Degradation of di-*n*-butyl phthalate using photoreactor packed with TiO$_2$ immobilized on glass beads

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Abstract

This study evaluated the performance of a photoreactor packed with TiO$_2$/glass, TiO$_2$ immobilized on glass beads, initiated by UV irradiation, denoted as UV/TiO$_2$/glass, to decompose di-*n*-butyl phthalate (DBP) in an aqueous solution. The photodegradation rate of DBP by this UV/TiO$_2$/glass process was found to obey pseudo first-order kinetics represented by the Langmuir–Hinshelwood model. The experimental results of this study show that the influence of pH value of an aqueous solution to reaction rate was negligible at the pH values 4.5–9. The effect of cations on the photodegradation rate of DBP reveals that the larger the charge and size of cations contained, the more the inhibition of reaction rate increased. The UV/TiO$_2$/glass process yielded a 75% degradation efficiency of DBP with initial concentration of 5 mg L^{-1} at 80 min reaction time.
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Keywords: Photodegradation; Packed-bed reactor; UV/TiO$_2$/glass; di-*n*-butyl phthalate

1. Introduction

Phthalic acid esters (PAEs) are widely used as plasticizers in different resins, especially PVC resin [1] and important additives in special paints and adhesives. The United States Environmental Protection Agency (USEPA) [2] and some of its international counterparts have classified the most common PAEs as priority pollutants and as endocrine-disrupting compounds.

PAEs, especially di-*n*-butyl phthalate (DBP) [3], have become widespread in the environment and they have been found in sediments, waters, and soils [4,5]. As a result of their low water solubility and high octanol/water partition coefficients, PAEs tend to accumulate in soil and sediment and in the biota living in waters containing phthalate. Also, DBP is a rather stable compound in the natural environment, and its toxic properties are even more important with the consideration of its high bioaccumulation rate in different organisms [4]. Huang et al. [6] found that some PAEs, such as DBP and di-2-ethylhexyl phthalate (DEHP), were the main refractory organic compounds in municipal wastewater. In conventional activated sludge plants, a large number of these organic pollutants are difficult to be degraded when passed through the treatment facilities.

According to Fujishima et al. [7,8], the photocatalytic reaction of TiO$_2$ attracted a lot of attention during the last two decades. The photocatalytic activity of TiO$_2$ for the degradation of organic [9–11] and inorganic water pollutants [12] and its characteristics have been well examined [13]. Basically, the photodegradation via TiO$_2$ is initiated by the photogeneration of hole/electron pairs in the semiconductor valence (h_{VB}^+) and conduction bands (e_{CB}^-), respectively, upon absorption of ultra-violet (UV) light with energy equal to or higher than the corresponding band gap (>3.2 eV) as shown in Eq. (1).

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

The charges carriers, h_{VB}^+ and e_{CB}^-, can recombine, or h_{VB}^+ can be scavenged by oxidizing species (for example, H$_2$O, OH$^-$, organic compound), and e_{CB}^- by reducing species (for example, O$_2$) in the solution as showed in the following equations.

$$h_{VB}^+ + H_2O \rightarrow {}^\bullet OH + H^+ \tag{2}$$

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

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$$R\text{–}H(\text{organic compound}) + h_{VB}^{+} \rightarrow R^{\bullet} + H^{+} \qquad (4)$$

$$e_{CB}^{-} + O_2 \rightarrow {}^{\bullet}O_2^{-} \qquad (5)$$
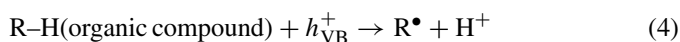
These free radicals produced from Eqs. (2)–(5) are generated on the surface of TiO_2. It has been interpreted that the oxidation of organic compounds by TiO_2 takes place either indirect oxidation by hydroxyl radicals or directly by h_{VB}^{+} [14,15]. Further, a profound reaction mechanism has been also proposed that the rate determining step is the reaction of surface-bound $^{\bullet}OH$ with adsorbed organic compounds [16,17]. Therefore, owing to the forgoing reason and the high reactivity of hydroxyl radical, Eqs. (2) and (3) would be the important parameters during the degradation of organic compounds by TiO_2 in aqueous solution.

