



Photodegradation of bisphenol-A in a batch TiO₂ suspension reactor

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ABSTRACT

In this work, the photocatalytic behaviors of bisphenol-A (BPA), which has been listed as one of endocrine disrupting chemicals, were carried out in a batch TiO₂ suspension reactor. The photodegradation efficiency has been investigated under the controlled process parameters including initial BPA concentration (i.e., 1–50 mg L⁻¹), TiO₂ dosage (i.e., 5–600 mg/200 cm³), initial pH (i.e., 3–11), and temperature (i.e., 10–70 °C). It was found that the optimal conditions in the photoreaction process could be coped with at initial BPA concentration = 20 mg L⁻¹, TiO₂ dosage = 0.5 g L⁻¹ (100 mg/200 cm³), initial pH = 7.0, and temperature = 25 °C. According to the Langmuir–Hinshelwood model, the results showed that the photodegradation kinetics for the destruction of BPA in water also followed the first-order model well. The apparent first-order reaction constants (k_{obs}), thus obtained from the fittings of the model, were in line with the destruction–removal efficiencies of BPA in all the photocatalytic experiments. Based on the intermediate products identified in the study, the possible mechanisms for the photodegradation of BPA in water were also proposed in the present study.

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1. Introduction

The environmental pollution of endocrine disrupting chemicals (EDCs) in water sources and factory effluents has aroused the concern of the public in recent years. Among these anthropogenic chemicals, bisphenol-A (abbreviated to BPA), which has been listed as one of EDCs, has received wider attention [1,2], because it has been widely used in the plastic industry for the production of polycarbonate plastics and epoxy resin. The main consumer products developed from BPA are baby bottle, drinking water bottle, lining of food can, dental sealant, and so on. It was reported that the contamination routes of BPA in the aquatic environment include effluents from wastewater treatment plants and waste landfill sites, and migration from BPA-based products [3]. As expected, its environmental distribution will be highly widespread. Because of its reported threats to human health, reproductive biology and its endocrine-disruptive effects on aquatic organisms [3,4], an effective environmental technology for the substantial removal of BPA from the water body is required to prevent its release into the natural waters.

Common methods for destroying and removing organic pollutants in effluents may be divided into three main categories:

physical, chemical, and biological. However, conventional water and wastewater treatment plants using activated sludge and/or carbon adsorption systems are inefficient in removing and degrading many phenolic EDCs including BPA and alkylphenols [5]. In the past two decades, the advanced oxidation processes in the destructive oxidation of organic pollutants have shown that they are promising techniques for the purpose of removing EDCs from effluents of biological treatment plants and/or surface waters [5,6]. In particular, the photocatalytic oxidation with titanium dioxide (TiO₂) has attracted much attention as an efficient method for degrading the refractory pollutants in water because these organic contaminants can be nearly mineralized by radiation energy in the near-UV range. On the other hand, titanium dioxide (TiO₂), the most used photocatalyst, bears the characteristics of the high activity, insolubility, resistance to corrosion, very low toxicity, and relatively moderate cost [7]. A number of researches were devoted to the enhancement of photocatalytic activity by improving photocatalyst with deposition of transition metals (e.g., Au, Ag and Pt) [8–13], adding promoter (e.g., β-cyclodextrin) [14], assisting photocatalysis by external energy (e.g., microwave and high-frequency ultrasound) [15,16], using composite TiO₂ with mineral materials (e.g., carbon, ceramic and zeolite) [17–19] and TiO₂ immobilized on the films or supports (e.g., activated carbon, glass materials, clay, and plastic mesh sheets) [8,20–22]. However, the simplest photoreaction system is to use an aqueous dispersion or slurry of the photocatalyst for the photodegradation of BPA.

With respect to the destruction and removal of BPA with photocatalysis by TiO₂, few studies reported in the literature involve

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the use of TiO₂ powder in the suspension reaction system using artificial UV light source. Using a commercial TiO₂ with suspension concentration of 1.0 g L⁻¹ irradiated by 365 nm from Hg-Xe lamp, Ohko et al. [23] investigated the photocatalytic degradation of BPA in water (40 mg L⁻¹). They found that BPA and its intermediate products were finally mineralized for the UV irradiation of 20 h. Watanabe et al. [24] reported the possible photoreaction pathway for the degradation of BPA (0.1 mM, 50 mL, pH = 4.4) based on the investigation with a commercial TiO₂ (100 mg) irradiated UV-illumination from Hg lamp. To investigate the feasibility of natural solar radiation as an alternative to the energy-intensive artificial UV sources, the photocatalytic degradation of BPA in water using a commercial TiO₂ under sunlight illumination was studied by Kaneco et al. [25]. They also found that the organic substrate could be completely mineralized in the TiO₂-catalyzed process under the UV-illumination of 11 h at the optimal conditions: initial BPA concentration of 20 mg L⁻¹, TiO₂ dosage of 10 mg L⁻¹, temperature of 40 °C, initial pH of 6.0, and solar light intensity of 0.35 mW cm⁻². Chiang et al. [9] compared the efficiencies of three commercial TiO₂ and the prepared TiO₂-platinized catalysts (100 mg L⁻¹) on the mineralization of BPA (20 mg L⁻¹) at the initial pH values of 3 and 10 using an annular jacket reactor (50 mL min⁻¹). They found that the photocatalytic activity could be enhanced by 3–6 times, but the degree of mineralization at pH 10 was relatively low because of the negative charge on TiO₂ particle surfaces that thus inhibits the adsorption of substrate. Horikoshi et al. [26] examined the UV-driven photodegradation of BPA (0.1 mM, 30 mL; initial pH = 6.7) in a plain, thermal and microwave-assisted non-thermal hybrid systems using a commercial TiO₂ (loading, 60 mg). It was found that only ca. 67% mineralization was accomplished in the plain reactor after the UV-illumination of 90 min, but the efficiency was increased to 90% in the hybrid reactor with either microwave irradiation or external heating. They also proposed the degradation mechanisms for BPA based on the organic intermediates identified by liquid chromatography-mass spectral detector (LC-MSD).

