Establishment of activity indicator of TiO$_2$ photocatalytic reaction—Hydroxyl radical trapping method

Chen-Yu Chang [a,*], Yung-Hsu Hsieh [b], Ling-Ling Hsieh [c], Kuo-Shan Yao [a], Ta-Chih Cheng [a]

[a] Department of Life Science, Ming-Dao University, 369 Wen-Hua Road, Peetow, Chang-Hua County 52345, Taiwan
[b] Department of Environmental Engineering, National Chung-Hsing University, 250 Kuo-Kuang Road, Taichung, Taiwan
[c] Department of Radiological Technology, Central Taiwan University of Sciences and Technology, 11 Pu-Tze Lane, Pei-Tun District, Taichung, Taiwan

ARTICLE INFO

ABSTRACT

In this study, a new, low cost and easy method, hydroxyl radical trapping method, was employed to investigate the photo-activity of UV/TiO$_2$ photocatalytic reaction. The Taguchi method was utilized to optimize the preparation of titanium dioxide (TiO$_2$) thin-film reactor through the modified chemical vapor deposition (CVD) method. The optimal yield of hydroxyl radicals was then evaluated by calculating the conversion ratio of salicylic acid under the optimal conditions. In the experiments, salicylic acid was used as the free-radical scavenger and the formation of three different intermediates were examined to shed light on the trend and kinetics of reaction of hydroxyl radical with organic substance under different operation conditions. The results indicated that the yield of hydroxyl radicals increased with increasing irradiation intensity and dissolved oxygen level. The optimal experimental conditions obtained in this study were irradiation with intensity of 2.9 mW cm^{-2} on salicylic acid at concentration of 250 mg L^{-1} by both agitation and aeration processes (dissolved oxygen level = 8.2 mg O$_2$ L^{-1}) at pH 5. Such conditions could achieve the optimal hydroxyl radical yield of 5.1 × 10^{-17} M.

1. Introduction

In recent years, advanced oxidation processes (AOPs) have been extensively utilized for the decomposition of hazardous or recalcitrant pollutants in the environment. The photocatalytic technology combining semiconductors with ultraviolet light is one of the technologies with the greatest potential. Among the semi-conductive metal oxides, titanium dioxide (TiO$_2$) is the photocatalyst popularly used in photochemical reactions owing to its low cost, stable properties, and high photocatalytic efficiency. In the field of environmental engineering, many studies on AOPs are closely related to the applications of free radicals, such as the UV/TiO$_2$ photocatalytic process in this study. Owing to their extremely high reaction rate ($k = 10^7$–10^{10} M^{-1} s^{-1}) and their exceptionally short presence in the environment, it is not easy to evidence the action of free radicals. In recent studies on free radicals, Electron Paramagnetic Resonance (EPR) is applied to measuring the final or immediate products derived by free radicals reacting with specified materials. However, their use is limited by the high cost involved. Therefore, most of the studies in environmental engineering have focused on investigating the relationships between different experimental parameters

and decomposition of pollutants by AOP-generated free radicals [1–6]. Moreover, the "radical scavenging or trapping methods" are newly developed technologies that quantify the free radicals indirectly and are becoming alternative analysis methods. Among the many tapping reagents, salicylic acid is increasingly applied in the detection of hydroxyl radicals [7–15], especially in biological or medical studies. Salicylic acid is a good trapping reagent and it reacts with hydroxyl radicals to produce three products, namely 2,3-dihydroxybenzoic acid (2,3-DHBA), 2,5-dihydroxybenzoic acid (2,5-DHBA) and catechol. These hydroxyl compounds can be easily determined using general instruments, such as High Performance Liquid Chromatography (HPLC). In view of the above, this study used salicylic acid as a trapping reagent in combination with HPLC to quantify the hydroxyl radicals formed in the UV/TiO$_2$ photocatalytic process.

This study had two objectives. First, the optimal conditions for preparing the thin-film reactor of the UV/TiO$_2$ photocatalytic process were explored using experimental design involving orthogonal arrays. Second, the effects of dose, pH value, amount of dissolved oxygen, and irradiation intensity on the formation of hydroxyl radicals during photocatalytic reaction were examined using salicylic acid as the scavenger [16] of hydroxyl radicals. The reactivities between each intermediate and hydroxyl radicals were also investigated from the perspective of reaction kinetics in order to obtain the yield of hydroxyl radicals in the photocatalytic system of this
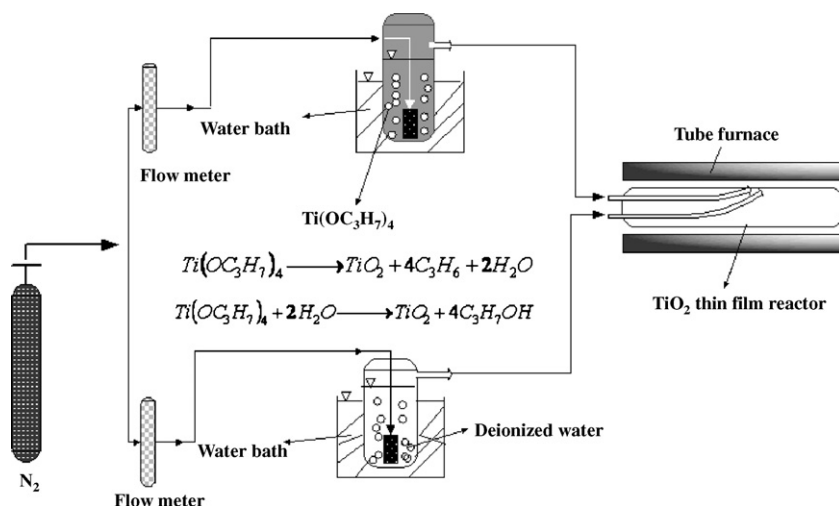