The finely divided TiO_2 can be either dispersed in the irradiated aqueous solution as slurry [18], or anchored on a suitable support in a fixed or fluidized bed [19]. However, from a practical point of view it may not be possible to use catalyst suspension in slurry because of the filtration problems linked to the small size of the TiO_2 particles for catalyst recycling and obtaining clean, powder-free water. Because of this reason, attempts have been made to immobilize the catalyst on rigid supports. It has been shown that it is possible to deposit TiO_2 on various rigid supports of different nature such as glass, quartz, and stainless steel, and it was found that quartz (fused silica) is the most appropriate support for optimum quantum efficiency [20]. The problem with the packed-bed reactor is the high resistance to solution flow due to dense packing of granular rigid support [21,22]. This can be improved without a great reduction of photo-efficiency by using larger glass beads, 2 mm in diameter, because all TiO_2 photocatalyst in the reactor will thus be excited due to incident flux passing through the large gaps between glass beads and also penetrating through glass beads covered with a thin TiO_2 layer.

The present study assessed the function of UV light on enhancing the catalytic efficiency of TiO_2 immobilized on glass beads, denoted as the UV/TiO_2/glass process, in a fixed-bed reactor to decompose DBP. The concentration analyzed using HPLC was chosen as a degradation index of the degradation of DBP by this UV/TiO_2/glass process. The effects of pH value, variable cations, KNO_3 concentration, and initial concentration of DBP on the degradation of DBP were examined. Related kinetic equations were also established based on the observed experimental results.

2. Materials and methods

Di-*n*-butyl phthalate ($C_{16}H_{22}O_4$, MW = 278), with high quality was purchased from Acros Organics (Belgium) and used without any further purification. Triton® X-100, polyethylene glycol mono [4-(1,1,3,3-tetramethylbutyl)phenyl] ether ($C_{34}H_{62}O_{11}$, MW = 646), was also acquired from Acros Organics. $Ca(NO_3)_2$, $Mg(NO_3)_2$, $NaNO_3$, and KNO_3 were purchased from Sigma (St. Louis, MO, USA). All the other chemicals used in this study are reagent grade obtained from several suppliers. De-ionized water from a Milli-Q system (Millipore, Bedford, MA, USA) was used to prepare all sample solutions.
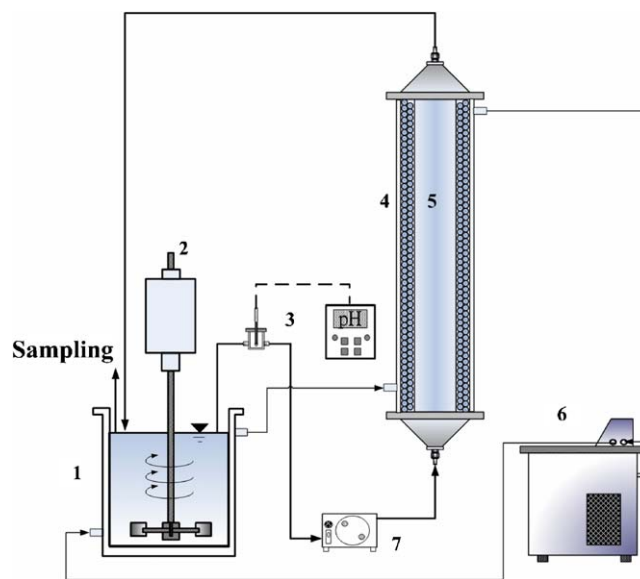

Fig. 1. Sketch of the experimental apparatus. Components: (1) reaction vessel, (2) stirrer, (3) pH meter, (4) photoreactor, (5) UV lamp, (6) thermostate, and (7) syringe pump.

The packed-bed photoreactor is shown in Fig. 1. The inner diameter of the outer tube is 35 mm and the outer diameter of the inner tube is 26 mm. Degussa P-25 TiO_2 was deposited on the silicate glass beads ($d_p = 2$ mm), denoted as TiO_2/glass, using the method described by Arabatzis et al. [23]. The procedure is as the following. 0.5 g TiO_2 with 1 mL water containing 0.1 mL acetylacetone produces a viscous paste, and then the paste was diluted by very slow addition of 1.7 mL water. Finally 1 drop of Triton® X-100 was added to the paste and then the mixture is mixed with 15 g glass beads. After drying at 100 °C for about 10 min, the TiO_2 with glass beads mixture was annealed in an oven at 450 °C for 30 min. Subsequently, the TiO_2/glass obtained was packed in the reactor and washed by 20 mL min⁻¹ distilled water to remove the uncoated TiO_2, which was collected and weighted. From the calculation, each gram TiO_2/glass contains 0.02 g TiO_2. The procedures of determining the pH_{zpc} of TiO_2/glass were described as follows [24]. In the pH range of 2–10, each 50 mL solution of pH interval of 0.5 was prepared and added with 1 g TiO_2/glass. Then, the suspension was shaken at 25 °C for 3 h and followed by acid–base titration with 0.01N NaOH and HNO_3. Consequently the surface charges of TiO_2/glass at different pH were calculated and the consequence showed the pH_{zpc} of 3.8.