On the basis of the above discussion and data, it is necessary to investigate the optimal photodegradation performance of BPA in water under a variety of process factors, to deduce the reaction kinetics, and to identify the intermediates for the proposed degradation mechanisms in the TiO₂ suspension reaction system. Thus, the objectives of this work were to (1) determine the extent of the effects of process factors such as initial BPA concentration, initial pH, temperature, and photocatalyst dosage on the photodegradation of BPA, (2) to evaluate the usefulness of the Langmuir–Hinshelwood model for analyzing the photocatalytic system, and (3) to elucidate the possible BPA photodegradation mechanism based on the identification of intermediate products.

2. Methods

2.1. Materials

BPA with the purity of over 99% was purchased from Aldrich Chemical Co. (Milwaukee, USA) and used without further purification as target compound in the present study. Its molecular structure was given in Fig. 1, indicating that the chemical name of this compound should be 4,4'-isopropylidenediphenol or 2,2'-bis(4-hydroxyphenyl)-propane (HOC₆H₄C(CH₃)₂C₆H₄OH; molecular weight 228). The photocatalyst nano-TiO₂ was purchased

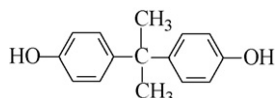


Fig. 1. Chemical structure of bisphenol-A (BPA).

from Degussa AG Co. (Frankfurt, Germany). H₂SO₄ (96 wt%; Merck Co., Germany) and NaOH (99% purity; Mallinckrodt Chemical Co., USA) were used for adjusting initial pH value of aqueous solution to obtain the extent of the destruction-removal of BPA in the photocatalytic system. To identify the possible products from the photodegradation of BPA, hydroquinone (99.9% purity; Merck Co., Germany) and 4-hydroxyacetophenone (99.9% purity; Merck Co., Germany), which have been recognized as main intermediate products by other studies [23–26], were tested to confirm the assignment of high performance liquid chromatography (HPLC) peaks based on the retention time at the same analytical conditions. The commercial standards are reagent grade with the purity of 99.9% and were purchased from Merck Co. (Whitehouse Station, USA).

2.2. Characterization of photocatalyst powder

Before being used in the analytical measurements and photoreaction experiments, the commercial photocatalyst was dried at about 100 °C and then stored in a desiccator. Its pore structures relating to Brunauer–Emmett–Teller (BET) and Langmuir surface areas (S_{BET} and S_{L} , respectively), total pore volume (V_{T}) and average pore size were obtained by measuring the nitrogen adsorption-desorption isotherms at -196 °C in a surface area & porosity analyzer (Model ASAP 2010; Micromeritics Co., Norcross, USA). The measurements were repeatedly made at least twice to evaluate its precision. The X-ray diffraction (XRD) was employed to observe the crystal components in the photocatalyst powder using a Siemens D5000 instrument (Cu-K α) between 2 θ of 10–60° with a scanning velocity of 2.4°/min.

2.3. Photocatalytic experiments

In this work, the photodegradation reactions of BPA in water were carried out in a commercial photochemical reactor (Model RPR-100; The Southern New England Ultraviolet Co., Branford, USA), equipped with magnetic stirrer and cooling fan and surrounded with sixteen UV (365 nm) lamps (Winstar Lighting Co.; Taipei, Taiwan) with the following specifications: diameter 16 mm, length 289 mm, lamp voltage 60 V, lamp current 0.17 A, UV power 0.9 W). All the experiments of photodegradation reaction were carried out in an about 250 cm³ batch Pyrex glass apparatus, which was put into the RPR-100 reactor. The Pyrex glass cylindrical apparatus (dimensions: o.d. 8.5 cm, i.d. 5.5, height ca. 14 cm) was equipped with double walls, surrounded by a thermostatic jacket (using outer-circulating refrigerated circulating-water bath) at desired temperature, and mounted with two ports for sampling and monitoring pH/temperature in the photoreaction system. For each experiment, 200 cm³ of the BPA solution with the specified compositions and conditions to be studied was poured into the apparatus. In the initial experiment, the TiO₂ suspension containing 100 mg L⁻¹ of BPA was equilibrated to study the adsorption behavior in the dark (no UV radiation). Another control experiment was carried out to investigate the photodegradation extent of the solution with 100 mg L⁻¹ of BPA in the UV radiation. In the subsequent experiments, the photodegradation system containing TiO₂ was further used to study the extent of destruction-removal efficiency in BPA at initial BPA concentration (i.e., 1, 5, 10, 20, and 50 mg L⁻¹), initial pH (i.e., 3, 5, 7, 9, and 11), TiO₂ dosage (i.e., 5, 10, 30, 50, 100, 200, 400, and 600 mg), and temperature (i.e., 10, 25, 40, 55, and 70 °C). All of the experiments were carried out at least twice to obtain the precise data for calculating the photochemical kinetics. Samples were taken from the photoreaction apparatus at predetermined intervals (i.e., 1, 3, 5, 7, 10, 15, 30, 45, and 60 min), and then filtrated with fiber membrane (Cat. No.: A045A025A; ADVANTEC MFS, Inc.). The BPA concentration analysis of filtrate solution was immediately

determined by high performance liquid chromatography-ultra violet (HPLC-UV), which was described below.