Fig. 1. Schematic diagram of TiO$_2$ thin-film reactor.

study. Our results can enhance the understanding of hydroxyl radicals formed in the UV/TiO$_2$ photocatalytic process and the method used in this study can also be applied to other AOPs.

2. Experimental/Materials and methods

2.1. Materials

Tetraisopropyl orthotitanate (Ti(OC$_3$H$_7$)$_4$) (TTIP, >98%, Merck Co.) was used for the preparation of the catalyst by chemical vapor deposition (CVD). Salicylic acid (Riedel-del Haen Co.), 2,3-dihydroxybenzoic acid (Sigma), 2,5-dihydroxybenzoic acid (Sigma), catechol (J.T. Baker), and all the other chemicals are of either analytical or reagent grade. The deionized water ($\geq$18 MΩ cm^{-1}) used for preparing the chemical solutions was processed by the Milli-Ultrapure R/O System (Millipore, USA) to ensure the quality of the prepared solution.

2.2. Procedure

2.2.1. Optimal preparation of photocatalytic reactor

In this study, the TiO$_2$ thin-film reactor was prepared using the modified chemical vapor deposition method [17] and the schematic diagram is shown in Fig. 1. First, tetraisopropyl orthotitanate (>98%, Merck Co.) solution and deionized water were put into two separate aeration bottles. The bottles were then placed in a water-bath of 60 °C and flushed with high-purity nitrogen gas (99.999%, Ho Chun Gas Co.) to carry the gas containing titanium dioxide and water vapor out of the bottles into the reactor through a Teflon tube. The tube was wrapped with heating tape (Glas-Col, made in USA) and heated to 95 ± 5 °C to prevent condensation. The reactor to be sprayed with the catalyst was placed in the tube furnace (Cherng Huei Co. CH-40MF) in order to maintain the reaction at the fixed temperature. During the preparation, the reactor was rotated by a motor to ensure that TiO$_2$ was evenly sprayed on the inner wall of the entire reactor. Finally, the reactor underwent high-temperature calcination for 24 h to remove impurities, enrich purity of TiO$_2$, and form the anatase crystal structure.

Table 1 lists the parameters employed to control the preparation of the catalyst. As can be seen, they include water-bath temperature (60, 80 °C), Ti(OC$_3$H$_7$)$_4$/H$_2$O ratio (2, 4, 6), flow rate of carrier gas (550, 1000, 1500 mL min^{-1}), oxidation temperature (200, 300, 400 °C), oxidation duration (6, 8, 10 h), calcination temperature (350, 450, 550 °C), rotation speed of furnace (20, 30, 40 rpm), and

speed of geared motor (55, 75, 95 cm min^{-1}). They were chosen according to the work of Qiu [18]. The orthogonal arrays in the experimental design proposed by Taguchi [19] were adopted to conduct the multiple-factor experiment and obtain the best combination of conditions for experimental photocatalytic conversion of salicylic acid. The eight parameters of various levels yield 18 different combinations as summarized in the L$_{18}$ orthogonal array shown in Table 2.

The different reactors were prepared according to the above-mentioned combinations and the salicylic acid conversion rate was

Table 1
Parameters employed to control the preparation of catalyst in Table L$_{18}$.

Factors	Designed value of controlled factors		
	1	2	3
(A) Water-bath temperature (°C)	60	80	–
(B) Ti(OC$_3$H$_7$)$_4$/H$_2$O ratio	2	4	6
(C) Carrier gas flow rate (mL min^{-1})	550	1000	1500
(D) Oxidation temperature (°C)	200	300	400
(E) Oxidation duration (h)	6	8	10
(F) Calcination temperature (°C)	350	450	550
(G) Spraying speed (rpm)	20	30	40
(H) Furnace linear motion geared motor speed (cm min^{-1})	55	75	95

Table 2
L$_{18}$ orthogonal array.