The photoreactor was packed with 150 g TiO_2/glass, and the void volume of the photoreactor after packing is 55 mL. The total volume of the target DBP solution used in one experiment was 500 mL. The UV irradiation source was an 8 W lamp encased in a quartz tube. UVX Radiometer (UVP Inc., USA) was employed for the determination of UV light intensity. The UV intensity of one 8 W UV lamp at 365 nm is 1.67 mW cm⁻². The DBP solution was circulated by a syringe pump with a constant flow rate of 10 mL min⁻¹.

The degradation efficiencies of DBP were monitored by concentration measurement using high performance liquid chro-

matography (HPLC). Analyses were achieved by a Hitachi HPLC system equipped with a UV–vis detector and a reverse phase Hypersil C-18 column (250 mm × 4.6 mm, i.d., 5 μm particle size). The mobile phase was a mixture of H_2O and CH_3OH (50:50, v/v) with flow rate of 1.0 mL min^{-1}. The determination was performed at wavelength 280 nm ($\lambda = 280$ nm) by UV absorption. The TOC of sample was analyzed by a TOC analyzer (Tekmar Dohrmann Phoenix 8000).

The effect of pH value of the solution on system performance was studied at various pH values of 4.0, 6.5, 7.5, and 9.0 with the initial DBP concentrations at 5 mg L^{-1}. A pH controller was used to control pH value of the solution at a constant value during the whole reaction time by adding 0.001 M HNO_3 or NaOH solution into the reactor. The influence of UV irradiation on the system performance was evaluated with and without UV at DBP of 5 mg L^{-1} without controlling the pH value of the solution. The effect of cation and anion on the decomposition efficiency was evaluated by adding 0.1 mole L^{-1} (M) $NaNO_3$, KNO_3, $Ca(NO_3)_2$, and $Mg(NO_3)_2$ at DBP of 5 mg L^{-1}. The effect of KNO_3 concentration was investigated at various concentrations of 0.025, 0.05, 0.075, 0.1, 0.25, and 0.5 M. The effect of the initial concentration of DBP was evaluated in the range 2.5–12.5 mg L^{-1}. The temperatures of the above experiments were maintained at 298 K. The effect of temperature was evaluated at 288, 298, and 308 K with 5 mg L^{-1} DBP.

