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Photocatalytic degradation of Bisphenol A (BPA) using immobilized TiO_2 and UV illumination in a horizontal circulating bed photocatalytic reactor (HCBPR)

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ABSTRACT

Photocatalytic degradation of Bisphenol A (BPA) in the presence of titanium dioxide (TiO_2) and ultraviolet (UV) illumination was performed in a self-designed horizontal circulating bed photocatalytic reactor (HCBPR). TiO_2 catalyst was immobilized on the surface of polyurethane foam (PF) cubes via microwave-assisted liquid phase deposition. The effects of initial BPA concentration, initial pH, TiO_2 dosage and temperature on BPA photodegradation were investigated in order to obtain the optimum operational conditions. The results reveal that the BPA degradation efficiency can be effectively improved by increasing pH from 3.4 to 12.3 or decreasing the initial BPA concentration from 50 to 10 ppm. The optimum TiO_2 carrier dosage (the ratio of the volume of PF carriers to the effective reaction volume of HCBPR) was about 1%. Besides, the effect of temperature on BPA photodegradation was found to be unremarkable in the range of 21.2–30.5 °C. Total organic carbon (TOC) was used to evaluate the mineralization of BPA during the photodegradation process. Under the optimum conditions, 95% removal of TOC and 97% removal of BPA can be achieved after 6 h of UV radiation, which demonstrates the high photodegradation efficiency of BPA in HCBPR.

1. Introduction

Bisphenol A (2,2-bis(4-hydroxyphenyl)propane or BPA) has been widely used as a raw material in the production of polycarbonate plastics and epoxy resins [1,2]. Because of its wide usage and its endocrine disrupting effects, BPA has been regarded as a representative material among endocrine disruptors and causes reproductive damage to aquatic organisms [3–7]. Therefore, in the last decade, there is an increasing interest in effective remediation technologies for the destruction of BPA in contaminated water environments.

Various methods have been put forward by researchers in recent years, involving biochemical [8–13], electrochemical [14], sonochemical [15] and photochemical [16–23] reactions. One of the most promising methods is photocatalytic degradation due to its high mineralization efficiency, low toxigenicity, ideally producing carbon dioxide, water and inorganic mineral ions as end products [24]. Among the photocatalysts used, titanium dioxide (TiO_2) is considered a very efficient one because of its photoactivity, physical and chemical stability, low cost and easy access. In general, photoinduced electrons (e^-) and positive holes (h^+) are produced from TiO_2 surface under illumination of UV light ($\lambda < 380$ nm). These species can further produce hydroxyl free radicals ($^\bullet OH$), which is a kind of strong oxidants, contributing to the destruction of contaminants into CO_2 and H_2O. Some studies were conducted recently about photocatalytic degradation of BPA [16–23], slurry reactor system was used in most of the cases, in which TiO_2 particles were suspended in the form of colloid and employed as photocatalyst. In slurry reactor systems, the photocatalytic reaction rate is mainly regulated by the UV light intensity, the quantum efficiency of the catalyst and the adsorption characteristics of both the reacting and non-reacting components in solution [25]. However, the requirement of separation of the ultra fine catalyst particles from the treated liquid hinders the wide application of slurry photocatalytic reaction systems. For instance, Chin et al. [26] developed a submerged membrane photocatalytic reactor using membrane to separate TiO_2 from the effluent; however, the problem of membrane fouling happened occasionally.

The above problems can be avoided in photocatalytic reactors where the catalytic particles are immobilized on a support or carrier. Hence, it is promising to employ the TiO_2-immobilized photocatalytic reactors. Nakashima et al. (2002) [17] had investigated the photocatalytic decomposition of BPA by use of TiO_2 immobilized on polytetrafluoroethylene (PTFE) mesh sheets. In reactor I, the TiO_2-modified PTFE mesh sheets were stacked with 5 mm gaps in a 2-L glass cylinder in which the solution was circulated by use

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of a rotary pump. In reactor II, the TiO_2-modified PTFE mesh sheets were attached to a bar-rotator in a fan-type arrangement and were rotated at 60 rpm. The apparent mass-transfer rate of the BPA to the TiO_2 in reactor II is about 4.5 times higher than in reactor I. It was found that BPA was decomposed more quickly in Reactor II than in Reactor I. Therefore, enhancing the mass transfer of pollutants from bulk liquid to TiO_2 surface is essential for developing and optimizing the TiO_2-immobilized photocatalytic reactors. On the base of this principle, we developed a novel TiO_2-immobilized photocatalytic reactor, named horizontal circulating bed photocatalytic reactor (HCBPR), in which photocatalyst TiO_2 is immobilized on polyurethane foam (PF) cubes and the PF cubes are suspended and circulated in the reactor, so as to get high mass transfer rate of pollutant to TiO_2 surface.

Hence, the purpose of this study is to investigate the removal efficiency of BPA in the self-designed horizontal circulating bed photocatalytic reactor and the effects of different operating parameters, such as, initial BPA concentration, initial pH, TiO_2 dosage and temperature. Additionally, the kinetics of BPA degradation and the complete mineralization process of BPA in HCBPR were discussed.

