Degradation of *n*-butyl benzyl phthalate using TiO$_2$/UV

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ABSTRACT

n-Butyl benzyl phthalate (BBP) has been classified as endocrine disrupting compound and priority pollutant. Effects of TiO$_2$ dosage, pH, initial BBP concentration and co-existing substances on the degradation of BBP by TiO$_2$/UV process were investigated. The optimal TiO$_2$ dosage and pH value for the BBP degradation were $2.0\,g\,L^{-1}$ and 7.0, respectively. The degradation rate of BBP by TiO$_2$/UV process could be fitted pseudo-first-order kinetics. The effects of co-existing substances on the degradation rate of BBP revealed that some anions (such as BrO_3^-, ClO_4^- and $Cr_2O_7^{2-}$) could enhance BBP degradation, and other anions would restrain BBP degradation. The sequence of inhibition was $PO_4^{3-} > CO_3^{2-} > NO_3^- > SO_4^{2-} > Cl^-$. The cations K^+, Na^+, Mg^{2+} and Ca^{2+} had the restrained effect on the BBP degradation, and the effect of Ca^{2+} was the strongest among four cations tested. The organic compounds acetone and methanol decreased the degradation rate of BBP. The major intermediates of BBP degradation were identified as mono-butyl phthalate, mono-benzyl phthalate and phthalic acid, and a primary degradation mechanism was proposed.

1. Introduction

Phthalate esters (PAEs) represent a large family of chemicals most widely used as plasticizers, primarily in the production of polyvinyl chloride (PVC) resins, adhesives, and cellulose film coating to improve mechanical properties of the plastic resin, particularly flexibility [1]. The worldwide yield of PAEs has reached 2.7 million metric tones per year [2]. However, PAEs have been classified as priority pollutants and endocrine disrupting compounds by the United States Environmental Protection Agency and similar regulatory agencies in several other countries. They are suspected of interfering with reproductive systems and behavior of humans and wildlife through disturbance of the endocrine system even at very low concentrations [1,3,4]. *n*-Butyl benzyl phthalate (BBP) is one of the most frequently identified phthalates in diverse environmental samples including groundwater, river water, drinking water, ocean water, soil, lake sediment and marine sediments. BBP exerted estrogenic activities in several tests [3,5,6]. BBP can be biologically degraded [7,8]. Although these microbial systems function in the laboratory under defined culture conditions, the bactericidal toxicants (such as heavy metals) that may be found in many wastes

would limit their actual effectiveness. Therefore, there is a strong need to look for physical and chemical methods as alternative and faster treatment processes for such pollutant.

The semiconductor photocatalysis is based on the reactive properties of electron–hole pairs generated in the semiconductor particles under illumination by light of energy greater than the semiconductor band gap [9,10]. Both hydroxyl and superoxide radicals are thought to be the primary oxidizing species in photocatalytic degradation process [10], which in turn react with an organic substrate, resulting in the degradation of the compound. They are formed by a reaction of electron–hole pairs with surface adsorbed oxygen and water (Eqs. (1)–(3)).

$$TiO_2 + h\nu \rightarrow e_{CB}^- + h_{VB}^+ \tag{1}$$

$$O_2 + e_{CB}^- \rightarrow O_2^{\bullet-} \tag{2}$$

$$H_2O + h_{VB}^+ \rightarrow {}^{\bullet}OH + H^+ \tag{3}$$

In recent years, this technology as an alternative for the treatment of water polluted by hazardous organic compounds has received considerable attention [11–14]. Several kinds of phthalates were also degraded by this technology [15–24]. However, no report about BBP degradation by TiO$_2$/UV process could be found in the literature.

In this paper, effects of TiO$_2$ dosage, pH, initial BBP concentration and co-existing substances on the degradation of BBP by TiO$_2$/UV process were studied. The major intermediates of the BBP degradation were identified, and a primary degradation mecha-

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nism was proposed. The findings of this study could be useful for the treatment of water contaminated with BBP.

2. Materials and methods

2.1. Chemicals

n-Butyl benzyl phthalate was of analytical grade and purchased from Sigma (St. Louis, MO, USA). Titanium dioxide (P25, Degussa), a mixture of 70% anatase and 30% rutile, was used as a photocatalyst. All other reagents were purchased from Aldrich (Milwaukee, WI, USA). Doubly distilled water was used for the preparation of all solutions.