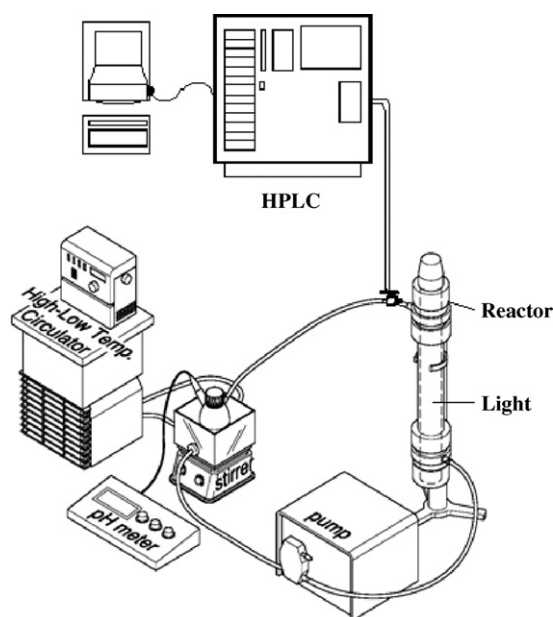| Number of combinations	Parameters							
	A	B	C	D	E	F	G	H
1	1	1	1	1	1	1	1	1
2	1	1	2	2	2	2	2	2
3	1	1	3	3	3	3	3	3
4	1	2	1	1	2	2	3	3
5	1	2	2	2	3	3	1	1
6	1	2	3	3	1	1	2	2
7	1	3	1	2	1	3	2	3
8	1	3	2	3	2	1	3	1
9	1	3	3	1	3	2	1	2
10	2	1	1	3	3	2	2	1
11	2	1	2	1	1	3	3	2
12	2	1	3	2	2	1	1	3
13	2	2	1	2	3	1	3	2
14	2	2	2	3	1	2	1	3
15	2	2	3	1	2	3	2	1
16	2	3	1	3	2	3	1	2
17	2	3	2	1	3	1	2	3
18	2	3	3	2	1	2	3	1

Fig. 2. Schematic diagram of continuous TiO_2 photocatalytic system.

also obtained in the photocatalytic experiments. In this study, the response level was representative of the conversion effect of salicylic acid under different combination conditions and the main effect represented the difference between the maximum and the minimum value for each variable. In comparison, the larger the main effect of variable, the greater its contribution to the conversion rate of salicylic acid would be.

2.2.2. Test of photocatalytic activities – free-radical scavenging experiment

The results from the catalyst preparation experiment described above were employed to establish the optimal conditions for preparing the photocatalytic reactor. Dose, pH value, aeration rate, and irradiation intensity [20–25] were used as variables for the heterogeneous photocatalysis experiment (shown as Fig. 2). The samples collected at different reaction times were analyzed by the High Performance Liquid Chromatography-Ultraviolet Detector (HPLC-UV, Agilent Co., Model HP1100 Series) equipped with the LC-8 58297 column (25 cm × 4.6 mm, 5 μm, Supelco Inc.). The buffer solution (pH 3.3) containing citric acid and acetic acid, 10% methanol solution, 10% acetonitrile solution, and deionized water was used as the eluent for HPLC to determine the yields of products (2,3-DHBA, 2,5-DHBA and catechol) from the reaction of salicylic acid and hydroxyl radical (optimal absorption wavelengths at 298, 305, 326 and 275 nm). The residual amount of salicylic acid was also determined. The yield of hydroxyl radical during photocatalysis was evaluated from the yields and decomposition rates of the three major products (2,3-DHBA, 2,5-DHBA and catechol).

3. Results and discussion

3.1. Optimal preparation conditions

The controlling factors, which include oxidation temperature, calcination temperature, flow rate of carrier gas, rotating speed of motor were listed in the L_{18} table. Different reactors were prepared according to different combinations of controlling factors for conducting the heterogeneous photocatalytic reactions to obtain the conversion rates of salicylic acid. The salicylic acid conversion rates thus obtained were then statistically analyzed by the F test to determine the significance and variability of each factor. The result showed that oxidation temperature had the greatest effect on conversion rates of salicylic acid in the photocatalysis system (51.38%) followed by calcination temperature (43.05%). In general, oxidation temperature changed the activity of photocatalyst by influencing the spraying condition, crystal structure, and formation of crystal during the spraying process. The effect of calcination temperature was more significant due to its function in removing impurities and increasing crystal strength. Table 3 shows the contributions and major effects of different parameters. The optimal preparation condition of TiO_2 thin-film reactor was achieved under water-bath temperature of 80 °C, Ti $(OC_3H_7)_4/H_2O$ ratio of 4, carrier gas flow rate of 1000 mL min^{-1}, catalytic oxidation temperature of 400 °C, oxidation duration of 8 h, calcination temperature of 550 °C, spraying speed of 30 rpm and furnace linear motion geared motor speed of 75 cm min^{-1}. In the subsequent experiments, the photocatalyst was prepared under the above optimal experimental conditions.