2.4. Analysis and calculation

The residual amount of BPA in the filtrate solution was determined by the use of a HPLV-UV (Hitachi Co., Tokyo, Japan), which includes a high pressure pump (Model L-2130), a UV detector (Model L-2400), and a Supelco 516 C-18 column (dimensions; 25 cm × 4.6 mm i.d., 5 μm beads). The mobile phase used in the analytical instrument was a mixed solvent of acetonitrile (Merck Co.; purity of over 99.9%) and water (50/50, v/v) with a flow rate of 1 cm³/min. According to the characteristic absorbance peaks recorded with spectrophotometer UV-1601 (Shimadzu Co.; Kyoto, Japan), BPA concentration was determined at 275 nm by the UV detector as demonstrated by Ohko et al. [23]. Levels of BPA in the aqueous solution were determined with standard curves ($R^2 = 0.9999$) by injecting known amounts (i.e., 0.5, 1, 3, 5, and 10 mg L⁻¹) of standards and measuring the areas under the peaks. The destruction-removal efficiency (DRE) of BPA in the photodegradation system was determined as follows:

$$\text{DRE} = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

where C_0 and C_t are the initial BPA concentration and residual BPA concentration at t time (mg L⁻¹), respectively. In order to evaluate the significance of data in the photodegradation kinetic experiments, a preliminary adsorption experiment was carried out at photocatalyst dosage = 100 mg, initial BPA concentration = 20 mg L⁻¹, initial pH = 7.0, and temperature = 25 °C, showing that the extent of adsorbed BPA amount within 3% seemed to be negligible.

To elucidate the photodegradation mechanism of BPA, a gas chromatography-mass spectrometry (GC-MS) with HP 6890N (Hewlett-Packard Co.; Palo Alto, USA) equipped with a HP 5973A mass selective detector (MSD) was used to identify the intermediate products from the photodegradation of BPA, using a 60 m × 0.25 mm i.d. × 0.25 μm film thickness HP-1 capillary column. The intermediate products were tentatively extracted by means of solid-phase microextraction (SPME). The extraction was performed by directly immersing the SPME fiber into the vial with magnetic mixing. When equilibrium was reached, the fiber was introduced into the GC injector, where the adsorbed analytes were thermally desorbed and determined by GC-MS. The temperature program at the chromatographic process was carried out as follows: 40 °C (initial temperature; hold 5 min) → (heating rate at a 5 °C/min) → 200 °C (intermediate temperature; hold 5 min) → (heating rate at a 10 °C/min) → 350 °C (final temperature; hold 2 min). The injector temperature and detector temperature were 250 °C and 280 °C, respectively. Helium with 99.999% purity was used as a carrier gas at a constant flow rate of 1 mL/min. The MS operated in scan mode and its mass range was 45–500 a.m.u. The compounds were tentatively identified by comparing their mass spectra and retention times with those from the MS search file (HP MS ChemStation). On the other hand, the possible intermediate products (i.e., hydroquinone and 4-hydroxyacetophenone) were also identified by comparing their retention times on HPLC with those of corresponding standards under the same analytical conditions.

3. Results and discussion

3.1. Characterizations of photocatalyst TiO₂

Commercial TiO₂ (P-25, Degussa Co., Germany), which is cubic particles having an average primary particle size of 20 nm and BET

Table 1

Main physical properties of TiO₂ photocatalyst in the present study^a.

Physical property	Value ^a
BET surface area (S_{BET} , m ² /g)	50.16 ± 0.02
Langmuir surface area (S_L , m ² /g)	412.49 ± 28.7
Total pore volume (V_t , cm ³ /g)	0.25 ± 0.033
Pore diameter (Å) ^b	19.74 ± 2.65

^a Average ± standard deviation from two measurements.

^b Estimated as follows: $4 \times S_{\text{BET}}/V_t$.

surface area of $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$, was used as a photocatalyst for the destruction-removal of BPA in the present study. The data in Table 1 indicated its main physical properties including surface areas, total pore volume, and average pore diameter. The determination value of the BET surface area was approximately $50 \text{ m}^2 \text{ g}^{-1}$, which was very close to the data (i.e., $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$) from the manufacturer's brochure. The data on total pore volume and pore size might be attributable to the fine voids between the nonporous nanoparticle (size 20–30 nm) with the crystal phases (i.e., anatase and rutile). In Fig. 2, the XRD pattern of nano TiO₂ showed the presence of three main peaks at $2\theta = 25.4^\circ$ (1 0 1), 37.8° , and 48.1° , which should be an attributive indication of anatase TiO₂ [11]. On the other hand, minor diffraction peaks appeared at $2\theta = 27.5^\circ$ (1 1 0) and 36.5° , which should correspond to rutile TiO₂. The results were in agreement with its mineral composition bearing an anatase to rutile ratio of 83:17 [26].