2.2. Adsorption experiments

Batch adsorption experiments were performed for all equilibrium studies. TiO_2 suspensions in water were dispersed by sonication for 30 s. After mixing BBP solution with a predetermined amount of TiO_2 particle in a quartz reactor, the mixture was maintained in suspension by a magnetic stirrer. The pH values of the suspensions were adjusted to the desired values using 0.1 M HCl or NaOH. Measurements were made using Orion model 320 pH meter (Beverly, MA, USA), fitted with a Cole-Parmer combination electrode (Barrington, IL, USA). The total volume of the suspension in the photoreactor was 150 mL for all cases. The samples were withdrawn at given time intervals, and immediately filtered through 0.45 μm Teflon syringe filters to minimize the continuing-adsorption of BBP after sampling.

2.3. Photocatalytic degradation experiments

The photocatalytic degradation experiments were carried out in a laboratory-scale photoreactor (Luzchem Research Inc., Quebec, Canada), and a sketch map of the photoreactor is shown in Fig. 1. The length, width and height of the photoreactor are 33, 33 and 22 cm, respectively. The diameter and height of the quartz cylinder are 6 and 8 cm, respectively. The distance of the left, right and top lamps to the quartz cylinder are 13.5, 13.5 and 14 cm, respectively. The diameter and length of the magnetic stirrer are respectively 0.5 and 4.9 cm, and the speed of agitation is 80 rpm. A quartz cylinder of 200 mL capacity, filled with 150 mL sample solutions was placed inside the reactor. A magnetic stirrer was located at the reactor's base so that a homogeneous TiO_2 suspension could be maintained throughout the reaction. A cooling fan was installed in the reactor to maintain the experimental temperature at $24 \pm 1\,°C$, which was the environmental temperature of the air-conditioned laboratory. Sixteen 350 nm black blue fluorescent UV lamps, each with approximately 8 W maximum output, were used as the light sources and

located around the cylinder. The light emission is ranged from 290 to 420 nm, with peaks at 350, 375 and 410 nm. The photon-intensity used throughout the experiments was $30\,W\,m^{-2}$. The suspensions were equilibrated in the dark for 30 min prior to illumination. The control samples in the darkness were also carried out.

At regular time intervals, the sample aliquots were taken from the reactor and then filtered through 0.45 μm Teflon syringe filters to remove TiO_2 particles. To measure the residual BBP after a certain reaction time, 5 mL of filtrate was extracted with 1 mL of mixture of n-hexane and ethyl acetate (1:1, v/v) by liquid–liquid extraction procedure. The recovery of BBP was 94%.

Each experiment was conducted three times. The data presented in the text and figures were the mean values.

In order to investigate effects of co-existing anions on the degradation of BBP by TiO_2/UV process, NaCl, $NaNO_3$, $NaClO_4$, $NaBrO_3$, Na_2CO_3, Na_2SO_4, $Na_2Cr_2O_7$ and Na_3PO_4 were tested, respectively. In addition, $NaNO_3$, KNO_3, $Mg(NO_3)_2$ and $Ca(NO_3)_2$ were used to study effects of co-existing cations on the degradation of BBP. Furthermore, acetone and methanol were also tested to investigate effects of co-existing organic compounds on the degradation of BBP. The concentration of BBP was $1\,mg\,L^{-1}$, pH value of the solution was 7.0, the dosage of TiO_2 was $2.0\,g\,L^{-1}$, and the concentrations of the co-existing substances are all 0.01 M.

2.4. Determinations of BBP and total organic carbon (TOC)

Concentration of BBP was analyzed using a Hewlett-Packard 6890 gas chromatograph (GC) equipped with a flame ionization detector (FID). The GC column was a Petrocol™ DH nonpolar bonded methyl silicone capillary column ($100\,m \times 0.25\,mm \times 0.5\,μm$ film thickness). The column temperature was kept at $280\,°C$ for 20 min. The injection port temperature and the detection port temperature were 250 and $290\,°C$, respectively. One microlitre of the extract was injected into the GC by splitless mode. Helium was used as a carrier gas at a flow rate of $1\,mL\,min^{-1}$. Flow rates of gases for FID detection were as follows: hydrogen at $40\,mL\,min^{-1}$, air at $350\,mL\,min^{-1}$, helium (make-up gas) at $30\,mL\,min^{-1}$.