3. Results and discussion

3.1. Degradation efficiency of DBP under various conditions

In this study, glass beads of 2 mm diameter coated with TiO_2 were chosen as the solid supports and photocatalyst (TiO_2/glass). To confirm the role of TiO_2/glass in the photocatalysis reaction, three sets of experiments were performed to compare degradation efficiency of DBP, $\eta_{DBP} = (C_0 - C)/C_0$, as a function of time and the results are shown in Fig. 2. Case (a) in Fig. 2 presents the experiment of TiO_2/glass only, without UV irradiation, and shows that the less obvious reduction of DBP (about 5%) is attributed to the adsorption of DBP by the TiO_2/glass surface after 80 min reaction time (t). The low DBP adsorption capacity of TiO_2/glass may be caused by competition with water for adsorption site. On the other hand, in case (b) of Fig. 2, which was only with clean glass beads and UV radiation (denoted as UV/glass), the η_{DBP} is 21% at $t = 80$ min. However, the degradation efficiency of UV/glass is contributed to the adsorption by glass beads and UV photolysis, and the result of case (b) reveals that the effects of adsorption and photolysis are insignificant. As for case (c) in Fig. 2, the decomposition of DBP, η_{DBP}, is 75% at $t = 80$ min with TiO_2/glass under UV irradiation, denoted as UV/TiO_2/glass. Therefore, the introduction of UV radiation to TiO_2/glass results in higher efficiency in the enhancement of η_{DBP} compared to cases (a) and (b) in Fig. 2. According to Eq. (2), the improvement of the degradation efficiency in the UV/TiO_2/glass process is significant when generating hydroxyl radicals which could degrade DBP efficiently. As a result, the degradation effi-
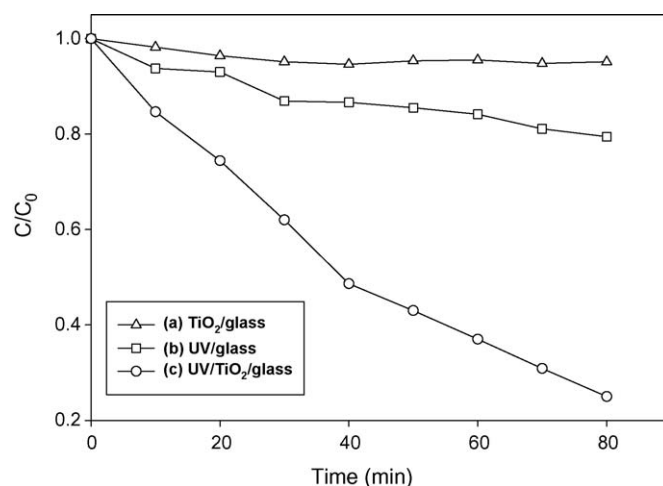
Fig. 2. Dependence of degradation of DBP on time at various conditions. Experimental conditions—case (a): 150 g TiO_2/glass; case (b): UV (λ_{365}) = 1.67 mW cm^{-2}, 150 g glass; case (c): UV (λ_{365}) = 1.67 mW cm^{-2}, 150 g TiO_2/glass. The other conditions are $C_{DBP0} = 5$ mg L^{-1} (initial concentration of DBP), reactor volume = 55 mL, $V_{tot} = 500$ mL, $T = 298$ K, catalyst amount = 150 g TiO_2/glass, and flow rate = 10 mL min^{-1}.

ciency of DBP under various conditions followed the sequence: UV/TiO_2/glass > UV/glass > TiO_2/glass.

Fig. 3 presents the variations of TOC and pH of DBP solution under the UV/TiO_2/ glass process as a function of time. As shown in Fig. 3, the removal of TOC is near 70% at $t = 80$ min, indicating that the UV/TiO_2/glass process could degrade and further mineralize DBP efficiently. Furthermore, the pH value of the reaction solution without buffer system decreased very slightly, from 6.1 to 5.9, during the whole reaction time. Note that buffer system was not introduced in the later experiments, except the experiment of pH effect.