3.2. Hydroxyl radical formation experiment

3.2.1. Scavenger dosing experiment

The present study used salicylic acid as the hydroxyl radical scavenger. The intermediates formed from the reaction of salicylic acid and hydroxyl radical, namely 2,3-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, and catechol, were examined to shed light on the formation of hydroxyl radicals in the photocatalysis system. Owing to the rapid reaction of hydroxyl radicals, the addition of salicylic acid at the optimal dose was required for their removal. The photocatalytic reactions were conducted in the presence of 100–500 ppm of salicylic acid at fixed pH for 8 h. The results showed that photocatalysis began to slow down after 5–6 h. Therefore, the reaction time was set to be 5 h for the subsequent hydroxyl radical formation experiments, which were conducted under the optimal conditions. The concentrations of salicylic acid and the intermediates produced after 5 h of reaction are shown in Fig. 3. As can be seen, the maximum total yields of the three products: 60% for 2,3-DHBA being the major product, 25% for 2,5-DHBA and 15% for catechol were achieved in the presence of 250 ppm of salicylic acid. As a result, 250 ppm of salicylic acid was used in the subsequent experiments to investigate the factors affecting the formation of hydroxyl radicals in the photocatalysis system.

3.2.2. pH experiment

In general, the yield of hydroxyl radicals in the photocatalytic reaction increases with increasing pH of the aqueous solution.
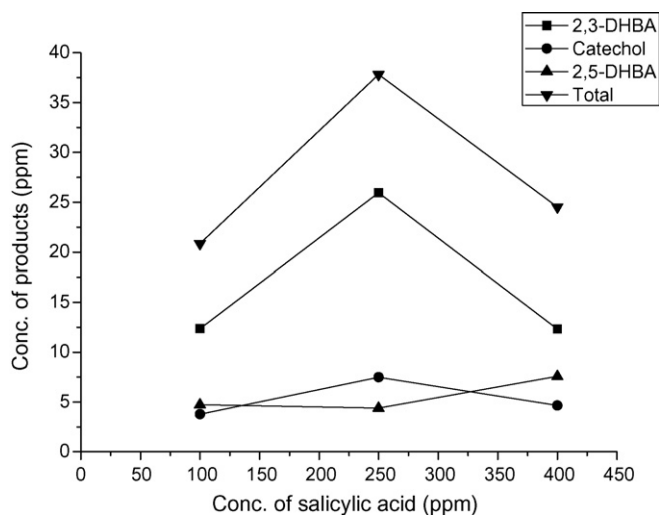
Table 3
Parameters and levels used in this experiment.

Factors	Water-bath temperature (°C)	Ti$(OC_3H_7)_4/H_2O$ ratio	Carrier gas flow rate (mL min^{-1})	Oxidation temperature (°C)	Oxidation duration (h)	Calcination temperature (°C)	Spraying speed (rpm)	Furnace linear motion geared motor speed (cm min^{-1})
Level 1	48.33%	53.38%	40.76%	63.39%	46.61%	26.94%	43.60%	56.49%
Level 2	59.25%	62.99%	68.48%	23.30%	51.93%	69.99%	59.48%	57.75%
Level 3	–	45.01%	52.13%	74.68%	62.82%	64.44%	58.29%	47.13%
Main effect	10.92%	17.98%	27.72%	51.38%	16.21%	43.05%	15.88%	10.61%

Fig. 3. Relationship between concentrations of intermediates and doses of salicylic acid in early photocatalytic reactions at irradiation intensity of 2.0 mW cm^{-2}, and constant pH and dissolved oxygen level.

However, the distribution ratios of the intermediates produced in the solution were directly related to the pH values. Moreover, the pH value alters the electrical behavior on the surface of the photocatalyst leading to changes in the absorption and desorption properties and capabilities of the intermediates produced by the catalyst. Therefore, the control of pH during the operation had significant impact on the efficiency of the overall treatment.

The pH$_{zpc}$ value of TiO$_2$ is 6.4. Therefore, the TiO$_2$ surface carries a positive charge at pH below 6.4. However, more and more oxygen ions dissociate from the TiO$_2$ surface at pH above 6.4, causing a negative charge to develop on the catalyst surface. The substances formerly attached to the catalyst surface as a result of electrostatic adsorption begin to leave the catalyst under the influence of electric repulsion between the substances and the catalyst, thus lowering the oxidation/reduction rate of the reactants. Therefore, the ionic reactants are more affected by the pH of the environment due to electrostatic interaction. The pKa value of salicylic acid is 2.98. When the pH value of the solution is higher than its pKa, it exists mainly in ionic form and is more affected by the electric nature of the TiO$_2$ surface. More salicylic acid is adsorbed on the TiO$_2$ surface at pH between the pKa of salicylic acid and the pH$_{zpc}$ of TiO$_2$ due to electrostatic attraction. The absorption process is the first step in the photocatalytic reaction mechanism. Therefore, the conversion rate of salicylic acid increases with increasing opportunities for hydroxyl radicals to attack salicylic acid. However, the amount of salicylic acid adsorbed decreases due to the increase in negative charge on the TiO$_2$ surface and the formation of repulsion to the negatively charged salicylic ions after dissociation at pH higher than pH$_{zpc}$. As a consequence, the salicylic ions adsorbed are less likely to be attacked by hydroxyl radicals in the photocatalytic reaction, leading to decrease in oxidation intermediates with increasing pH.