3.2. Photocatalytic performance of BPA with the process parameters

3.2.1. Effect of initial BPA concentration

Fig. 3 showed the dependence of the degradation efficiency on initial BPA concentration at TiO₂ dosage of 100 mg/200 cm³, initial pH of 7.0, reaction time of 60 min, and temperature of 25 °C. It is evident that the destruction-removal efficiency (DRE) decreased gradually, ranging from 100 to 97% when the initial substrate concentration increased from 1 to 20 mg L⁻¹. However, the BPA concentration increased from 20 to 50 mg L⁻¹, while the corresponding data on DRE were on the significantly decreasing trend, ranging from 97 to 67%. The result was consistent with other studies [25]. The reduction in DRE could be attributed to the amount of adsorption areas determined by a given TiO₂ dosage. This result indicates that the adsorption rate will increase with initial BPA concentration ranging from 1 to 50 mg L⁻¹ when the mass transfer from the concentration gradient increases. However, the concentration effect will inversely impact on its adsorption frequency which is indicative of the degradation efficiency because of the limited adsorption sites available for the uptake of BPA.

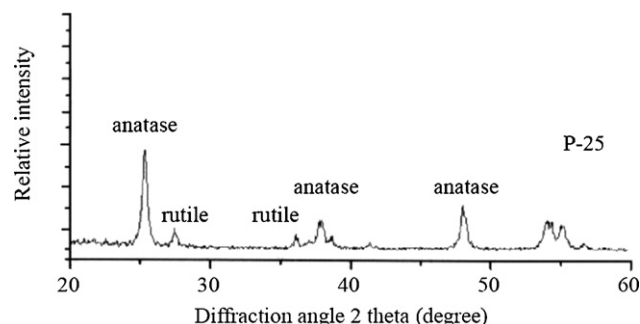


Fig. 2. XRD pattern of photocatalyst P-25 used in the present study.

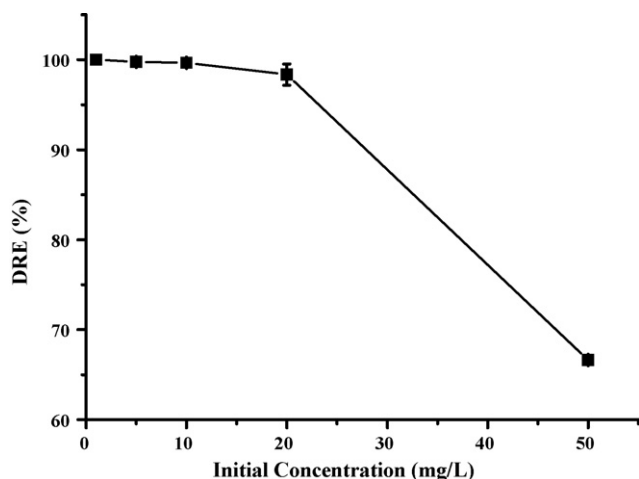


Fig. 3. Plot of bisphenol-A (BPA) destruction-removal efficiency (DRE) versus initial BPA concentrations (photoreaction conditions: TiO_2 dosage = $100 \text{ mg}/200 \text{ cm}^3$, initial pH = 7.0, reaction time = 60 min, and temperature = 25°C).

3.2.2. Effect of photocatalyst dosage

In order to obtain the optimal TiO_2 suspension dosage in the slurry reaction system, the effect of various photocatalyst dosages (i.e., 5, 10, 30, 50, 100, 200, 400, and $600 \text{ mg}/200 \text{ cm}^3$) on the degradation efficiency of BPA in water was investigated at the initial BPA concentration of 20 mg L^{-1} , pH of 7.0, and temperature of 25°C . The results were shown in Fig. 4. Evidently, the photodegradation efficiency increased when the dosages increased up to $100 \text{ mg}/200 \text{ cm}^3$, and then the efficiency was very close to 100% in the TiO_2 dosage range $100\text{--}600 \text{ mg}/200 \text{ cm}^3$. The results are consistent with those studied by Kaneco et al. [25]. It was thus suggested that the optimal amounts of photocatalyst for the degradation-removal of BPA should be 100 mg of TiO_2 in the present study, which corresponds to the TiO_2 suspension concentration of $100 \text{ mg}/200 \text{ cm}^3$. As explained by Kaneco et al. [25], the efficiency may increase with the rise in the number of active sites for the photocatalytic reaction, which is in parallel with increasing TiO_2 dosage. The residual BPA concentration in the solution was expected to rapidly decrease; as a result, the rate constant, described in Section 3.3, increased at a larger value as the photocatalyst dosage rose. This result leads to a suggestion that higher initial BPA concentrations should be tested in conjunction with appropriate dosage in order to obtain the optimal TiO_2 dosage.