3.2. Effect of initial DBP concentration

Since the target compound concentration is an important parameter affecting degradation efficiency in the photocatalytic
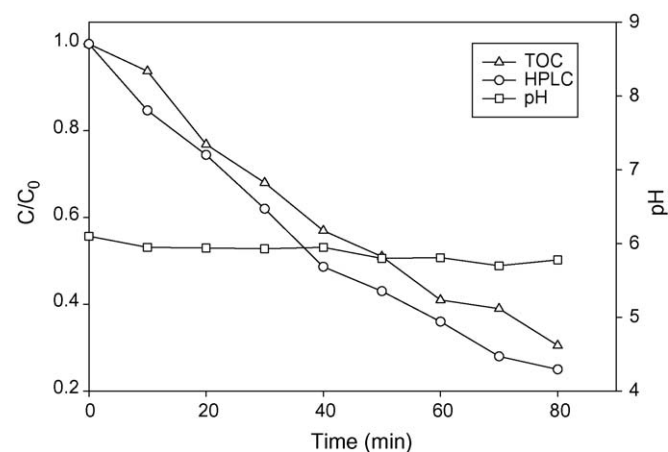
Fig. 3. Time variation of TOC, HPLC, and pH using the UV/TiO_2/glass process. Experimental conditions: $C_{DBP0} = 5$ mg L^{-1}, reactor volume = 55 mL, $V_{tot} = 500$ mL, $T = 298$ K, catalyst amount = 150 g TiO_2/glass, flow rate = 10 mL min^{-1}.
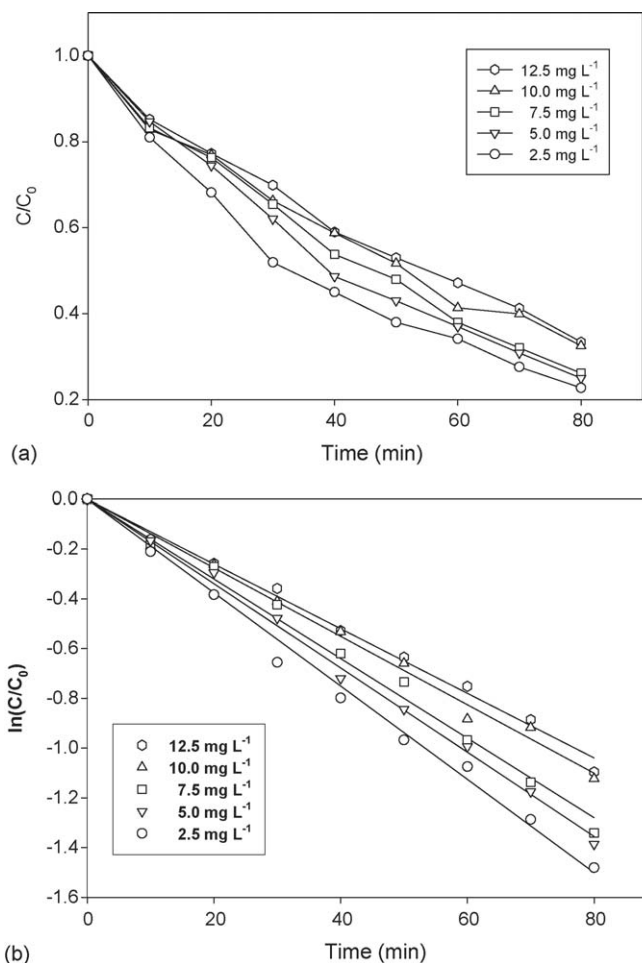
(a)

(b)

Fig. 4. Effect of initial concentration of DBP on removal efficiency. (a) Dependence of degradation of DBP on time at various initial concentrations of DBP; (b) analysis of degradation kinetics of DBP simulated by pseudo first-order reaction. Experimental conditions: reactor volume = 55 mL, V_{tot} = 500 mL, T = 298 K, catalyst amount = 150 g TiO$_2$/glass, and flow rate = 10 mL min^{-1}.

reaction, the effect of initial DBP concentration on the photocatalytic degradation rate was investigated over the concentration range of 2.5–12.5 mg L^{-1} of DBP, and the experimental results are presented in Fig. 4. Fig. 4(a) shows that the degradation efficiency decreases as the initial DBP concentration increases. This result indicates that the DBP degradation kinetics is not simple first-order but pseudo first-order.

The Langmuir–Hinshelwood kinetic expression has been used for heterogeneous photocatalysis to describe the relationship between the initial degradation rate and the initial concentration [25–27]. In this model, the reaction rate for second-order surface decomposition of DBP is as follows [26]:

$$\text{rate} = -\frac{d[\text{DBP}]}{dt} = k_c \frac{K_{\text{DBP}}[\text{DBP}]}{1 + K_{\text{DBP}}[\text{DBP}]_0} \tag{4}$$

where [DBP] is the DBP concentration at time t, k_c the second-order rate constant, K_{DBP} the equilibrium adsorption constants of DBP onto TiO$_2$/glass, and [DBP]$_0$ is the initial concentration of DBP. According to Eq. (4), the photocatalytic degradation of DBP in the TiO$_2$/glass reactor exhibits pseudo first-order kinet-

Table 1
The pseudo first-order rate constant k_{obs}, $1/k_{\text{obs}}$, half-life $t_{1/2}$, and correlation coefficients for photocatalytic degradation of DBP at different initial concentrations of DBP

Initial DBP (mg L^{-1})	k_{obs} (min^{-1})	$1/k_{\text{obs}}$ (min)	$t_{1/2}$ (min)	R^2
2.5	0.0188	53.19	36.87	0.992
5.0	0.0169	59.17	41.01	0.997
7.5	0.0160	62.50	43.32	0.991
10.0	0.0138	72.46	50.23	0.991
12.5	0.0130	76.92	53.32	0.993

Experimental conditions: as shown in Fig. 4.