2. Materials and methods

2.1. Reactor configuration

Photocatalytic degradation experiment was carried out in a self-designed horizontal circulating bed photocatalytic reactor, as shown in Fig. 1. A low-pressure UV lamp (Guoda Co. Ltd. Shanghai, China, 25 W, with peak emission at $\lambda = 254$ nm, outer diameter of 4.5 cm) was set in the center of reactor. The UV irradiation intensity was 18 $mW\,cm^{-2}$. The reactor was covered tightly by foil to minimize light energy lost. The main reaction zone of HCBPR was a tube-like chamber with diameter of 20 cm and length of 42 cm (the effective reaction volume is 12.5 L), where the PF carriers were suspended. The aerators used for fluidizing the PF carriers were fixed at one side near the bottom of the HCBPR reactor. The air bubbles from aerators could not only provide the oxygen needed in photocatalytic oxidation but also enhance the contact efficiency between contaminants and photocatalyst, which further increased the degradation efficiency. Moreover, taking advantage of immobilized photocatalytic carriers, continuous treatment without extra separation process of TiO_2 could be conveniently achieved in HCBPR.

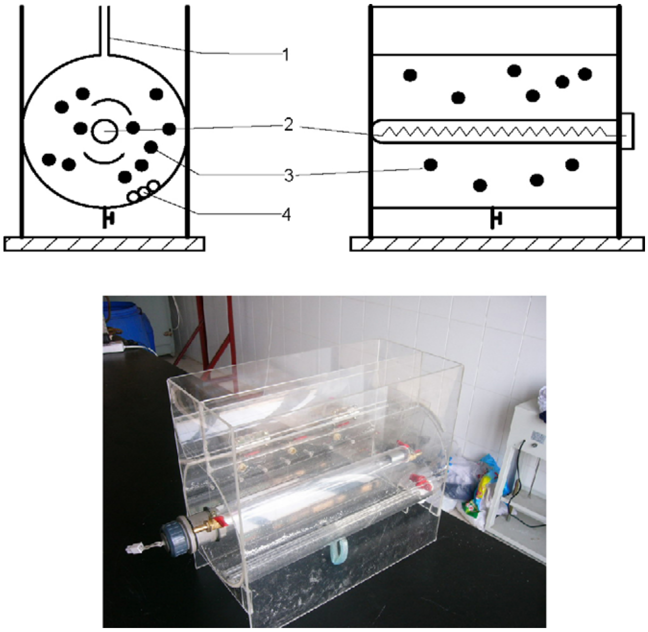

Fig. 1. Schematic and photo of horizontal circulating bed photocatalyst reactor (HCBPR) (1, air outlet; 2, UV lamp; 3, photocatalyst carriers; 4, aerators).

2.2. Photocatalyst immobilization

The P25 Titanium dioxide (TiO_2) (Degussa AG, Germany) was used as the photocatalyst in this study. Porous polyurethane foam (PF) cube (1 cm^3 by volume) was used as photocatalyst carrier. The density of PF cube is about 30 $kg\,m^{-3}$ and its specific surface area is about 1.1×10^5 $m^2\,m^{-3}$. Microwave-assisted liquid phase deposition method was applied to immobilize TiO_2 on PF carriers, because the PF carriers are irresistible to high temperature exposure. First, ammonium hexafluorotitanate and boric acid were dissolved into deionized water to give a concentration of 0.1 mM and 0.3 mM, respectively. Then, a small amount of P25 was added into the mixture serving as crystallization-inducing reagent; and the mixture was vigorously stirred for 30 minutes and afterwards was filtered to get transparent deposition liquid. Polyurethane foams, which were pretreated under supersonic in 10% (v/v) HNO_3, ethanol, and deionized water beforehand, were emerged into that liquid and then radiated to deposition in microwave oven for 30 min. After deposition, the carriers were sieved out from the liquid and washed with deionized water to remove the non-firmly attached TiO_2 particles. Finally, the TiO_2 immobilized carriers were dried under room temperature. The SEM images of polyurethane foam before and after the TiO_2 immobilization are shown in Fig. 2(a) and (b), respectively. X-ray diffraction (XRD, Rigaku D/Max 2550) results proved that the deposited TiO_2 has a good photocatalyst performance, which was mainly constituted of anatase with its particle size of 10–15 nm [27].

2.3. Start-up and operation

After placing certain number of carriers into the reactor, the system was operated in the absence of UV irradiation (Dark) for 3 h to achieve adsorption equilibrium of BPA on carrier's surfaces. Then, the UV lamp was turned on (Under UV) and photocatalytic degradation was conducted for next 6 h. For every 1 h, 5 mL sample was collected from the reactor. Each sample was filtered with 0.45 μm microfiltration membrane before chemical analysis. In this study, 10% HCl and 10% NaOH were used as pH adjustor. The aeration flow rate was set at 100 $L\,h^{-1}$.

2.4. Chemical analysis

High purity BPA used in this study was supplied by Sigma–Aldrich. The chemical structure of BPA is presented in Fig. 3. The concentration of BPA in samples was measured using a high performance liquid chromatograph (Varian Prostar), interfaced with a photodiode array detector. The separation was carried out by a Suplecosil LC-18 column (4.6 mm × 150 mm, 5 μm) with a mobile phase consisting of 50% water and 50% acetonitrile (flow rate, 1 $mL\,min^{-1}$). The TOC of samples was measured by Shimadzu TOC-$V_{CPH/CPN}$.