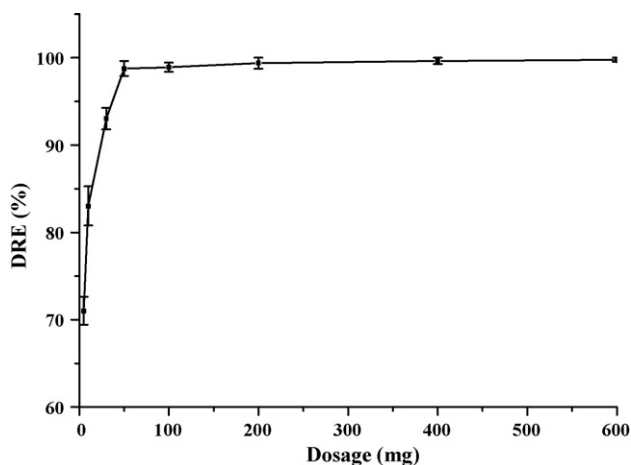
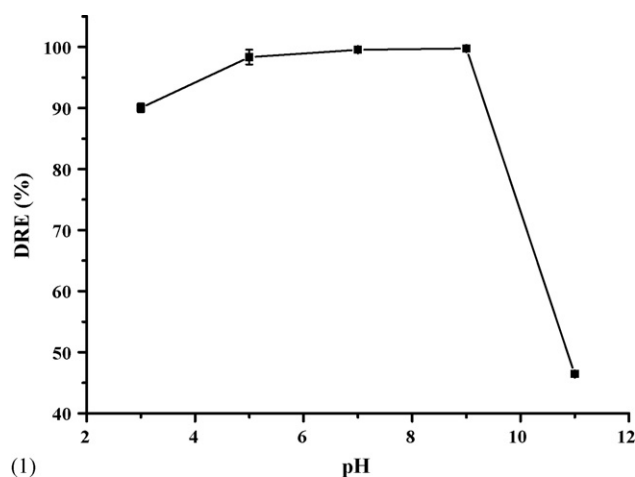


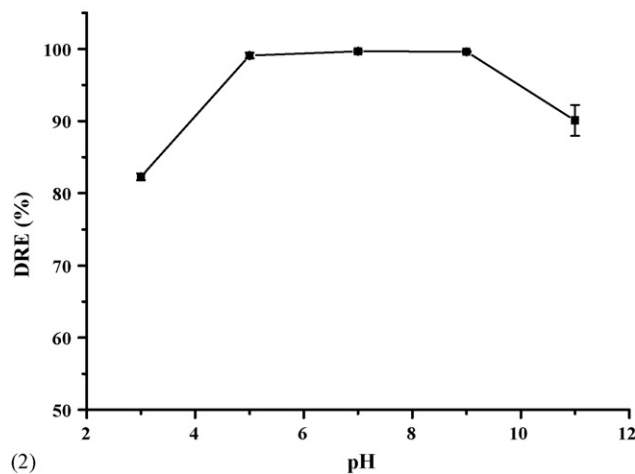
Fig. 4. Plot of bisphenol-A (BPA) destruction-removal efficiency (DRE) versus TiO_2 dosage (photoreaction conditions: initial BPA concentration = 20 mg L^{-1} , initial pH = 7.0, reaction time = 60 min, and temperature = 25°C).

3.2.3. Effect of initial pH

In heterogeneous media, the surface charges of most semiconductor oxides are dependent on the extent of hydrogen ion (H^+) or hydroxide ion (OH^-) in the water environment, resulting in the available surface sites for the adsorption potential and photocatalytic reactivity. As a consequence, the effect of the initial pH (i.e., 3, 5, 7, 9, and 11) on the photodegradation efficiency of BPA in water was investigated at the initial BPA concentrations of 10 and 20 mg L^{-1} , TiO_2 dosage of $100 \text{ mg}/200 \text{ cm}^3$, reaction time of 60 min, and temperature of 25°C , as shown in Fig. 5. Obviously, the degradation efficiency significantly increased as the pH was increased from 3 to 5, and then approached a maximum (ca. 100%) as the pH increased from 5 to 9, while it showed a decreasing trend at a higher pH from 9 to 11. It was elucidated that the ionization of BPA occurred at around pH 9–10 to form the bisphenolate anion due to the pK_a value of BPA ranging 9.6–10.2 [27]. It has also demonstrated that the zero point charge in the TiO_2 particles ranges from 6 to 7 (around 6.25 for Degussa P-25) [25,28], implying that the surface charge of the TiO_2 particles is slightly negative under alkaline condition. Therefore, the reduction in the adsorption frequency at basic pH range may be probably due to the electrostatic repulsion between the anion and the negatively charged surface, resulting in the decrease in the reactivity of the photodegradation of BPA occurring on the TiO_2 particle surface. This result was mostly consistent with those achieved by other researchers [25,29]. However, as elu-



(1)



(2)

Fig. 5. Plot of bisphenol-A (BPA) destruction-removal efficiency (DRE) versus initial pH at (1) initial BPA concentration = 10 mg L^{-1} , and (2) initial BPA concentration = 20 mg L^{-1} (photoreaction conditions: TiO_2 dosage = $100 \text{ mg}/200 \text{ cm}^3$, reaction time = 60 min, and temperature = 25°C).

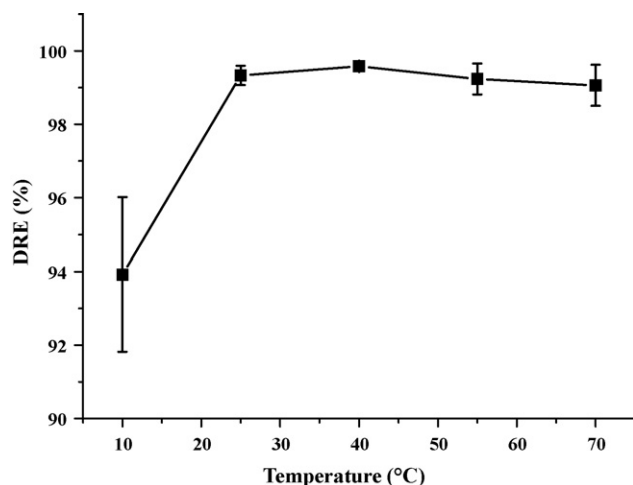


Fig. 6. Plot of bisphenol-A (BPA) destruction-removal efficiency (DRE) versus temperature (photoreaction conditions: TiO₂ dosage = 100 mg/200 cm³, initial BPA concentration = 20 mg L⁻¹, initial pH = 7.0, and reaction time = 60 min).

culated by Kaneco et al. [25], the efficiency continued to be on the increase in the pH range 8–10 because more hydroxide ions (OH⁻) at high initial pH increased the generation of hydroxyl radicals (•OH).