ics with respect to DBP concentration as shown in Eq. (5):

$$-\frac{d[\text{DBP}]}{dt} = k_{\text{obs}}[\text{DBP}] = k_c \frac{K_{\text{DBP}}}{1 + K_{\text{DBP}}[\text{DBP}]_0}[\text{DBP}] \tag{5}$$

where k_{obs} is the observed pseudo first-order rate constant for the photocatalytic oxidation of DBP. Therefore, the integration of Eq. (5) results in

$$\ln\left(\frac{[\text{DBP}]_0}{[\text{DBP}]}\right) = k_{\text{obs}}t \tag{6}$$

Based on Eq. (6), the linear relationship of ln([DBP]$_0$/[DBP]) with irradiation time was observed as indicated in Fig. 4(b) and Table 1. The relationship between k_{obs} and [DBP]$_0$ from Eq. (6) can be expressed as follows:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_c K_{\text{DBP}}} + \frac{[\text{DBP}]_0}{k_c} \tag{7}$$

Eq. (7) shows that the linear expression can also be obtained by plotting the reciprocal of degradation rate ($1/k_{\text{obs}}$) as a function of the initial DBP concentration. Based on this equation, the values of k_{obs} at different initial DBP concentrations were fitted and plotted in Fig. 5. The values of the adsorption equilibrium constant (K_{DBP}), and the second-order rate constant (k_c) were obtained by means of a least-square best fitting procedure, and these values were found to be K_{DBP} = 0.0521 L mg^{-1} and k_c = 0.4115 mg min^{-1} L^{-1} (R^2 = 0.974), respectively. Previous
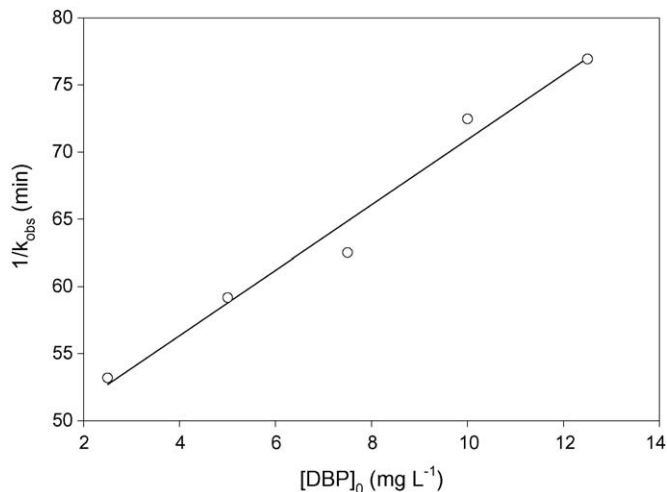

Fig. 5. The relationship between $1/k_{\text{obs}}$ with initial concentration of DBP. Experimental conditions: as shown in Fig. 4, R^2 = 0.974.

Table 2
The pseudo first-order rate constant k_{obs}, half-life $t_{1/2}$, and correlation coefficients for photocatalytic degradation of DBP at different temperature

Temperature (K)	k_{obs} (min^{-1})	$t_{1/2}$ (min)	R^2
288	0.0117	59.24	0.957
298	0.0169	41.01	0.965
308	0.0214	32.39	0.969

Experimental conditions: except temperature, the other conditions were as shown in Fig. 3.

Table 3
The pseudo first-order rate constant k_{obs}, half-life $t_{1/2}$, and correlation coefficients for photocatalytic degradation of DBP at different pH values

pH	k_{obs} (min^{-1})	$t_{1/2}$ (min)	R^2
4.5	0.0170	40.77	0.988
6.0	0.0169	41.01	0.965
7.5	0.0172	40.30	0.981
9.0	0.0176	39.38	0.996

Experimental conditions: pH values adjusted by HNO$_3$ and NaOH, the other conditions are as shown in Fig. 3.

studies about the photodegradation of organics by TiO$_2$ were performed. The experimental values of these studies were $k_c = 0.57$ mg min^{-1} L^{-1} and $K_{4\text{-nitrophenol}} = 0.072$ L mg^{-1} for 4-nitrophenol [25], $k_c = 1.78$ mg min^{-1} L^{-1} and $K_{TNT} = 0.093$ L mg^{-1} for TNT [26], and $k_c = 3.3$ mg min^{-1} L^{-1} and $K_{ethanol} = 3.8 \times 10^{-3}$ L mg^{-1} for ethanol [27], which were closed to the values of our experiments.