To measure the total organic carbon after a certain reaction time, the sample aliquots were taken from the reactor and then filtered through 0.45 μm Teflon syringe filters to remove TiO_2 particles. Ten milliliter of the filtrate was placed in a graded tube, and freeze-dried with a Heto Drywinner freeze dryer to dryness. Distilled water was added drop by drop to dissolve the residue in the graded tube, and the volume of the solution was recorded to calculate TOC, which was measured using a Shimadzu TOC 5000A Analyzer by directly injecting the aqueous solution. The concentrated solution was manually injected using a 20 μL of syringe, and no dilution was needed.

2.5. Identification of BBP degradation intermediates

A Waters Sep-Pak C_{18} cartridge (500 mg) was conditioned by 2 mL of methanol, and then 5 mL of water. Ten milliltre of the sample was taken and centrifuged. The supernatant was filtered through 0.2-μm membrane prior to solid-phase extraction (SPE). The sample was acidified to pH 2 with 0.1 M HCl, and then passed through the cartridge at a flow rate of $2\,mL\,min^{-1}$. The analytes retained on the SPE cartridge was eluted with methanol ($1\,mL \times 2$), and the eluate was purged to dryness with pure nitrogen gas. Finally, the residue was dissolved in 0.5 mL of methanol prior to determination by HPLC and gas chromatography–mass spectrometry (GC–MS). The relationships, differences and functionality between HPLC and GC/MS when identify the intermediates could be found in literature [8].
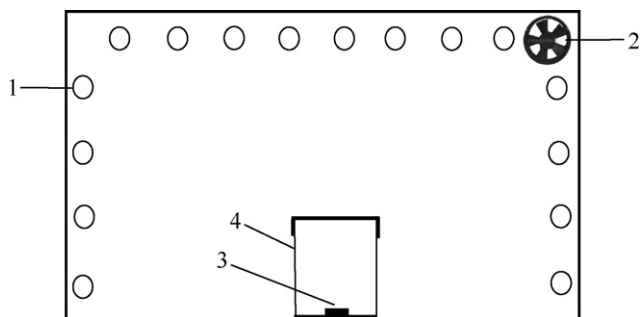

Fig. 1. Sketch map of the photocatalytic reactor. 1: lamp; 2: cooling fan; 3: magnetic stirrer; 4: quartz reactor.

The HPLC analysis was carried out using an Agilent 1100 series HPLC system consisting of a G1322A degasser, a G1311A QuatPump, a G1316A COLCOM and a G1315B diode array detector (DAD, Agilent, USA). A personal computer equipped with a HP ChemStation (HP, USA) was used to acquire and process chromatographic data. An Agilent Zorbax Eclipse XDB-C$_8$ column (150 mm × 4.6 mm, particle size 5 μm) was used as separation column. A gradient elution mode was carried out in order to obtain well-separated intermediates and parent compound. The mobile phase was a binary gradient mixture of 50 mM phosphoric acid and methanol. The gradient started at 35% (v/v) methanol maintained isocratically for the first 10 min, thereafter the methanol content was raised linearly to 65% within 2 min, and held for in 7 min, finally being returned to the original condition (35% methanol) in 1 min. The total run time was 20 min. The flow-rate was maintained at 1.00 mL min^{-1}.

The intermediate products of BBP degradation were identified by GC–MS, which was performed on a Hewlett-Packard 6890 gas chromatograph equipped with an Agilent 5973 mass selective detector (MSD). An HP-5MS 5% phenyl methyl siloxane-coated capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used. The operative gas chromatographic conditions were the following: the column temperature during injection was 50 °C, then after 2 min, it was linearly programmed to increase to a final temperature of 300 °C at 6 °C min^{-1}, and then isothermally held for 16 min. The injection volume was 1 μL, and injection temperature was 220 °C. The carrier gas was helium at a flow-rate of 1.5 mL min^{-1}. A mass range of 30–550 amu was scanned in all electron ionization mass spectroscopy studies where the electron energy was 70 eV. Instrumental library searches, comparison with available standard compounds, and mass fragmentation pattern were used to identify the degradation intermediates.