3.2.4. Effect of temperature

The information about the effect of temperature on the photocatalytic reactivity of BPA in water with TiO₂ was very scarce in the literature. Therefore, the effect of temperature ranging from 10 to 70 °C on the degradation efficiency of BPA in water using TiO₂ was investigated at the initial BPA concentrations of 20 mg L⁻¹, TiO₂ dosage of 100 mg/200 cm³, reaction time of 60 min, and pH of 7. Fig. 6 showed that the temperature played a less important role in the photocatalytic reaction system, although the appreciable change in the enhancement of degradation efficiency was observed in the range of 10–25 °C. These results are consistent with those studied by Kaneco et al. [25] and Machado et al. [30]. From the viewpoint of application and energy saving, the photodegradation system should be performed at room temperature.

3.3. Photocatalytic kinetics of BPA

The heterogeneous photodegradation process in an illuminated stirring suspension chamber generally involves complicated reaction mechanisms with the hydroxyl radical •OH and the organic solutes adsorbed on the TiO₂ surface. Although many theoretical model equations have been proposed for describing the kinetics based on mass balance, chemical kinetics and initial/boundary conditions, these equations are not only complicated and impractical while being used, but they also require detailed data such as the characteristics of TiO₂ and reactants. It was often suggested that the dependence of TiO₂-oxidation rate on the concentration of the organic solutes follows the Langmuir–Hinshelwood kinetic model [7]:

$$R = \frac{k \cdot K \cdot C}{1 + K \cdot C}$$

where C is the concentration of organic solute (i.e., BPA), K represents the Langmuir adsorption constant, and k is a reactivity constant. At low solute concentrations, the rate R is thus proportional to the solute concentration, with k_{obs} being the observed or apparent first-order rate constant.

$$R = k \cdot K \cdot C = k_{\text{obs}} \cdot C$$

Further, the photocatalytic reaction equation can be formed as an apparent first-order rate:

$$R = k_{\text{obs}} \cdot C = -\frac{dC}{dt}$$

The integral form of the pseudo-first-order rate equation is generally expressed as follows:

$$\ln \frac{C}{C_0} = -k_{\text{obs}} \cdot t$$

where C_0 is the initial concentration of organic solute, and C is the residual concentration of the solute at time t . The linear dependence of $\ln(C/C_0)$ versus t can be used to obtain the data of k_{obs} .

Using the fittings of pseudo-first-order model, the values of k_{obs} were listed in Table 2. On the basis of the results shown in Table 2, the noteworthy features are as follows:

1. Using the regression analysis (least square method), the pseudo-first-order kinetic model, also demonstrated by Lee et al. [22], Watanabe et al. [24], Wang et al. [29], and Chin et al. [31], appeared to be in agreement with the experimental data on the photodegradation of BPA because of the correlation coefficients of higher than 0.95 for all the photocatalytic experiments except for the case investigated at temperature of 10 °C.
2. It was observed that the variations of rate constants (k_{obs}), listed in Table 2, with the process parameters (i.e., initial BPA concentration, TiO₂ dosage, initial pH, and temperature) were in parallel with the data shown in Figs. 3–6. For example, the rate constants (k_{obs}) decreased from 0.396 to 0.019 min⁻¹ as the BPA concentration increased from 1 to 50 mg L⁻¹. Consistently, the degradation efficiency decreased gradually as the BPA concentration increased from 1 to 20 mg L⁻¹, but it decreased significantly in the BPA concentration range 20–50 mg L⁻¹.

Table 2

Apparent first-order reaction model parameters for the photodegradation of BPA using TiO₂ at various photoreaction conditions.

Process parameter	Value	First-order reaction model	
		k (min ⁻¹)	R^2
Initial BPA concentration ^a	1 mg L ⁻¹	0.396 ± 0.246	0.987
	5 mg L ⁻¹	0.150 ± 0.036	0.985
	10 mg L ⁻¹	0.096 ± 0.002	0.995
	20 mg L ⁻¹	0.075 ± 0.002	0.967
	50 mg L ⁻¹	0.019 ± 0.000	0.956
TiO ₂ dosage ^b	5 mg/200 cm ³	0.021 ± 0.001	0.987
	10 mg/200 cm ³	0.028 ± 0.001	0.985
	30 mg/200 cm ³	0.043 ± 0.004	0.995
	50 mg/200 cm ³	0.065 ± 0.009	0.967
	100 mg/200 cm ³	0.081 ± 0.009	0.956
	200 mg/200 cm ³	0.098 ± 0.006	0.937
Initial pH ^c	3	0.027 ± 0.001	0.988
	5	0.068 ± 0.009	0.946
	7	0.081 ± 0.009	0.956
	9	0.086 ± 0.002	0.973
	11	0.037 ± 0.004	0.993
Temperature ^d	10 °C	0.034 ± 0.026	0.913
	25 °C	0.081 ± 0.009	0.956
	40 °C	0.091 ± 0.011	0.961
	55 °C	0.084 ± 0.008	0.957
	70 °C	0.079 ± 0.012	0.953

^a Photoreaction conditions: TiO₂ dosage = 100 mg/200 cm³, initial pH = 7.0, reaction time = 60 min, and temperature = 25 °C.