Fig. 4 illustrates the concentrations of intermediates produced after 5 h of photocatalytic reaction. As can be seen, the yields of 2,3-DHBA, 2,5-DHBA and catechol were higher under acidic to neutral conditions, with the highest total yield at pH 5. According to the results obtained, the yield of hydroxyl radicals was higher at pH 5.

3.2.3. Dissolved oxygen experiment

Dissolved oxygen plays an important role in the liquid-phase photocatalytic reactions. It captures electrons, thus preventing the recombination of electrons and pairs of electron holes. After the formation of superoxide free radicals, dissolved oxygen reacts with water molecules to generate hydroxyl free radicals and enhances the oxidation rate of the photocatalytic reaction. The experiment involved three different dissolved oxygen conditions at 8.2, 6.8 and 4.1 mg O$_2$ L^{-1} generated by different aeration conditions and mixing effects of solutions for the photocatalytic reactions. Salicylic acid of 250 ppm was exposed to irradiation with intensity of 2.0 mW cm^{-2} for 5 h. The conversion rates of salicylic acid at 8.2, 6.8 and 4.1 mg O$_2$ L^{-1} were 21.6, 20.8 and 14.9%, respectively, thus confirming the effect of dissolved oxygen on oxidation efficiency of the photocatalytic reaction. The formation of hydroxyl radicals was inhibited due to insufficient dissolved oxygen. Therefore, the ability of salicylic acid in scavenging hydroxyl radicals and forming intermediates was reduced at lower dissolved oxygen levels, leading to decrease in oxidation efficiency of the entire photocatalytic system. The yield of hydroxyl radicals usually increases with increasing dissolved oxygen level. However, the experimental results were similar at the dissolved oxygen levels of 8.2 and 6.8 mg O$_2$ L^{-1}, indicating that the formation of hydroxyl radicals was not significantly improved even after reaching a certain dissolved oxygen level. Further aeration to increase the dissolved oxygen level in the system was not considered necessary as long as adequate mixing was available to sustain sufficient dissolved level for conducting the photocatalytic reaction. However, both mixing and aeration were still used in the subsequent experiment for achieving the highest dissolved oxygen level in order to obtain the optimal and the highest yield of hydroxyl radicals.

3.2.4. Irradiation intensity experiment

The theory of photocatalytic reaction indicates that treatment efficiency is directly proportional to irradiation intensity. As irradiation intensity increases, the number of photons received by the photocatalyst per unit time and unit area also increases. Because the collision probability between the active reaction sites and the photons increases, the oxidation efficiency of the photocatalytic reaction is significantly increased. Fig. 5 illustrates the concentrations of intermediates produced by photocatalytic reaction after irradiation with intensities of 1.0, 2.0 and 2.9 mW cm^{-2} for 5 h. The distribution curves show that the total yield of intermediates is directly proportional to the intensity of irradiation.

3.2.5. Optimal combination experiment

The optimal salicylic acid dose (250 ppm), pH value (pH = 5), aeration rate (8.2 mg O$_2$ L^{-1}), and irradiation intensity (2.9 mW cm^{-2}) obtained in each experiment described above were used for the
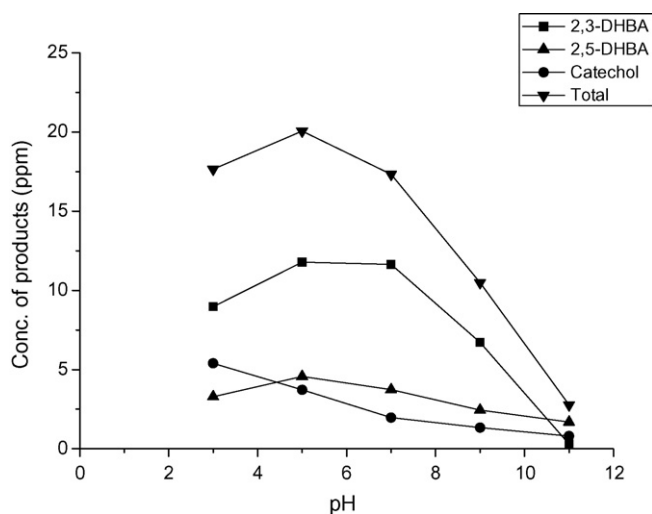