2.5. Photodegradation kinetic parameters

Under the experimental conditions, it can be assumed that the first step in reaction is able to adsorb BPA molecules and their degradation products on the surface of TiO_2 photocatalyst, and the second step is all substrates adsorbed to be decomposed. The kinetic model for BPA photocatalytic degradation is based on the following assumptions: (1) photocatalytic oxidation is mainly completed via the hydroxyl groups absorbed on the surface of the TiO_2

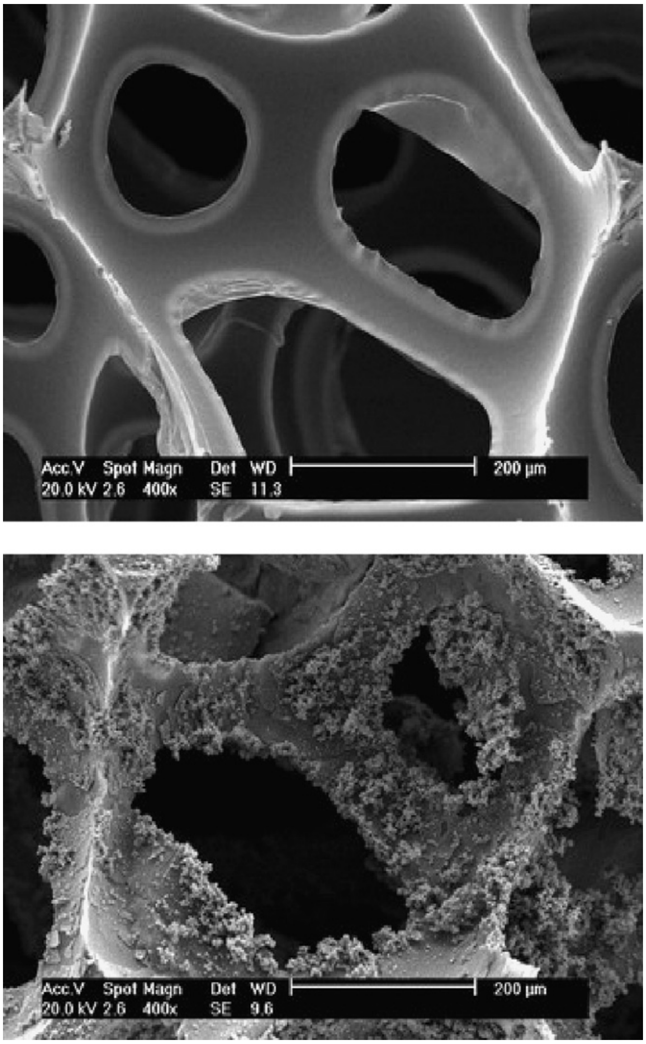

Fig. 2. SEM images of polyurethane foam used (a) and polyurethane foam after microwave-assisted liquid phase deposition treatment (b).

particles, which attacks the organic compounds and related intermediates, and the interaction of hydroxyl with compounds is the rate-limiting step for photocatalytic degradation. (2) The combination of H_2O/OH^- with the photo-induced hole h^+ to form hydroxyl is a reversible process, and the $^{\bullet}OH$ radicals should be mainly formed from the adsorbed H_2O molecules. (3) The combination rate of h^+/e^- is much higher than the hydroxyl forming rate of the reaction between h^+, H_2O and OH^-; and the concentration of H_2O/OH^- which is available to combine with h^+ is far higher than that of h^+. (4) The concentration of hydroxyl radicals is constant at a steady state (Bodenstein steady state assumption); and (5) the concentration of h^+ is constant at steady state (Bodenstein steady state assumption). Acknowledging the above-mentioned reaction steps for photocatalysis, the elementary reaction equations are expressed as the following equations:

$$\mathrm{TiO_2} + h\nu \xrightarrow{h\nu>3.2\,\mathrm{eV}} \mathrm{TiO_2}(\mathrm{e^-_{CB}} + \mathrm{h^+_{VB}}) \tag{1}$$

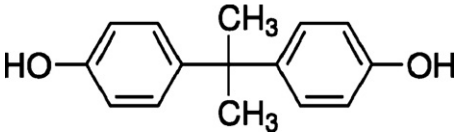

Fig. 3. Chemical structure of Bisphenol A (BPA).

$$\mathrm{h^+_{VB}} + \mathrm{OH^-} \rightarrow \cdot\mathrm{OH} \tag{2}$$

$$\mathrm{h^+_{VB}} + \mathrm{H_2O} \rightarrow \cdot\mathrm{OH} + \mathrm{H^+} \tag{3}$$

$$^{\bullet}\mathrm{OH} + \mathrm{BPA} \rightarrow\rightarrow \text{Oxidative intermediates} \rightarrow\rightarrow \mathrm{CO_2} + \mathrm{H_2O} \tag{4}$$

The Langmuir-Hinshelwood (L-H) model is commonly used to describe these processes, which is considered to follow pseudo-first-order decay kinetics [28].