^b Photoreaction conditions: initial BPA concentration = 20 mg L⁻¹, initial pH = 7.0, reaction time = 60 min, and temperature = 25 °C.

^c Photoreaction conditions: TiO₂ dosage = 100 mg/200 cm³, initial BPA concentration = 20 mg L⁻¹, reaction time = 60 min, and temperature = 25 °C.

^d Photoreaction conditions: TiO₂ dosage = 100 mg/200 cm³, initial BPA concentration = 20 mg L⁻¹, initial pH = 7.0, and reaction time = 60 min.

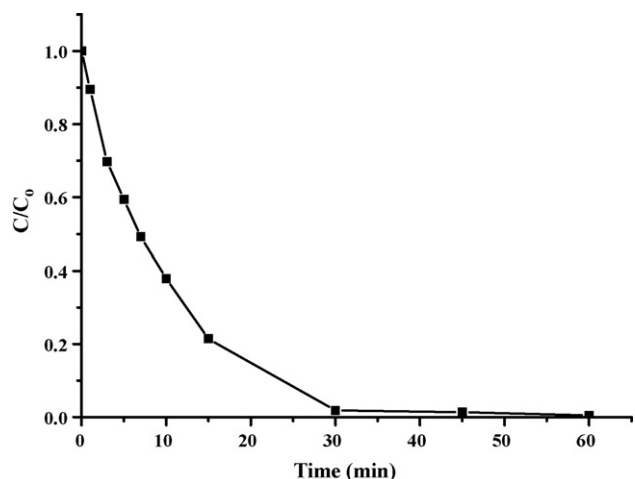


Fig. 7. Plot of normalized bisphenol-A (BPA) concentration versus irradiation time (photoreaction conditions: initial BPA concentration = 10 mg L^{-1} , TiO_2 dosage = $100 \text{ mg}/200 \text{ cm}^3$, initial pH = 7.0, and temperature = 25°C).

3.4. Intermediate products and proposed photodegradation mechanism

More than 99% of the initial BPA was degraded after 1 h of UV irradiation in the photodegradation of BPA, as shown in Fig. 7. Photocatalytic degradation of BPA in the TiO_2 suspension process proves to be an efficient method for quickly lowering the concentration of the endocrine disrupting compound in an effluent. To identify the intermediate products from the photodegradation of BPA and further induce the possible reaction mechanisms, the intermediates formed in the UV-driven photodegradation of BPA (20 mg L^{-1}) in the aqueous TiO_2 suspension (dosage, $100 \text{ mg}/200 \text{ mL}$) at pH of 7.0 and temperature of 25°C for the illumination time of 30 min were preliminarily identified by GC-MS and HPLC, which have been described in Section 2.4. Fig. 8 illustrated the HPLC profile of the BPA solution, showing that unreacted BPA and few intermediate products existed. In comparison with mass spectra information of standard chemicals and retention time on existing GC-MS data, only the compound "A" has been identified

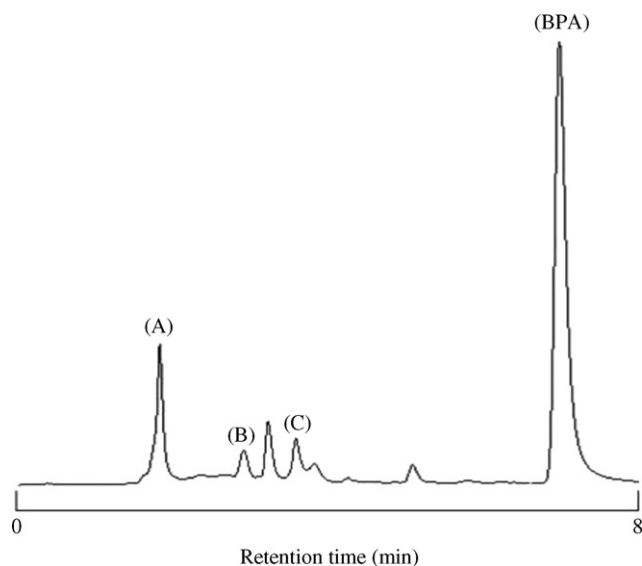
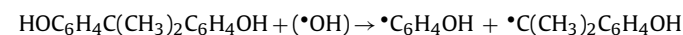


Fig. 8. HPLC chromatogram of BPA and its photodegradation products obtained from the photoreaction conditions of TiO_2 dosage = $100 \text{ mg}/200 \text{ cm}^3$, initial BPA concentration = 20 mg L^{-1} , initial pH = 7.0, temperature = 25°C and reaction time = 30 min.