Fig. 4. Concentrations of intermediates produced at various pH under irradiation intensity of 2.0 mW cm^{-2} and salicylic acid of 250 ppm.
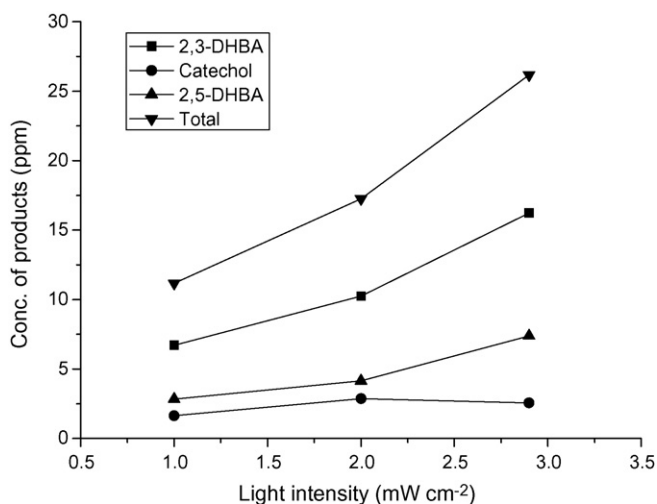
Fig. 5. Concentration of intermediates produced under different irradiation intensities with salicylic acid of 250 ppm, and constant pH and dissolved oxygen level.

experiment to identify the conditions for obtaining the optimal yield of hydroxyl radicals. The concentrations of products after 12-h photocatalysis are illustrated in Fig. 6. As can be seen, the concentrations of the three major intermediates, 2,3-DHBA, 2,5-DHBA and catechol, increased with increasing reaction time, but started to decrease after 9 h. In the early phase of reaction, the yield of products increased with decreasing concentration of salicylic acid. As a result, most of the hydroxyl radicals reacted with salicylic acid, resulting in higher formation rates of the three products. However, with increasing reaction time, the amount of products formed increased while the amount of salicylic acid decreased. The formation rates of products continued to increase till the depletion rates could no longer be offset. As a result, the concentrations of products started to decrease with increasing reaction time.

From the above discussion, we also understand that the reaction of salicylic acid with hydroxyl radicals produces 2,5-DHBA, 2,3-DHBA and catechol that further react with hydroxyl radicals to be consumed. The reaction mechanism is illustrated as follows:
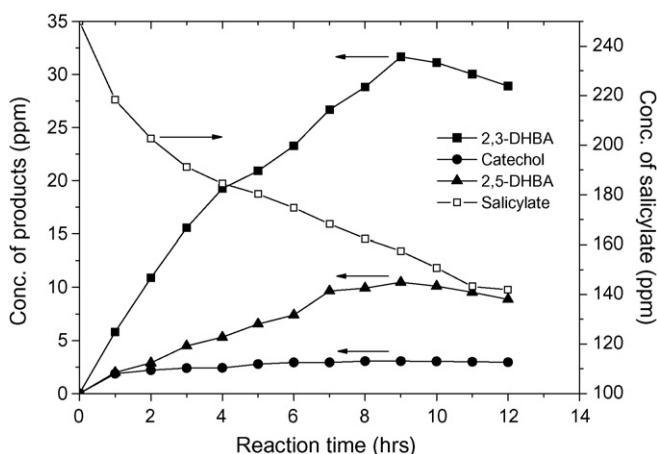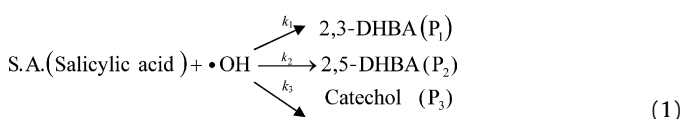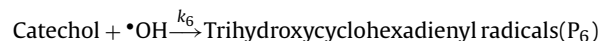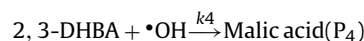
$$
\text{S.A.(Salicylic acid)} + {}^{\bullet}\text{OH} \quad
\begin{array}{l}
\xrightarrow{k_1} \text{2,3-DHBA}\,(P_1) \\
\xrightarrow{k_2} \text{2,5-DHBA}\,(P_2) \\
\xrightarrow{k_3} \text{Catechol}\;\;(P_3)
\end{array}
\tag{1}
$$

Fig. 6. Optimal yield of hydroxyl radicals under salicylic acid of 250 ppm, pH 5, dissolved oxygen level of 8.2 mg O_2 L^{-1} and irradiation intensity of 2.9 mW cm^{-2}.