3. Results and discussion

3.1. Adsorption of BBP on TiO$_2$

The adsorption experiments were conducted to study the adsorption behavior of BBP on TiO$_2$ particles at pH 3.0, 7.0 and 9.0. The adsorption amounts of BBP by TiO$_2$ particles at pH 3.0, 7.0 and 9.0 were 12.1%, 18.5% and 13.6%, respectively. The adsorption constants at pH 3.0, 7.0 and 9.0 were respectively 0.039, 0.096 and 0.052 min^{-1}, which were calculated according to the method in literature [25]. The results showed that neutral pH favored the adsorption of BBP on TiO$_2$ particles. This is because TiO$_2$ particles at the point of zero charge (isoelectric point, about pH 6.2–7.5) [10,25,26] could adsorb more BBP molecules. When pH is below isoelectric point of the P-25 TiO$_2$, the surface of TiO$_2$ particles is electropositive, which does not favor the adsorption of BBP molecules. On the contrary, when pH is above isoelectric point, the surface of TiO$_2$ particles is electronegative, which does also not favor the adsorption of BBP molecules.

3.2. Effect of TiO$_2$ dosage on the degradation of BBP

BBP is only slightly soluble in water with a reported maximum of solubility of approximately 2.7 mg L^{-1} [27]. BBP is stable in aqueous solution. No degradation was observed in the dark at room temperature after 10 days. In general, BBP exhibits weak absorption of light at λ higher than 300 nm. The UV–VIS spectrum comprises only a weak maximum absorption at 275 nm (ε_{275} = 0.00937 M^{-1} cm^{-1}). The experimental results showed that the degradation of BBP did not occur after 3 h irradiation at 350 nm, which indicated that BBP was extremely inert and difficult to be degraded. However, the concentration of BBP continuously decreased when photocatalyst TiO$_2$ was added into BBP solution at 350 nm irradiation. Effect of TiO$_2$
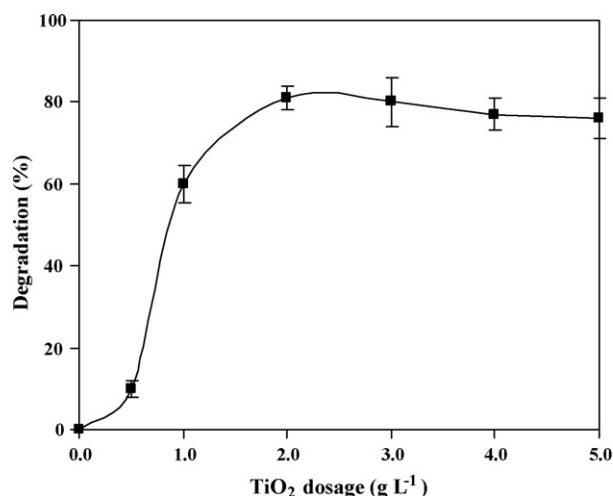

Fig. 2. Effect of TiO$_2$ dosage on the photocatalytic degradation of BBP in aqueous solution. [BBP]$_0$ = 1.0 mg L^{-1}, pH 7.0, and illumination time = 120 min.

dosage on the degradation of BBP is shown in Fig. 2. The degradation efficiency of BBP increased with increasing amounts of TiO$_2$ up to 2.0 g L^{-1}. Then, the degradation efficiency kept nearly constant with the enhanced amount of the catalyst. The increase in the degradation efficiency of BBP was because of the increase in the total surface area of the catalyst, namely number of active sites, available for the photocatalytic reaction as the dosage of catalyst increased. However, when the dosage of TiO$_2$ was overdosed, the number of active sites on the TiO$_2$ surface would become almost constant due to the decreased light penetration, the increased light scattering and the loss in surface area occasionally by agglomeration at high solid concentration [28]. Therefore, 2.0 g L^{-1} of TiO$_2$ was chosen as the optimal amount for the later photocatalytic degradation of BBP. It should also be pointed out that the different design of reactor (such as larger exposed area, more UV lamp or faster agitation), type of catalyst, characteristics of target pollutant as well as kinds and concentrations of co-existing substances in the mixture might affect the optimal TiO$_2$ dosage [22].