$$r = \frac{dC}{dt} = \frac{kKC}{1+KC} \tag{5}$$

where C is the BPA concentration, k is the BPA degradation rate constant, and K represents adsorption equilibrium constant. In this study, BPA concentration C was less than $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$, which made $KC \ll 1$; hence, Eq. (5) can be transformed to Eq. (6) [25].

$$r = \frac{dC}{dt} = kKC = k_{ap}C \tag{6}$$

A linear form of (6) is:

$$\ln\left(\frac{C_0}{C}\right) = k_{ap}t \tag{7}$$

where C_0 and C are the BPA concentration at times zero and t, repectively, and k_{ap} represents the apparent degradation rate constant. The apparent degradation rate constants were determined by regression analysis. Half-lives $t_{1/2}$ were calculated using Eq. (8) which was derived from Eq. (7) by replacing C with $C_0/2$:

$$t_{1/2} = \frac{\ln 2}{k_{ap}} = \frac{0.6931}{k_{ap}} \tag{8}$$

The kinetic parameters k_{ap} and $t_{1/2}$ for the photocatalytic degradation of BPA were investigated in order to compare the effects of various factors on BPA photodegradation efficiency. The experimental design is listed in Table 1.

The TiO_2 dosage (R) is defined as the ratio of the PF carrier volume ($V_{carriers}$) to the effective volume of reaction zone in HCBPR ($V_{reactor}$) (Eq. (9)), with the assumption that the TiO_2 particles were homogenously immobilized on the PF cubes.

$$R = \frac{V_{carriers}}{V_{reactor}} \tag{9}$$

Table 1
Experimental design for photocatalytic degradation of BPA in HCBR.

Factors	Values	Other conditions
Initial BPA concentration (ppm)	10	Initial pH 7.4
	20	TiO_2 dosage: 1%
	30	Temperature: 24.3 °C
	40	
	50	
Initial pH	3.4	Initial BPA: 10 ppm
	5.1	TiO_2 dosage: 1%
	7.4	temperature: 24.3 °C
	9.7	
	12.3	
TiO_2 dosage (%, v/v)	0.0	Initial BPA: 10 ppm
	0.5	Initial pH 7.4
	1.0	Temperature: 24.3 °C
	1.5	
	2.0	
	3.0	
Temperature (°C)	21.2	Initial BPA: 10 ppm
	24.3	Initial pH 7.4
	30.5	TiO_2 dosage: 1%

3. Results and discussion

3.1. Effect of initial BPA concentration

It is significant from both the mechanistic and application point of view to investigate the dependence of the photocatalytic reaction on the initial BPA concentration. The effect of initial BPA concentration on the BPA degradation kinetics was investigated by employing different initial BPA concentrations (10 ppm, 20 ppm, 30 ppm, 40 ppm and 50 ppm, 1 ppm = 4.4 × 10^{-3} mmol L^{-1}). The experiments were carried out at fixed pH 7.4, TiO_2 dosage 1%, temperature 24.3 °C and the solution volume is 12.5 L. As shown in Fig. 4, the greatest BPA removal rate was reached when BPA initial concentration was 10 ppm (0.044 mmol L^{-1}). The BPA removal rate after the same reaction time decreased when the initial BPA concentration increased from 10 ppm (0.044 mmol L^{-1}) to 50 ppm (0.220 mmol L^{-1}).

The active sites for photocatalytic reaction remain the same at a fixed TiO_2 dosage. Almost no inhibition of the catalyst action occurs when the BPA initial concentration is relative low. However, as the BPA initial concentration increases, more and more BPA molecules are adsorbed on the surface of TiO_2 particles. The accumulation of BPA molecules in the inner layer spacing on the TiO_2 surface results in the adsorption competition for active sites between BPA molecules and the inhibition of TiO_2 photocatalytic activity, which thereby decreases the amount of reactive hydroxyl free radicals attacking BPA molecules and leads to the decrease of BPA photodegradation efficiency [29].

Since some intermediates are formed during photocatalytic degradation and may interfere with the total kinetics, some calculations were done at the beginning of UV irradiation. During a short time interval, any changes such as intermediates effects could be considered as negligible. Hence, the initial photocatalytic degradation rate can be expressed as a function of initial BPA concentration, see Eq. (10).

$$r_0 = \frac{kKC_0}{1 + KC_0} \tag{10}$$

The inverse of Eq. (10) gives the following expression (Eq. (11)), which indicates the dependence of $1/r_0$ values on the appropriate $1/C_0$ values of BPA concentration:

$$\frac{1}{r_0} = \frac{1}{k} + \frac{1}{kK}\frac{1}{C_0} \tag{11}$$

The applicability of L–H equation for BPA photodegradation has been confirmed by the linear plot obtained by plotting the reciprocal of initial reaction rate (1/r) against reciprocal of initial concentration ($1/C_0$) as shown in Fig. 5. The values for K and k are found to be 6.00 L $mmol^{-1}$ and 0.303 mmol L^{-1} h^{-1}, respectively.