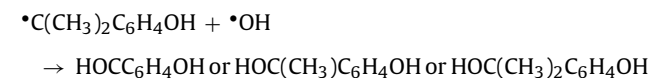
as acetic acid in this work. The compounds "B" and "C" were confirmed as *p*-hydroquinone ($\text{HO C}_6\text{H}_4\text{OH}$; molecular weight 110) and *p*-hydroxyacetophenone ($\text{C(O)CH}_3\text{C}_6\text{H}_4\text{OH}$; molecular weight 136), respectively, in comparison with the standard chemicals and their corresponding retention times on HPLC analysis. However, a few components were not clearly identified by GC-MS and HPLC analyses in this study since no analytical standards were injected. The peak between the compounds "B" and "C" was possibly attributable to *p*-hydroxybenzaldehyde ($\text{C(O)HC}_6\text{H}_4\text{OH}$; molecular weight 122) on the basis of molecular weight and retention time. Similarly, the peak between the compounds "C" and "BPA" could be assigned to 4-hydroxyphenyl-2-propanol ($\text{HO C(CH}_3)_2\text{C}_6\text{H}_4\text{OH}$; molecular weight 152). These analytical results were consistent with those reported by some researchers [9,18,23–26,32–34].

Based on the intermediate products identified in the study, it is relevant to propose the possible mechanisms for the photodegradation of BPA in water in the following sequence:

Step 1: In the initial photo-oxidation, the aqueous photocatalytic reaction proceeded mainly by electrophilic hydroxyl radicals ($\cdot\text{OH}$) produced from the oxidation of water molecules. The photocleavage of electro-rich carbons in the phenyl groups of BPA or the excited BPA molecules was attacked by hydroxyl radicals ($\cdot\text{OH}$), forming phenol radical ($\cdot\text{C}_6\text{H}_4\text{OH}$) and isopropylphenol radical ($\cdot\text{C(CH}_3)_2\text{C}_6\text{H}_4\text{OH}$).



Step 2: Incorporating a hydroxyl radical ($\cdot\text{OH}$) into the intermediate radicals, phenol radical was then converted to *p*-hydroquinone ($\text{HO C}_6\text{H}_4\text{OH}$). At the same time, isopropylphenol radical was followed to form 4-hydroxyphenyl intermediates such as *p*-hydroxybenzaldehyde, *p*-hydroxyacetophenone and 4-hydroxyphenyl-2-propanol.



Step 3: Furthermore, these single-aromatic intermediates were subsequently oxidized through ring-opening reactions into aliphatic acids. It should be noted that these hydrophilic aliphatic

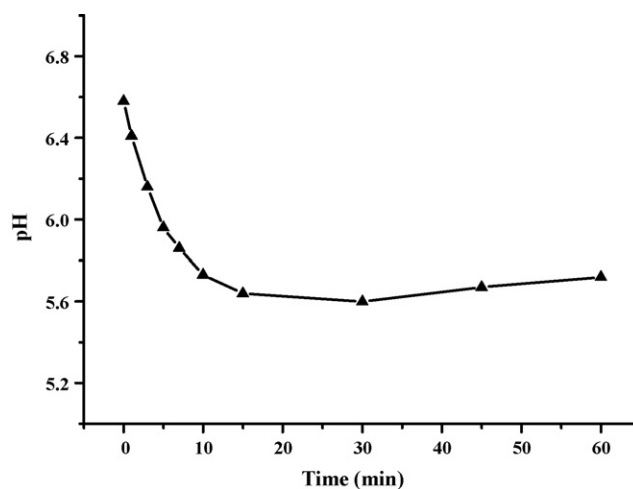


Fig. 9. Plot of variation in pH versus irradiation time (photoreaction conditions: initial BPA concentration = 10 mg L^{-1} , TiO_2 dosage = $100 \text{ mg}/200 \text{ cm}^3$, initial pH = 7.0, and temperature = 25°C).

acids were not identified in the literature. In the study, the identification of acetic acid was carried out by the use of GC-MS. The pH values in aqueous media would be expected to gradually decrease and approach an equilibrium level during the photodegradation of BPA, as shown in Fig. 9. Ultimately, these short chain intermediates were completely mineralized to form carbon dioxide (CO₂), which was slowly evolved from the aqueous media in the photodegradation of BPA.

Single-aromatic intermediates + ([•]OH)

→ aromatic ring opened products + ([•]OH)

→ CH₃COOH + ([•]OH) → CO₂ + H₂O

4. Conclusions

In order to obtain the optimal values of photocatalyst dosage, initial BPA concentration, initial pH and temperature, and in order to preliminarily identify main intermediate products during the advanced oxidation process, photocatalytic degradation of BPA, a commonly known endocrine disrupting compound, in the 365 nm-UV-driven suspension system using a commercial TiO₂ powder have been examined. It was found that the optimal conditions in the photoreaction process could be performed at initial BPA concentration = 20 mg L⁻¹, TiO₂ dosage = 0.5 g L⁻¹ (100 mg/200 cm³), initial pH = 7.0, and temperature = 25 °C. In all the photocatalytic experiments, the photodegradation kinetics for the destruction-removal of BPA in water can be well described by pseudo-first-order reaction model. The apparent first-order reaction constants (*k*_{obs}) thus obtained from the fittings of the model seemed to be proportional to TiO₂ dosage. However, the values of *k*_{obs} decreased gradually when the initial BPA concentration increased. In a preliminary analysis by the use of GC-MS and HPLC, some intermediate products during the photodegradation of BPA have been identified as acetic acid, *p*-hydroquinone and *p*-hydroxyacetophenone. Based on the intermediate products identified in the study, the possible mechanisms for the photodegradation of BPA in water were also proposed. In conclusion, the photocatalytic degradation of BPA in the TiO₂ suspension process proves to be an efficient method for quickly lowering the concentration of the endocrine disrupting compound in water.

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