$$
2,3\text{-DHBA} + {}^{\bullet}\text{OH} \xrightarrow{k4} \text{Malic acid}(P_4)
$$

$$
2,5\text{-DHBA} + {}^{\bullet}\text{OH} \xrightarrow{k_5} \text{Maleyl pyruvate}(P_5)\,[26\text{--}28]
\tag{2}
$$

$$
\text{Catechol} + {}^{\bullet}\text{OH} \xrightarrow{k_6} \text{Trihydroxycyclohexadienyl radicals}(P_6)
$$

where k_1, k_2 and k_3 represent the formation rate constants of 2,3-DHBA, 2,5-DHBA and catechol; k_4, k_5 and k_6 represent the reaction rate constants of these products with hydroxyl radical; and P_4, P_5 and P_6 represent the products from the reactions of 2,3-DHBA, 2,5-DHBA and catechol with hydroxyl radical, respectively. The kinetics of hydroxyl radical can be expressed as:

$$
\frac{-d[\text{S.A.}]}{dt} = k_T[{}^{\bullet}\text{OH}][\text{S.A.}] = k_1[{}^{\bullet}\text{OH}][\text{S.A.}] \\
+ k_2[{}^{\bullet}\text{OH}][\text{S.A.}] + k_3[{}^{\bullet}\text{OH}][\text{S.A.}]
\tag{3}
$$

$$
k_T = k_1 + k_2 + k_3
$$

$$
\frac{-d[P_i]}{dt} = k_f[{}^{\bullet}\text{OH}][\text{S.A.}] - k_r[{}^{\bullet}\text{OH}][P_i]
\tag{4}
$$

where P_i is the 2,3-DHBA, 2,5-DHBA and catechol ($i = 1$–3); k_T is the reaction rate constant of salicylic acid; sum of k_1, k_2 and k_3; k_f is the formation rate constants of 2,3-DHBA, 2,5-DHBA and catechol ($f = 1$–3); and k_r is the consumption rate constants of 2,3-DHBA, 2,5-DHBA and catechol reacting with hydroxyl radicals ($r = 4$–6).

Owing to the higher concentration of salicylic acid in the early phase of reaction, the formation rate of 2,3-DBHA is also higher. As the reaction proceeds, the amount of 2,3-DHBA formed increases while that of salicylic acid decreases. Therefore, the formation rate of 2,3-DHBA decreases as the depletion rate increases till the steady state where the formation rate equals the depletion rate and the highest concentrations of products formed are reached. Thereafter, the concentration of 2,3-DHBA starts to decline. At steady state, the formation and depletion rates of the product are the same, or $d[P_i]/dt = 0$. Therefore, Eq. (4) can be written as:

$$
k_f[{}^{\bullet}\text{OH}][\text{S.A.}] = k_r[{}^{\bullet}\text{OH}][P_i]
\tag{5}
$$

$$
\frac{[\text{S.A.}]}{P_i} = \frac{k_r}{k_f}
\tag{6}
$$

The result of Eq. (6) indicates that the ratio of the formation rate constant and the depletion rate constant at steady state (after 9 h of reaction in this study) becomes constant and is equal to the ratio of the salicylic acid concentration and the product concentration. Therefore, the ratios of the formation rate constants and the depletion constants of 2,3-DHBA, 2,5-DHBA and catechol at steady state and different pH values can be derived: $k_4/k_1 = 4.29$, $k_5/k_2 = 12.96$, $k_6/k_3 = 35.51$. As can be seen, the ratios of the formation rate constants and the depletion rate constants of the three products are all greater than 1, confirming that the reaction of each product with hydroxyl radicals at steady state is predominant.

The ratios of rate constants can only shed light on the relationships between formation and depletion of the three products. However, the formation of 2,3-DHBA, 2,5-DHBA and catechol occur at the same time when salicylic acid reacts with hydroxyl radicals. Therefore, it is very difficult to obtain their formation rate constants (k_1, k_2 and k_3) directly and individually. On the other hand, their relative formation can be obtained if the actual depletion constants of the products are available. The rate constants (k_4, k_5 and k_6) of 2,3-DHBA, 2,5-DHBA and catechol, with hydroxyl radicals can be obtained by allowing each product to react with hydroxyl radicals individually to determine the reaction orders. The formation rate constant (k_1, k_2 and k_3) of each product can be derived from the ratio of the rate constants. In the experiment, the relationship between product concentration and reaction time was

analyzed after allowing 2,3-DHBA, 2,5-DHBA and catechol to react with hydroxyl radicals in the photocatalysis system for different periods of time. The results revealed a linear relationship between product concentration and reaction time in the plot of the natural log of product concentration ($\ln[P_i]$) vs. reaction time (t). The statistical analysis results also showed that the reactions between the products and hydroxyl radicals are of first order. [•OH] can be considered constant because hydroxyl radicals in the reaction are constantly provided by the photocatalytic reaction. Therefore, the slope of the linear plot of $\ln[2,5\text{-DHBA}]$ vs. time is the observational rate constant (k_{4obs}) of the reaction of 2,5-DHBA and hydroxyl radicals. The equation is derived as follows:

$$\frac{d[P_i]}{dt} = -k_r[P_i][•OH] \tag{8}$$

After rearrangement, the integrations on both sides are calculated as

$$\int_0^t \frac{d[P_i]}{P_i} = \int_0^t (-k_r[•OH])dt \tag{9}$$

$$\ln[P_i]_t - \ln[P_i]_0 = -k_r[•OH]$$
$$\ln[P_i]_t = -k_r[•OH] + \ln[P_i]_0 \tag{10}$$