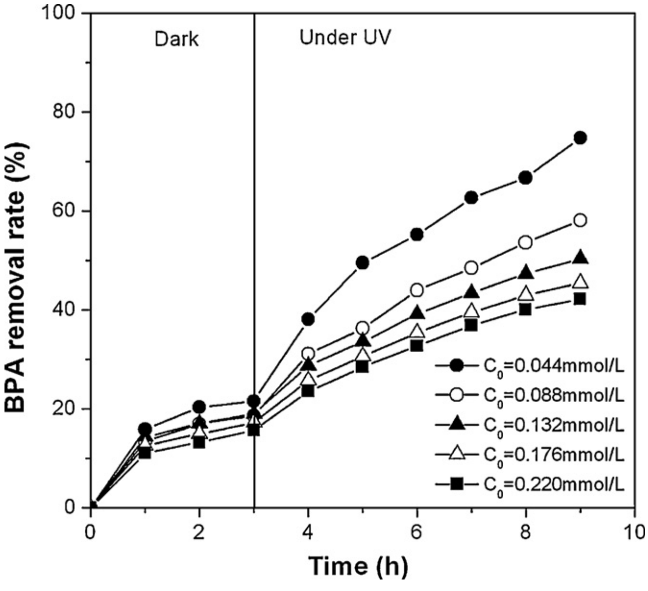

Fig. 4. Effect of initial BPA concentration on BPA removal rate in HCBPR. TiO_2 dosage (R) = 1%, initial pH 7.4, temperature (T) = 24.3 °C.

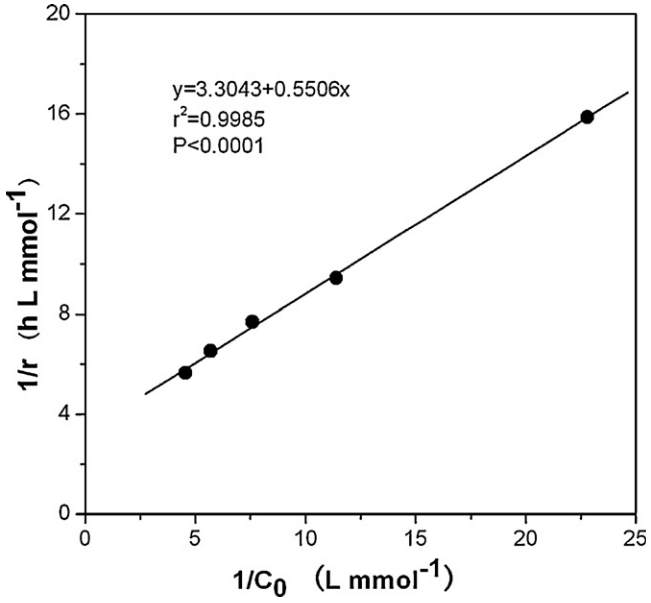

Fig. 5. Dependence of 1/r on the reciprocal of initial BPA concentration C_0.

3.2. Effect of initial pH

The amphoteric character of most semiconductor oxides casts a critical effect on the surface charge of the photocatalyst, which is directly related to the emergence of free radicals and the decomposition of contaminants on surface. Hence, pH is one of the main factors influencing the degradation rate of organic compounds in the photocatalytic process. The effect of pH on BPA degradation rate was investigated in the range of 3–12 at BPA concentration 0.044 mmol L^{-1} and TiO_2 dosage (R) 1.0%. The comparison of BPA removal rate at different pH values is shown in Fig. 6. The changes of k_{ap} and $t_{1/2}$ versus pH were illustrated in Fig. 7.

In general, the zero point of charge (zpc) of TiO_2 is around pH 6.25 [11]. That is, TiO_2 surface is positively charged in acidic media (pH < 6.25) whereas it is negatively charged in alkaline circumstance (pH > 6.25). On the base of the simulation of molecular point charge, it is found that the BPA molecule has two negative oxygen atoms at the hydroxyl groups and four negative carbon atoms at the phenolic group [19]. These properties determine the initial adsorption of BPA molecules on the TiO_2 surface. Hence, the acidic conditions (pH < 6.25) favor the initial adsorption of BPA on the positively charged TiO_2 surface. On the contrary, as the pH increases and is higher than 6.25, the TiO_2 surface gradually becomes more negatively charged, which results in the development of greater repulsive forces between TiO_2 surface and BPA molecules and thus the retardation of initial adsorption of BPA on the TiO_2 surface. These phenomena can be observed by the comparison of BPA removal rate during the three-hour dark stage at different pH conditions, as shown in Fig. 6. A lower BPA removal rate was observed when the pH value increased to 12.3. These results agree with those reported by other researchers [19,20,26].

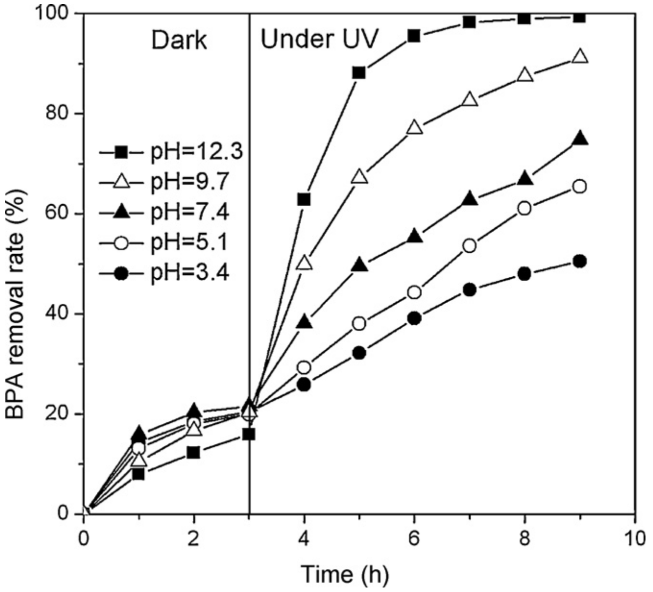

Fig. 6. Effect of initial pH on BPA removal rate in HCBPR. TiO_2 dosage (R) = 1%, initial BPA concentration C_0 = 10 ppm, temperature (T) = 24.3 °C.