The temperature dependence of kinetic parameter k_{obs} in Eq. (5) can also be described by the Arrhenius equation:

$$k_{obs} = A \exp\left(-\frac{E_a}{RT}\right) \tag{8}$$

where A, E_a, T, and R are the frequency factor, activation energy, temperature (K), and gas constant, respectively. The effect of temperature was evaluated at 288, 298, and 308 K, and the related k_{obs}, as shown in Table 2, are 0.0117, 0.0169, and 0.0214 min^{-1}, respectively. Plotting $\ln k_{obs}$ against $1/T$ (1/K), as shown in Fig. 6, gives A of 132.9 min^{-1} and E_a of 22.3 kJ mol^{-1}.

3.3. Effects of pH value

Two important mechanisms, surface adsorption and hydroxyl radical oxidation, make the pH value an important parameter in photodegradation that takes place on the surface of a photocatalyst [18,28–30]. For example, the TiO$_2$ coated on the surface of glass beads would leach out and DBP would be hydrolyzed
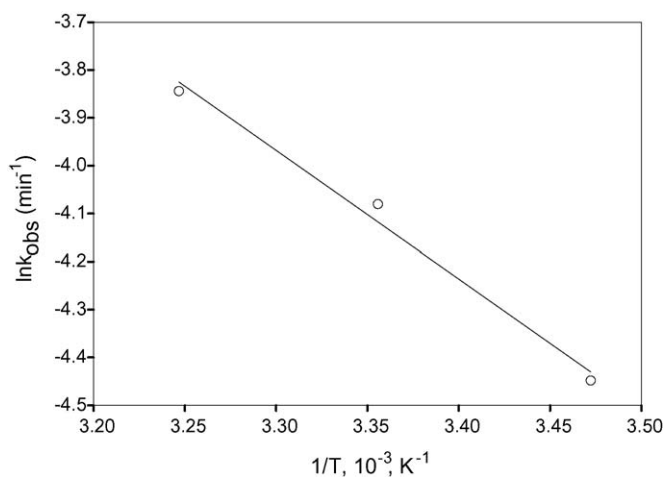

Fig. 6. Plot of k_{obs} and temperature (T) following Arrhenius law. Experimental conditions: $C_{DBP0} = 5$ mg L^{-1}, reactor volume = 55 mL, $V_{tot} = 500$ mL, catalyst amount = 150 g TiO$_2$/glass, and flow rate = 10 mL min^{-1}. $R^2 = 0.989$.

when the respective pH value goes below 4 and beyond 10 [9]. Therefore, the pH values of aqueous solution in this study were controlled between 4.5 and 9 for realizing the influence of pH effect to the photocatalysis of DBP by an UV/TiO$_2$/glass process. As the first-ordered photocatalysis hypothesized, Table 3 presents that the influence of pH value on reaction rate is negligible at the pH values in the range from 4.5 to 9. In previous researches [9,18], the suspended TiO$_2$ particles were applied to the degradation of organisms. As the pH value of suspension was controlled at 6, the pH$_{zpc}$ of TiO$_2$, the efficiency of photodegradation increased. This resulted from the fact that the TiO$_2$ with electroneutral surface is a marvelous adsorptive material of organisms. However, in our experiment, the results of variation of surface charge revealed that the pH$_{zpc}$ of TiO$_2$/glass was 3.8, which was similar to the experimental value of Vohra and Tanaka [31]. It was supposed that regarding TiO$_2$/glass, the coating of TiO$_2$ on the surface of glass beads was not uniform and complete. Furthermore, the photocatalyst used in this study was TiO$_2$/glass (TiO$_2$/SiO$_2$) with pH$_{zpc}$ around 3.8, and the surface charge was negative while the pH of solution was above 3.8. As a result, in the pH range of 4.5–9, the adsorption capacities of TiO$_2$/glass with regard to organisms were maintained for the negative charge of TiO$_2$/glass surface. According to experimental results in Fig. 2(a), very small amounts of DBP are adsorbed by TiO$_2$/glass from aqueous solution. Therefore, the removal efficiency of DBP may be largely caused by hydroxyl radical oxidation. It is clear from Eq. (3) that more hydroxyl radicals were produced at high pH values, subsequently enhancing the photodegradation rate of DBP. In contrast, the high OH$^-$ ion content of the system may trap the photogenerated CO$_2$ in the solution, and, as a result, bicarbonate and carbonate are formed in the alkaline system. Both bicarbonate and carbonate are efficient scavengers of hydroxyl radicals due to their very high rate constants with the hydroxyl radicals ($k = 3.9 \times 10^8$ M^{-1} s^{-1} for carbonate and $k = 8.5 \times 10^6$ M^{-1} s^{-1} for bicarbonate). Thus, according to the influence of the increase of hydroxyl radicals and the formation of scavengers, the comprised results causing the pH effect on the reaction is negligible during pH values of solution in the range from 4.5 to 9.0.

