2.2. TiO2 Coating

The drum was carefully washed before coating. Coating solution, which was prepared by mixing TTIP, ethyl alcohol, and HCl at a ratio of 10:100:1, was then applied to the dried drum at 35°C, 300 rpm for 3 hr. After coated, the drum was heated at 100°C. The temperature was increased at the rate of 10–20°C/minute up to 500°C, at which heating continued for 4 hr. This process was repeated for 5~10 times before use for experiments. The video microscope system (camscope, sometech, Korea) was used to examine the coating and SEM was used to measure the coating thickness.

2.3. RPODrum Reactor

Fig. 1 shows the RPODR used in this study. It was a batch type reactor with 5 liter of capacity. The light source was installed above the drums, which were connected into a horizontal axis. The drum was partially submerged (40%). While the drum was rotating, a water film formed onto the drum surface due to the shear force. The UV light, which was directed into the water film, induced oxidation of contaminants. The rotation also aided rapid diffusion of contaminants and supply of oxygen in the water.

2.4. Analytical Method

For the analysis of BPA, 1 liter of sample was first acidified to pH 2. Sodium chloride and 100 mL of dichloromethane were added into the acidified sample. The sample volume was then reduced using the concentrator (TurboVapII, Zymark, U.S.A.) until it became 0.5 mL. Then, 200 μL of N,O-bis (trimethylsilyl) trifluoro acetamide (Aldrich Chemical Co., U.S.A.) and dichloromethane were added so that the sample volume became 1 mL before an analysis. The BPA concentration was analyzed using GC/MSD (Agilent, U.S.A.). Table 1 summarized the GC/MSD conditions.

Table 1. Analytical Conditions of BPA by the GC/MSD
- Gas Chromatograph : Agilent 6890 N
- Mass Selective Detector : Agilent 5973 N, Electron Ionization mode
- Column : HP-5MS (30 m × ID 0.25 mm × 0.25 μm)
- Injection Temp. : 250°C, Detector Temp. : 280°C
- Oven Temp. : Initial Temp. 80°C, Hold 3 min, Increase rate of 20 °C/min, from 80°C to 300°C

3. Results and Discussion

Fig. 2 shows the drum surface before and after the TiO2 coating. Fig. 2(a) shows the surface picture before the coating. Fig. 2(b) and Fig. 2(c) show the surface picture after 5 times of the coating and 10 times of the coating. These figures clearly show the coating. After 5 times of the coating, rough surface formed on the surface. As the coating repeated, the surface became smooth. The thickness increased with the repeated coating. According to Fig. 3, it was 285 nm after 5 times of the coating, and 445 nm after 10 times of the coating.

Fig. 4 shows the BPA removal results according to the number of the coating. The light source was 2 W/L of blacklight lamp and the drum speed was 30 rpm. The BPA removal was not extensive without TiO2. When the drum was not coated with TiO2, only 14% of BPA was removed for 90 min of reaction. The UV wavelength was 365 nm. The light irradiates 1.5–6.1 eV of
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(a) Before coating  
(b) After 5 times of coating  
(c) After 10 times of coating

Fig. 2. Photograph of TiO$_2$ immobilized on stainless steel.

(a) After 5 times of coating  
(b) After 10 times of coating

Fig. 3. Film thickness of TiO$_2$ immobilized on a stainless steel by SEM.

energy at 200–800 nm of wavelength. Since this provides sufficient energy to break the molecular bond, contaminants were degraded into a simple form molecule when they were subject to the UV irradiation. The removal improved with TiO$_2$ coating. 22% of BPA was removed at 5 times of the coating and 52% of BPA was removed at 10 times of the coating. Since the beneficial effect of TiO$_2$ was evident, experiments were then conducted with the TiO$_2$ coated drum.

Fig. 5 shows an effect of the light source on the BPA removal. All drums were rotated at the same speed of 30 rpm. The lamp with visible light was ineffective for the oxidation of BPA, while the UV lamp was effective. The removal efficiency was 10% for 90 min by the vita-lite lamp. It was 52% by the blacklight lamp and 73% by the germicidal lamp. This result clearly indicates the importance of the light wavelength. The visible light seemed to have insufficient energy to induce the photocatalytic oxidation.

Fig. 6 shows an effect of the light intensity. The germicidal lamp was used at 0–6 W/L, and the drum speed was fixed at 30 rpm. BPA was not removed without the UV irradiation. As the
light intensity increased, the removal improved. The removal efficiency was 73% at 2 W/L, 86% at 4 W/L, and 97% at 6 W/L for 90 min of reaction. According to Aguado et al. (1994), the reaction rate is generally proportional to the light intensity in all photocatalytic reactions. However, when the light intensity was greater than 250 W/m², the dependency on the intensity reduced. The reaction rate became proportional to the square root of the intensity.

Fig. 7 shows the BPA removal results when air and nitrogen gas was added into the reactor at 0.5 L/minute. The light intensity was 6 W/L and the drum speed was 30 rpm. According to Butters and Powell (1995), addition of air, oxygen, hydrogen peroxide improved the photocatalytic oxidation through promotion of OH radical formation. However, such beneficial effect was not noted in this experiment. The dissolved oxygen concentration was constant at 8.0±0.2 mg/L during the 90 min of reaction, which indicated the oxygen supply was enough.