Generally, the pH variations cast a major influence not only on the adsorption mode of BPA on photocatalyst surface, but also on the redox reactions which are quite sensitive to surface charge [30]. It was observed that BPA photocatalytic degradation efficiency can be significantly improved via the increase of pH value, as illustrated in Fig. 7. When pH value is lower than 7.0, the values of k_{ap} are almost at the same level and lower than 0.20 h^{-1}. However, k_{ap} value increases dramatically from 0.148 ± 0.047 h^{-1} to 0.845 ±0.263 h^{-1} while pH value increases from 7.4 to 12.3. These results indicate that the alkaline conditions facilitate the photocatalytic decomposition of BPA. Similar results were reported earlier for the photocatalytic degradation of cyanosine dye [29], aniline [28], and chloramben [31]. Since BPA is difficult to be adsorbed on the TiO_2 surface at alkaline pHs, BPA would have a lesser chance to react with the photogenerated hole on the TiO_2 surface and tends to react with the diffused hydroxyl radicals in the bulk liquid [20]. This effect may be attributed to more efficient generation of hydroxyl radicals ($^\bullet OH$) on the TiO_2 surface with an increase of hydroxide ion (OH^-) concentration, and the high mass transfer efficiency of hydroxyl radicals ($^\bullet OH$) from the TiO_2 surface to the bulk liquid in HCBPR. Therefore in this case, the presence of large quantities of OH^- on the TiO_2 particle surface as well as in the reaction medium favors the production of hydroxyl free radicals and improves the BPA photocatalytic degradation efficiency in HCBPR.

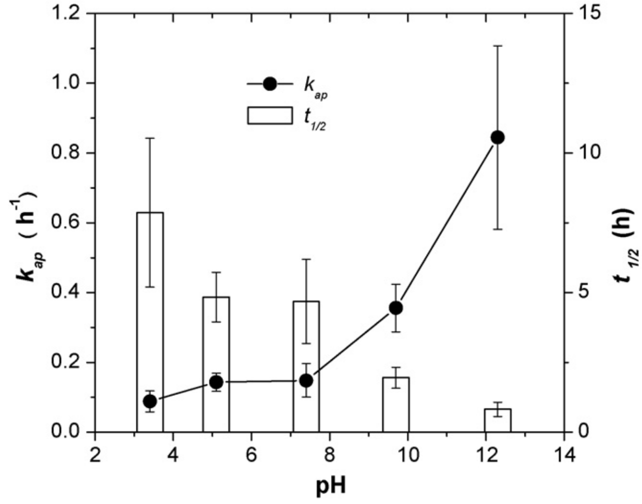

Fig. 7. Changes of the apparent BPA photocatalytic reaction constant k_{ap} and half-life time $t_{1/2}$ at different pH. TiO_2 dosage (R) = 1%, initial BPA concentration C_0 = 10 ppm, temperature (T) = 24.3 °C.

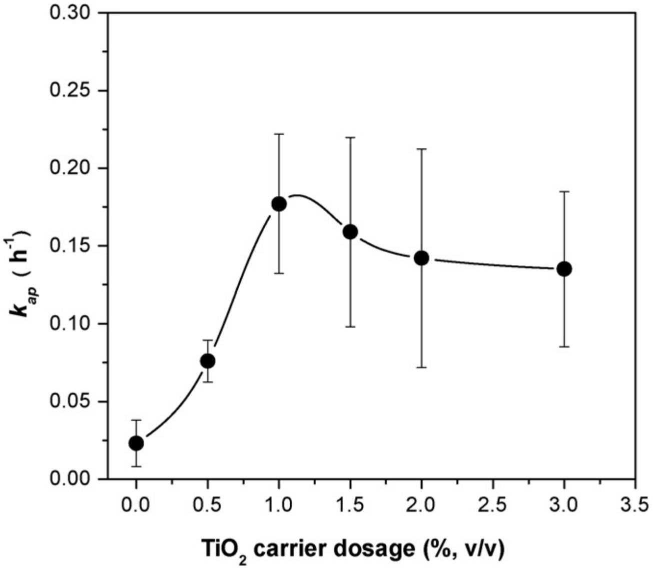

Fig. 8. Changes of the apparent BPA photocatalytic reaction constant k_{ap} at different TiO_2 dosage. Initial BPA concentration C_0 = 10 ppm, initial pH 7.4, temperature (T) = 24.3 °C.