3.3. Effect of pH on the degradation of BBP

The pH value of the solution was another important parameter affecting photocatalytic degradation of organic pollutant since the amphoteric behavior of most semiconductor oxide affects the surface charge of the photocatalyst. Therefore, role of initial pH on the degradation of BBP was investigated, as illustrated in Fig. 3. The efficiency of BBP degradation increased when pH value increased from 3.0 to 7.0. When pH value was above 7.0, the degradation efficiency kept nearly constant with increase in pH value. The phenomenon can be explained in terms of the location of the point of zero charge (about pH 6.2–7.5) of the TiO$_2$ particles. In acidic media, the surface of TiO$_2$ is electropositive, which does not favor the adsorption of BBP molecules on the TiO$_2$ particles. However, the neutral medium favored the adsorption of BBP on TiO$_2$ particles because TiO$_2$ particles at isoelectric point could adsorb more BBP molecules. In alkaline media, although the electronegative surface of TiO$_2$ particles does not favor the adsorption of BBP molecules, more hydroxide ions (OH$^-$) in the solution induced the generation of hydroxyl free radicals (OH$^\bullet$), which came from the photooxidation of OH$^-$ by holes forming on the surface of TiO$_2$ particles. Because OH$^\bullet$ is the dominant oxidizing species in the photocatalytic process, the degradation of BBP could be fast in alkaline media [28]. It should also be pointed out that high concentration of OH$^-$ ions in
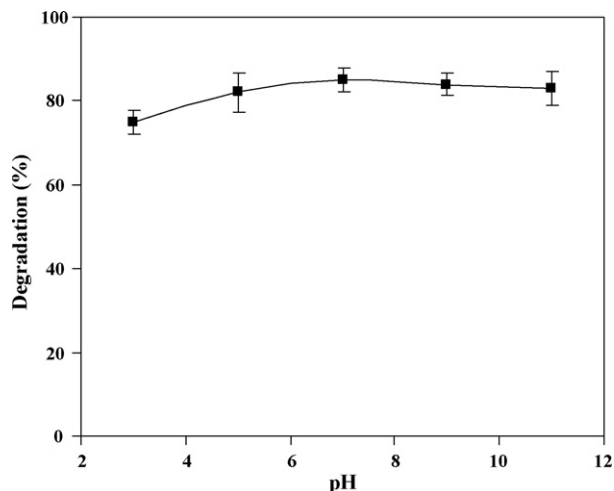
Fig. 3. Effect of pH on the photocatalytic degradation of BBP in aqueous solution. $[BBP]_0 = 1.0$ mg L^{-1}, $[TiO_2] = 2.0$ g L^{-1}, and illumination time = 120 min.

the medium might trap CO_2 generated by degradation of BBP, and as a result, bicarbonate and carbonate were formed in the alkaline medium, which would limit degradation rate of BBP because bicarbonate and carbonate are efficient scavengers of hydroxyl free radicals [21]. Therefore, pH 7.0 was selected as the optimal experimental condition because there was no need for a neutralization process. It need be pointed out that type of catalyst and characteristics of target compound would affect the optimal pH value [21,22].

3.4. Effect of initial BBP concentration on the degradation of BBP

Because the concentration of target compound is an important parameter affecting degradation efficiency in the photocatalytic reaction, the effect of initial BBP concentration on the degradation rate of BBP was investigated over the concentration range of 0.5–2.5 mg L^{-1}, and the results are presented in Fig. 4A. With increasing the initial BBP concentration, the degradation efficiency of BBP decreased. The results indicated that BBP degradation kinetics is not simple first order but pseudo-first-order. The photocatalytic degradation kinetics of organic pollutants is usually modeled with the Langmuir–Hinshelwood equation [29]. That is,

$$\text{rate} = -\frac{dc}{dt} = \frac{kKC}{1 + KC_0} = k_{obc}C \tag{4}$$

$$k_{obs} = \frac{kK}{1 + KC_0} \tag{5}$$

where k is the reaction rate constant, K is the adsorption equilibrium constant, C is BBP concentration at time t, C_0 is initial BBP concentration, and k_{obs} is the observed pseudo-first-order rate constant for the photocatalytic degradation of BBP. Therefore, the integration of Eq. (4) results in

$$\ln\left(\frac{C}{C_0}\right) = -k_{obs}t \tag{6}$$

Based on Eq. (6), the linear relationship of $\ln(C/C_0)$ with irradiation time was observed as indicated in Fig. 4A and Table 1. In addition, the relationship between k_{obs} and C_0 from Eq. (5) can be expressed as follows:

$$\frac{1}{k_{obs}} = \frac{1}{kK} + \frac{[C_0]}{k} \tag{7}$$

Eq. (7) shows that the linear expression could be obtained by plotting the reciprocal of degradation rate ($1/k_{obs}$) as a function
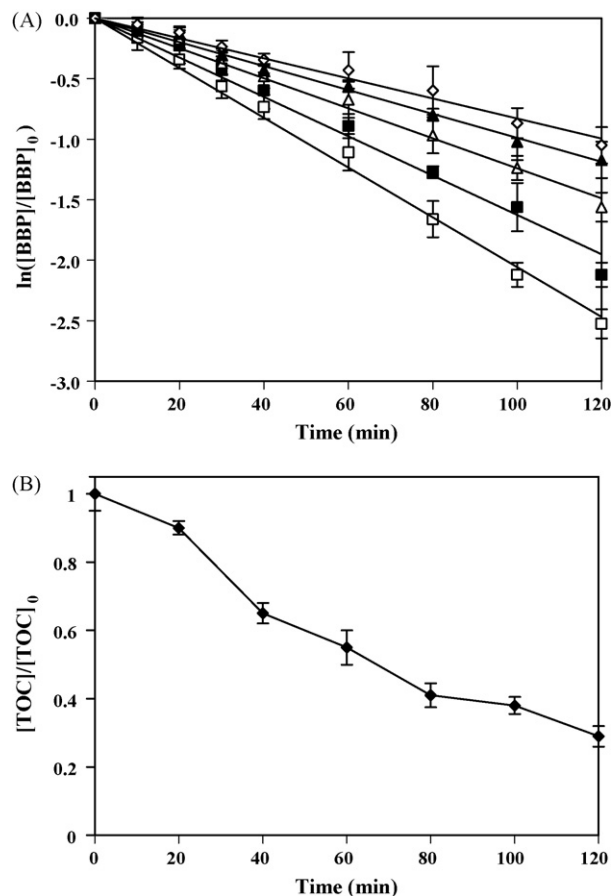

Fig. 4. Effect of the initial BBP concentrations on the photocatalytic degradation of BBP in aqueous solution (A), and variation of TOC with time (B). $[TiO_2] = 2.0$ g L^{-1} and pH 7.0. Concentration of BBP: (◇) 2.5 mg L^{-1}; (▲) 2.0 mg L^{-1}; (△) 1.5 mg L^{-1}; (■) 1.0 mg L^{-1}; (□) 0.5 mg L^{-1}. For Fig. 4B, $[BBP]_0 = 1.0$ mg L^{-1}.

of the initial BBP concentration. The values of adsorption equilibrium constant (K) and the reaction rate constant (k) can be calculated from the intercept and slope of the linear regression according to the data of $1/k_{obs}$ and $[BBP]_0$ in Table 1, and these values were found to be $K = 1.274$ L mg^{-1} and $k = 0.0292$ mg min^{-1} L^{-1} ($R^2 = 0.976$), respectively.

3.5. Effects of co-existing substances on the degradation of BBP

Usually, industrial wastewater is a mixture which contains inorganic and organic substances. Therefore, the influence of the co-existing inorganic and organic substances on BBP degradation efficiency was investigated, and the results are given in Table 2. It is interesting to note that some anions (such as BrO_3^-, ClO_4^- and $Cr_2O_7^{2-}$) could enhance BBP degradation, and other anions would restrain BBP degradation. The sequence of inhibition was

Table 1
The pseudo-first-order rate constant k_{obs}, $1/k_{obs}$, half-life $t_{1/2}$ (mean ± standard deviation) and correlation coefficient R^2 for photocatalytic degradation of BBP at different initial concentration of BBP with pH 7.0 and $[TiO_2] = 2.0$ g L^{-1}

$[BBP]_0$ (mg L^{-1})	k_{obs} (min^{-1})	$1/k_{obs}$ (min)	$t_{1/2}$ (min)	R^2
0.5	0.0209 ± 0.0013	47.85 ± 2.98	33.16 ± 2.06	0.991
1.0	0.0185 ± 0.0011	54.05 ± 3.21	37.46 ± 2.23	0.985
1.5	0.0124 ± 0.0009	80.64 ± 5.85	55.88 ± 4.06	0.993
2.0	0.0104 ± 0.0007	96.15 ± 6.47	66.63 ± 4.49	0.994
2.5	0.0089 ± 0.0008	112.4 ± 10.1	77.89 ± 7.01	0.984

Table 2
The pseudo-first-order rate constant k_{obs}, half-life $t_{1/2}$ (mean ± standard deviation) and correlation coefficient R^2 for photocatalytic degradation of BBP with different co-existing substances