An effect of the drum speed was shown in Fig. 8. The light intensity was 6 W/L, and the reaction continued for 90 min. According to Fig. 8, the drum speed was important for the photocatalytic oxidation. The faster the drum rotated, the better the BPA removal was. The removal efficiency was 97% at 30 and 60 rpm during 90 min. It was 99% at 120 rpm. As the speed increased to 240, the reaction was complete within 40 min. Further increase in the speed did not help. No improvement was noted at 360 rpm.

In Fig. 9, ln(C/Co) is plotted against time for various initial BPA concentrations. The approximately linear decrease in the logarithm of the BPA concentration with elapsed time is consistent with the first-order kinetic expression.

The reaction rate and the reaction time can be calculated by the following equation (1). The equation (2) can be used to calculate the half-life. The reaction rate and the half-lives under various conditions were calculated using these equations. The results are summarized in Table 2.

\[
C/Co = \exp(-k \cdot t) \quad (1)
\]
\[
t_{1/2} = 0.693 / k \quad (2)
\]

According to Table 2, the reaction rate increased by 2.25 times, 5.6 times as the number of the coating increased to 5 and 10. The reaction rate was the slowest under the visible light. It was 0.0012 min⁻¹. The rate increased to 0.0067, 0.0111 min⁻¹ for the blacklight and germicidal lamps. As the light intensity increased from 2 W/L to 4 W/L and 6 W/L, the reaction rate increased by 1.6 times and 2.4 times. As the rotating speed increased from 30 rpm to 60, 120, 240 rpm, the rate increased by 1.3, 2.2, 5.2 times. The optimum condition for the photocatalytic oxidation of BPA was when the germicidal lamp was used at the intensity of 6 W/L while the drum was rotating at 240 rpm. The time required to oxidize 50% of BPA at 1 mg/L was 5 min.
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Fig. 9. Pseudo-first order removal of BPA using RPOD drum.

Table 2. Kinetic constant, $k$ and $t_{1/2}$ values under various experimental conditions

<table>
<thead>
<tr>
<th>Number of TiO2 coating times (2 W/L, blacklight lamp, 30 rpm)</th>
<th>$k$ [min$^{-1}$]</th>
<th>$t_{1/2}$ [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0012</td>
<td>577.50</td>
</tr>
<tr>
<td>5 times</td>
<td>0.0027</td>
<td>256.67</td>
</tr>
<tr>
<td>10 times</td>
<td>0.0067</td>
<td>103.43</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Light Source (2 W/L, 30 rpm)</th>
<th>$k$ [min$^{-1}$]</th>
<th>$t_{1/2}$ [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vita-lite lamp</td>
<td>0.0012</td>
<td>577.50</td>
</tr>
<tr>
<td>Blacklight lamp</td>
<td>0.0067</td>
<td>103.43</td>
</tr>
<tr>
<td>Germicidal lamp</td>
<td>0.0111</td>
<td>62.43</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Light intensity (germicidal lamp, 30 rpm)</th>
<th>$k$ [min$^{-1}$]</th>
<th>$t_{1/2}$ [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 W/L</td>
<td>0.0003</td>
<td>2310</td>
</tr>
<tr>
<td>2 W/L</td>
<td>0.0111</td>
<td>62.43</td>
</tr>
<tr>
<td>4 W/L</td>
<td>0.0174</td>
<td>39.83</td>
</tr>
<tr>
<td>6 W/L</td>
<td>0.0268</td>
<td>25.86</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rotating speed (germicidal lamp, 6 W/L)</th>
<th>$k$ [min$^{-1}$]</th>
<th>$t_{1/2}$ [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 rpm</td>
<td>0.0268</td>
<td>25.86</td>
</tr>
<tr>
<td>60 rpm</td>
<td>0.0354</td>
<td>19.58</td>
</tr>
<tr>
<td>120 rpm</td>
<td>0.0599</td>
<td>11.57</td>
</tr>
<tr>
<td>240 rpm</td>
<td>0.139</td>
<td>4.99</td>
</tr>
<tr>
<td>360 rpm</td>
<td>0.137</td>
<td>5.06</td>
</tr>
</tbody>
</table>

4. Conclusions

This study evaluated the photocatalytic oxidation of BPA using the RPOD reactor under various conditions. This study found that the RPOD was effective for BPA degradation. It could reduce 1 mg/L of BPA by half within 5 min under the optimum conditions. According to the study results, TiO2 coating was important for the BPA oxidation. As the coating thickness increased, the removal efficiency improved. The light source, the light intensity and the rotating speed were important. The UV light was more effective for the BPA degradation than the visible light. The removal efficiency improved with increasing intensity. As the drum speed increased, the removal efficiency improved. The maximum speed was 240 rpm in this study. Addition of air and nitrogen was not beneficial for the BPA degradation in this study probably due to enough oxygen in the water.

References