3.3. *Effect of photocatalyst dosage*

The effect of photocatalyst (TiO_2) carrier dosage on the degradation of BPA in HCBPR was investigated. The experiments were conducted at various amounts of TiO_2 dosage R of 0, 0.5, 1.0, 1.5, 2.0 and 3.0%, while initial BPA concentration used was 10 ppm, initial pH was 7.4, and the temperature of bulk liquid was 24.3 °C.

The changes of k_{ap} versus R are illustrated in Fig. 8. The values of k_{ap} increased with increasing R up to 1.0%. Then, the apparent degradation rate constant k_{ap} decreased slightly, and became nearly flat when R was higher than 2.0%. The increase of k_{ap} seems to be the results of an increase in the total surface area of TiO_2, namely, an increase of the active sites and an increase in the hydroxyl radicals generation. However, when enough TiO_2 is present in the reactor for adsorbing BPA molecules, the extra higher quantities of TiO_2 carriers would not have more positive effect on the BPA degradation efficiency. On the contrary, when TiO_2 was overdosed, the number of active sites on the TiO_2 particle surface, which were available for the photocatalytic reaction, might approach constant or even decrease slightly because of the decrease of light penetration and the increase of UV light scattering. Therefore, there is an optimum TiO_2 dosage (R) for HCBPR, in this case, the optimal TiO_2 dosage (R) for BPA photodegradation in HCBPR was about 1.0% (v/v).

Similar phenomena have already been reported in other TiO_2 suspension photocatalytic systems. For example, the optimum TiO_2 dosage for the photocatalytic degradation of fungicide carbendazim is about 70 mg L^{-1} [32]. This is due to the increase of internal mass transfer resistance and light shielding effect, which can further result in the decrease of overall reaction rate at very high TiO_2 dosage [33].

3.4. *Effect of temperature*

The effect of temperature on the BPA photodegradation in aqueous solution with the presence of TiO_2 and UV was investigated in

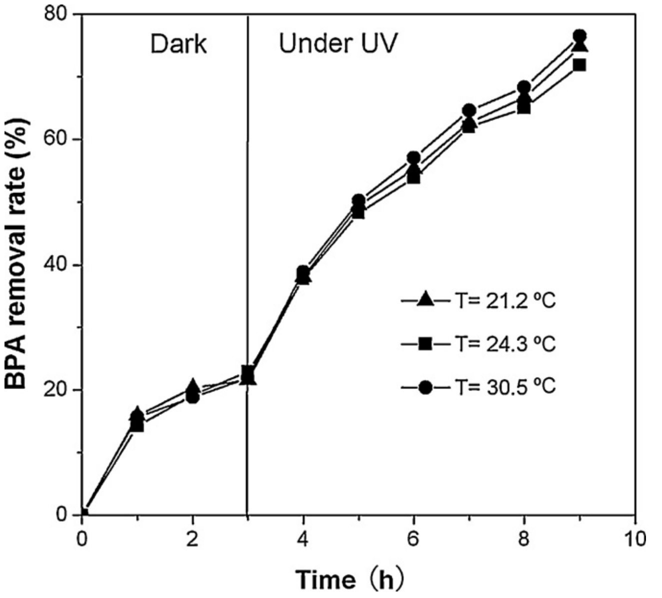

Fig. 9. Effect of temperature on BPA removal rate in HCBPR. Initial BPA concentration C_0 = 10 ppm, initial pH 7.4, TiO_2 dosage (R) = 1%.

the range of 21.2–30.5 °C. The results are demonstrated in Fig. 9 and Table 2.

It is generally accepted that temperature is a critical parameter determining the photocatalytic reaction rate [34]. The results in this study also showed that the apparent BPA degradation rate was increased slightly with increasing temperature (see Table 2). Some scientists pointed out that the speed of photocatalytic reaction is considerably fast; consequently photocatalytic reaction is not sensitive to temperature changes [35]. Hence, temperature has a limited influence on BPA degradation rate. It is unnecessary to control temperature in photocatalytic degradation when temperature changes from 20 °C to 30 °C.

It was reported that the optimum temperature for photocatalysis is generally comprised between 20 and 80 °C [25]. Because the apparent activation energy (E_a) is relatively low and was estimated to be 0.814 kJ mol^{-1}, the photocatalytic systems do not require heating and are generally operated at room temperature. The lower sensitivity of TiO_2 photocatalytic reaction to temperature changes is attractive for practical application of HCBPR in water and wastewater purification, because it implies the lower energy consumption and higher resistance to seasonal changes.

3.5. *Photocatalytic mineralization of BPA under optimum conditions*

Complete mineralization of BPA is of great significance in water and wastewater treatment processes. Thus, the monitoring of BPA concentration and TOC removal was employed to assess the mineralization extent of BPA during the photocatalytic reaction (after 3 h of dark stage). Experiments were performed under optimum conditions: initial BPA concentration of 10 ppm (0.044 mmol L^{-1}), initial pH of 12.3, TiO_2 dosage (R) of 1% and temperature of 24.3 °C. The results are illustrated in Fig. 10.

Table 2
Effect of temperature on photocatalytic degradation of BPA using TiO_2 under UV illumination in HCBR (Experimental conditions: initial BPA: 10 ppm; initial pH 7.4; TiO_2 dosage (R): 1%).