The line plotted by $\ln[P_i]$ against reaction time (t) had the slope of $-k_r[•OH]$, which represents the observational consumption rate constants (k_{robs}) of 2,3-DHBA, 2,5-DHBA and catechol, and the observational formation rate constant (k_{fobs}) will be obtained from the ratio of k_r/k_f. According to the data reported by Buxton et al. [29], both the consumption rate constants (k_r) and the formation rate constant (k_f) can be derived from the proportional coefficients.

After calculation, $k_{4obs} = 2.4 \times 10^{-5}$, $k_{5obs} = 2.7 \times 10^{-5}$, and $k_{6obs} = 1.9 \times 10^{-5}$. According to the above ratios of depletion rate constants, the formation rate constants (k_r/k_f), the observational depletion rate constants of the reactions of the three hydroxylation products with hydroxyl radicals, and the observational formation rate constants of the three products are obtained as follows: $k_{1obs} = 5.6 \times 10^{-6}$, $k_{2obs} = 2.1 \times 10^{-6}$, and $k_{3obs} = 5.4 \times 10^{-7}$. As described previously, the reaction rate constant k of the reaction of salicylic acid with hydroxyl radical is the sum of k_1, k_2 and k_3 (Eq. (4)). Therefore, the observational rate constant of salicylic acid is obtained as 8.2×10^{-6}. From the ratio of the rate constant $k = 2.8 \times 10^{11}$ of the reaction between salicylic acid and hydroxyl radicals obtained by Buxton et al. [29], the radioactive decomposition method at pH 5, the observational rate constant of the present study, and the formation rate constants of the three products, $k_1 = 1.9 \times 10^{11}$, $k_2 = 7.1 \times 10^{10}$, and $k_3 = 1.8 \times 10^{10}$, are obtained.

According to the formation rate of each product, the formation rate constant of 2,3-DHBA is the highest followed by that of 2,5-DHBA, and finally that of catechol. This result is consistent with the concentration of major products with the optimal yield of hydroxyl radicals. The concentration of hydroxyl radicals in the system at steady state can be indirectly obtained from the observational formation rate constant of each product and the formation rate constant obtained above:

$$k_{1obs} = k_1[•OH], k_{2obs} = k_2[•OH], k_{3obs} = k_3[•OH]$$

$$[•OH] = 5.1 \times 10^{-17} \text{ M}$$

4. Conclusions

The conclusions of this study are summarized as follows. The speed of rotating motor, oxidation temperature, and calcination temperature are the major influencing factors to be taken into consideration when preparing the photocatalytic thin-film reactor. The optimal combination of parameters for preparing the catalyst by CVD including water-bath temperature of 80 °C, Ti $(OC_3H_7)_4/H_2O$ of 4, carrier gas flow rate of 1000 mL min^{-1}, oxidation temperature of 400 °C, calcination temperature of 450 °C, oxidation duration of 8 h, rotation speed of furnace of 30 rpm, and speed of geared motor of 75 cm min^{-1} achieved the greatest preparation efficiency. In the investigation of the yield and formation condition of hydroxyl radicals, 250 mg L^{-1} of salicylic acid were found to render the best scavenging effect. In the pH experiment, the yield of hydroxyl radicals under acidic condition was higher than that under basic condition due to the favorable electric condition of the catalyst surface for the adsorption process. In the dissolved oxygen experiment, the yield of hydroxyl radicals was higher in the system with both aeration (dissolved oxygen level of 8.2 mg O$_2$ L^{-1}) and mixing. However, the yield of such system was not much different from that of the system with mixing alone. Therefore, the aeration cost can be saved in practical operation. In the irradiation intensity experiment, the yield of hydroxyl radicals was found to be proportional to irradiation intensity. The yield of hydroxyl radicals was higher when irradiated with the intensity of 2.9 mW cm^{-2}. In the final optimal combination experiment (250 ppm of salicylic acid, pH at 5, aeration rate at 8.2 mg O$_2$ L^{-1}, and irradiation intensity of 2.9 mW cm^{-2}), the concentration of hydroxyl radicals formed in the system was found to be 5.1×10^{-17} M, according to the reaction kinetics. Owing to the difficulty involved in the measurement and analysis of free radicals, expensive and advanced instruments or procedures, such as spin trapping method, were utilized. Other available methods were either less sensitive or required additional treatment. This study used salicylic acid as the hydroxyl radical scavenger to investigate the formation and reaction rate of hydroxyl radicals. The experimental results show that the method proposed in the present study is feasible and can be employed to examine the formation and control of hydroxyl radicals in other AOPs.

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