Co-existing substances	k_{obs} (min^{-1})	$t_{1/2}$ (min)	R^2
No	0.0185 ± 0.0011	37.46 ± 2.23	0.985
NaCl	0.0180 ± 0.0014	38.51 ± 3.01	0.965
Na$_2$SO$_4$	0.0157 ± 0.0009	44.15 ± 2.53	0.982
Na$_3$PO$_4$	0.0119 ± 0.0007	58.25 ± 3.43	0.909
Na$_2$CO$_3$	0.0131 ± 0.0011	52.91 ± 4.44	0.912
NaBrO$_3$	0.0192 ± 0.0016	36.10 ± 3.01	0.951
NaClO$_4$	0.0198 ± 0.0013	35.01 ± 2.31	0.927
Na$_2$Cr$_2$O$_7$	0.0204 ± 0.0016	33.98 ± 2.66	0.938
NaNO$_3$	0.0143 ± 0.0009	48.47 ± 3.05	0.958
KNO$_3$	0.0145 ± 0.0008	47.80 ± 2.64	0.931
Mg(NO$_3$)$_2$	0.0136 ± 0.0012	50.97 ± 4.51	0.973
Ca(NO$_3$)$_2$	0.0129 ± 0.0006	53.73 ± 2.49	0.947
Acetone	0.0154 ± 0.0009	45.01 ± 2.63	0.952
Methanol	0.0148 ± 0.0012	46.83 ± 3.81	0.934

$[BBP]_0 = 1.0\,mg\,L^{-1}$, pH 7.0 and $[TiO_2] = 2.0\,g\,L^{-1}$. The concentrations of the co-existing substances are all 0.01 M.

$PO_4^{3-} > CO_3^{2-} > NO_3^- > SO_4^{2-} > Cl^-$. The cations K$^+$, Na$^+$, Mg^{2+} and Ca^{2+} had the restrained effect on the BBP degradation, and the effect of Ca^{2+} was the strongest among four cations tested (Table 2), which were similar to the results reported in literature [21]. The rate retardation likely resulted from the adsorption of ions on the surface of TiO$_2$ and the isolation of the BBP molecules from the reaction or blocking the active sites of the TiO$_2$ catalyst surface. The cause of different extents of rate retardation was likely the different binding ability of ions at the surface of the TiO$_2$ particles. In addition, other effects such as the scavenging of hydroxyl free radicals by phosphate or carbonate could be partly contributed to the rate retardation. On the other hand, addition of electron acceptor BrO$_3^{2-}$, ClO$_4^-$ or Cr$_2$O$_7^{2-}$ could enhance the degradation of BBP. It is well known that semiconductor photocatalysis was based on the reactive properties of electron–hole pairs generated in the semiconductor particles under illumination by light of energy greater than the semiconductor band gap [9,10]. When electron acceptor was added to the reaction system, it would accelerate degradation of organic pollutant because electron acceptor might prohibit recombination of electron and hole by means of combination with electron [30,31]. In addition, acetone and methanol were chosen as co-existing organic compounds since both of them are commonly used solvents. The results showed that the photocatalytic degradation efficiency of BBP decreased with the addition of acetone or methanol. These could be resulted from the competition of hydroxyl radicals. Both acetone and methanol are small-molecule organic compounds which are easier to be oxidized when they co-existed with other organic compounds. Thus, in the case of the presence of other organic pollutants and inorganic ions, longer illumination time were needed in order to achieve the same degradation efficiency as that obtained in the case of BBP only.