With regard to the economical and practical aspects of treatment, the result of the study of pH effect implied that pH adjustment steps may not be required in the treatment of DBP contaminated water when using the UV/TiO$_2$/glass process.

Table 4
The pseudo first-order rate constant k_{obs}, half-life $t_{1/2}$, and correlation coefficients for photocatalytic degradation of DBP at different cations

Salt	k_{obs} (min^{-1})	$t_{1/2}$ (min)	R^2
NaNO$_3$	0.0161	43.05	0.997
KNO$_3$	0.0141	49.16	0.944
Mg(NO$_3$)$_2$	0.0143	48.47	0.990
Ca(NO$_3$)$_2$	0.0132	52.51	0.991

Experimental conditions: the concentration of all slats is 0.1 M, the other conditions are as shown in Fig. 3.

Table 5
The pseudo first-order rate constant k_{obs}, half-life $t_{1/2}$, and correlation coefficients for photocatalytic degradation of DBP at various KNO$_3$ concentrations

KNO$_3$ concentration (M)	k_{obs} (min^{-1})	$t_{1/2}$ (min)	R^2
0	0.0169	41.01	0.965
0.025	0.0166	41.76	0.995
0.05	0.0163	42.52	0.993
0.075	0.0160	43.32	0.981
0.1	0.0141	49.16	0.944
0.25	0.0101	68.63	0.972
0.5	0.0046	150.68	0.912

Experimental conditions: as shown in Fig. 3.

3.4. Effects of inorganic cations

The effects of inorganic cations, which are frequently present in industrial waste waters, on the degradation efficiency of DBP with UV/TiO$_2$/glass were evaluated as shown in Table 4. These species are likely to retard the rates of oxidation of organic compounds by competing for the oxidizing radicals or blocking the active sites of the TiO$_2$ catalyst. According to Table 4, when all of the salts were added into aqueous solution, the respective pH values of the solution were between 6.2 and 6.6. As described in previous section, the influence of pH value on reaction rate is negligible at the solution pH values in the range from 4.5 to 9. From the data of Table 4 it reveals that the larger the charge and size of cations contained, the more the inhibition of reaction rate increased. At the pH value from 6.2 to 6.6, the decrease in reaction rate that resulted from the adsorption of cations could be due to the negative charge of TiO$_2$/glass surface. However, some of the added cations might have blocked the active sites of the catalyst surface, thus deactivating the decomposition efficiency of catalyst towards organic molecules.

The effect of KNO$_3$ concentration on the degradation efficiency of DBP with UV/TiO$_2$/glass is shown in Table 5. The increased inhibition was formed as the concentration of KNO$_3$ increased. Especially, an apparent inhibition took place when the concentration of KNO$_3$ was more than 0.075 M.

4. Conclusions

The major results of applying the UV/TiO$_2$/glass process to mineralize DBP can be summarized as follows:

1. The rank of treatment conditions based on the mineralization efficiency of DBP has the sequence: UV/TiO$_2$/glass > UV/glass > TiO$_2$/glass. The packed-bed photoreactor containing UV/TiO$_2$/glass yielded a 75% degradation efficiency of DBP (5 mg L^{-1}) at 80 min reaction time.
2. The effect of pH value of aqueous solution on photodegradation rate of DBP using the UV/TiO$_2$/glass process is negligible while the pH range was 4.5–9.
3. The effect of cations on the photodegradation rate of DBP reveals that the larger the charge and size of cations contained, the more the inhibition of reaction rate increased.
4. The observed experimental data showed a reasonably good expression of the pseudo first-order kinetics represented by the Langmuir–Hinshelwood model. The values of the adsorption equilibrium constant (K_{DBP}), and the second-order rate constant (k_c) were obtained as 0.0521 L mg^{-1} and 0.4115 mg min^{-1} L^{-1}, respectively.

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