Temperature (°C)	k_{ap} (h^{-1})	$t_{1/2}$ (h)	r^2
21.2	0.161 ± 0.037	4.31 ± 0.99	0.991
24.3	0.177 ± 0.045	3.91 ± 0.99	0.989
30.5	0.188 ± 0.045	3.69 ± 0.88	0.990

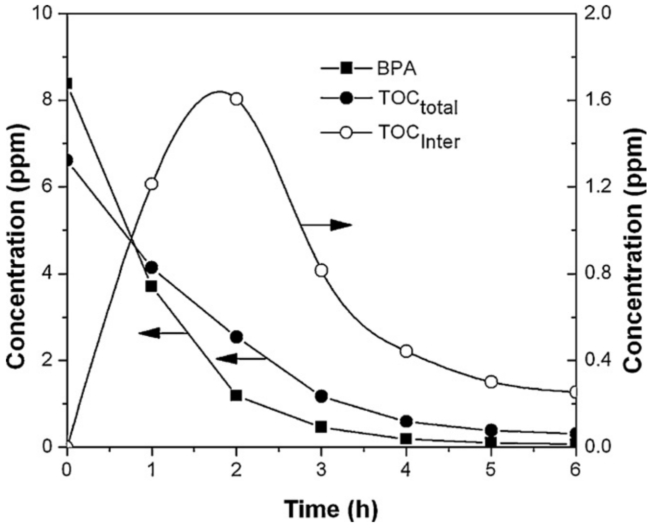

Fig. 10. Photocatalytic mineralization of BPA under the optimum conditions: Initial BPA concentration C_0 = 10 ppm, initial pH 12.3, TiO_2 dosage (R) = 1%, temperature (T) = 24.3 °C.

As shown in Fig. 10, BPA was gradually photodegraded in HCBPR and was lower than 0.2 ppm after four hour UV illumination. Likewise, the overall TOC (TOC_{total}) removal demonstrates the same trend, but the rate is a little bit slower. This discrepancy may result from the emergence of BPA's intermediates, whose amount (presented as TOC_{inter}) is also demonstrated in Fig. 10. The amount of intermediate reaches its peak after approximately 2 h of UV illumination, and then gradually decreases to lower than 0.4 ppm after 4 h of UV illumination. It was well-documented by other scientists [7] that such a peak trend exists because of the retardation of some intermediates. It was found that over 95% TOC and 97% BPA were removed and degraded into CO_2 and H_2O after 6 h of UV radiation. This illustrates that photocatalytic degradation has an outstanding advantage in its unselective strong oxidation ability, which could decompose contaminants into harmless CO_2 and H_2O rapidly and safely.

The photodegradation pathway of BPA has been investigated by other researchers [19]. It was reported earlier that the two methyl group in BPA were firstly attacked by $^{\bullet}OH$ and/or $^{\bullet}OOH$ radicals and followed by the cleavage of the two phenyl moieties. The mineralization to CO_2 finally occurred via oxidative processes involving carboxylic acids and aldehydes [19]. Moreover, it was found that the estrogenic activity was reduced to less than 10% of the initial activity for BPA after 6 h of UV illumination in a slurry photocatalytic reactor, even though 35% of the initial amount of BPA remained in the solution with some intermediate products [16]. When comparing the variation of toxicity during the photocatalytic degradation of BPA at pH 3 and 10 in a annular jacket photoreator, it was found that both TOC content and BPA concentration decreased as the UV illumination proceeded and a gradual decrease in toxicity was observed for BPA degradation at pH 10, but there was a significant increase in the toxicity of the system during the early stage of BPA oxidation when the experiment was performed at pH 3, which indicated the evolution of more hazardous intermediates during BPA degradation under acidic conditions [20]. Therefore, it can be concluded that solution pH plays a significant role in regulating the mechanisms of the photocatalytic degradation of BPA, which in turn determine the stability and toxicity of intermediates generated from the degradation process. In the view of application of photocatalytic oxidation in water and wastewater treatment, it is recommended that photocatalytic degradation of BPA should be performed under alkaline conditions, due to the higher BPA decomposition efficiency and the less hazardous intermediates. In addition, the toxicological changes of intermediates generated at different stages during BPA photocatalytic degradation under different conditions need to be further investigated.

4. Conclusions

The influences of initial BPA concentration, initial pH, carrier dosage and temperature on the degradation rate of BPA were investigated in a self-designed horizontal circulating bed photocatalytic reactor. The results show that too high initial BPA concentration compromises the degradation rate due to the limited active sites available on photocatalyst surface. The variation of pH has a pronounced effect on degradation rate: alkaline condition promotes the rate considerably because of change of surface charge, whereas acidic environment casts a negative effect on degradation. Besides, the dosage of photocatalyst carrier also influences the degradation rate, the rate constant reaches the peak when the ratio is 1%, and then decreases when increasing the ratio to 1.5%, 2% or 3%. Temperature exerts an insignificant enhancement on BPA degradation due to the high speed of photocatalytic degradation. Conclusively, an optimum condition for HCBPR operation was achieved as follows, initial BPA concentration at 10 ppm, initial pH at 12.3, TiO_2 dosage at 1% and temperature at 24.3 °C, under which 95% TOC removal and nearly 97% BPA degradation were achieved after 6 h of UV radiation.

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