3.6. Mechanism of BBP degradation

To explore the degradation mechanism of BBP, the intermediate products formed in the photocatalytic degradation of BBP in the aqueous suspensions of titanium dioxide were identified through HPLC and GC–MS methods according to literature [8] with minor modification. Comparison with available standard compounds, instrumental library searches, and mass fragmentation pattern were used to identify degradation intermediates. Mono-butyl phthalate, mono-benzyl phthalate and phthalic acid were identified as primary intermediate products of BBP degradation.
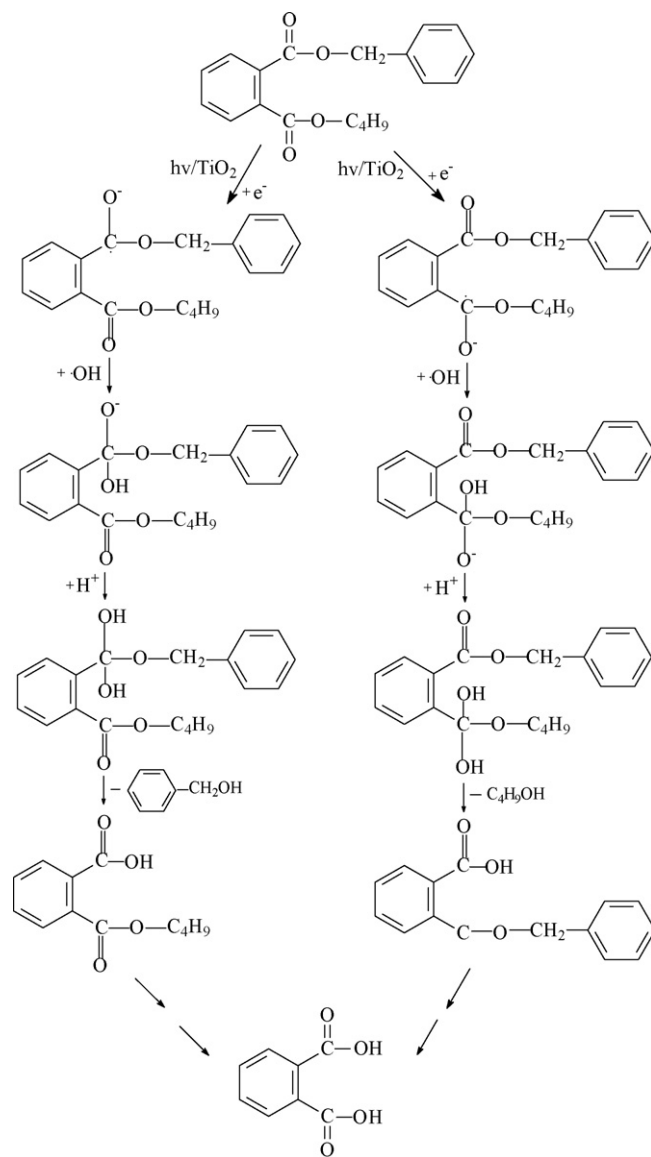

Fig. 5. Proposed pathways for the photocatalytic degradation of BBP.

Based on the identification of intermediates, we used a combination of literature [15,16] and our experimental data to elucidate a comprehensive pathway for the photocatalytic degradation of BBP. Fig. 5 shows the mechanism for the formation of three intermediate products involving electron transfer reactions and reactions with hydroxyl radicals. The model compound BBP upon the transfer of an electron could form a radical anion, which might undergo addition of a hydroxyl radical forming the anionic species. The loss of a butanol or benzyl alcohol from the species could lead to the formation of the observed products mono-butyl phthalate and mono-benzyl phthalate. Under the action of electrons and then hydroxyl radicals, mono-butyl phthalate and mono-benzyl phthalate would form phthalic acid by a similar process. Furthermore, the removal of TOC was approximately 70% after illumination time of 120 min (Fig. 4B), which indicated that most of BBP and the intermediate products would be mineralized to final products CO$_2$ and water with increased illumination time, although some intermediates could be adsorbed on TiO$_2$ particles [21,22].

4. Conclusions

Effects of TiO_2 dosage, pH, initial BBP concentration and co-existing substances on the degradation of BBP by TiO_2/UV process were investigated. The optimal TiO_2 dosage and pH value for the BBP degradation were $2.0\,g\,L^{-1}$ and 7.0, respectively. The degradation rate of BBP by TiO_2/UV process could be fitted pseudo-first-order kinetics. The effects of co-existing substances on the degradation rate of BBP reveal that some ions (such as BrO_3^-, ClO_4^-, and $Cr_2O_7^{2-}$) could enhance BBP degradation, and other ions would restrain BBP degradation. The sequence of inhibition was $PO_4^{3-} > CO_3^{2-} > NO_3^- > SO_4^{2-} > Cl^-$. The cations K^+, Na^+, Mg^{2+} and Ca^{2+} had the restrained effect on the BBP degradation, and the effect of Ca^{2+} was the strongest among four cations tested. The organic compounds acetone and methanol decreased the degradation rate of BBP. The major intermediates of BBP degradation were identified as mono-butyl phthalate, mono-benzyl phthalate and phthalic acid, and a primary degradation mechanism was proposed. The removal of TOC showed that most of BBP and the intermediate products would be mineralized to final products CO_2 and water with increasing illumination time. The results obtained are helpful for the treatment of water contaminated with BBP.

Acknowledgements

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