

Photocatalytic Degradation of Phytotoxic Substances in Waste Nutrient Solution by Various Immobilized Levels of Nano-TiO₂

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Abstract The photocatalytic degradation effectiveness of six selected typical phytotoxic substances (ferulic, benzoic, gallic, salicylic, tannic, and acetic acid) by two levels of 10 nm TiO₂ (11 and 22 g/m²) immobilized on tiles under 254 nm of UV light irradiation was investigated. The results showed that the immobilized nano-TiO₂ significantly degraded all phytotoxic substances dissolved in distilled water, and the cumulative degradation rates of ferulic, benzoic, gallic, salicylic, tannic, and acetic acid reached 22.2, 33.6, 48.2, 56.9, 57.5, and 76.0 % after 6 h of treatment, respectively. Furthermore, the cumulative degradation rates of six phytotoxic substances by immobilized nano-TiO₂ were different remarkably, i.e., salicylic acid > benzoic acid, gallic acid > ferulic acid, acetic acid > tannic acid. The maximal photocatalytic degradation efficiencies of all phytotoxic substances appeared at the first 2 h in the three experiments. During the 6-h treatment period, the photocatalytic

degradation efficiency of all phytotoxic substances decreased gradually. There was no significant difference in the photocatalytic degradation of benzoic acid and ferulic acid between the two levels of immobilized nano-TiO₂ treatments, whereas a significant difference was found in the photocatalytic degradation of salicylic acid, gallic acid, tannic acid, and acetic acid. In a word, nano-TiO₂ photocatalysis is an effective method to degrade phytotoxic substances. And the photocatalytic degradation effectiveness of six typical phytotoxic substances may be related to their structures.

Keywords Phytotoxic substance · Photocatalysis · Nano-TiO₂ immobilization · Degradation rate · Chemical structure

1 Introduction

Phytotoxic substances are released to the rhizosphere through plant residual decomposition and root secretion, and they restrain the plant growth (Rice 1971). It has been reported that phytotoxic substances are mainly consisted of phenolic acids and fatty acids (Tang and Young 1982; Einhellig and Souza 1992; Chou 1995; Asao et al. 2004), such as benzoic acid, 4-hydroxy-benzoic acid, cinnamic acid, ferulic acid, salicylic acid, gallic acid, tannic acid, acetic acid, palmitic acid, stearic acid, etc. (Politycka et al. 1984; Kil and Youb 1987; Yu and Matsui 1993; Gallet 1994; Chou 1995; Lee et al. 2006). The accumulation of

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phytotoxic substances is one of the key factors for causing continuous cropping obstacles of field crops and horticultural crops. It has been reported that aqueous extracts of soybean tissue and root exudates of soybean had a significant impact on the following planted soybean seedling growth, and phenolic acids isolated from aqueous extracts of soybean tissue and root exudates of soybean were directly related to continuous cropping obstacles (Du and Jin 1999). Strawberry root exudates inhibited root activity and plant growth in the second crop and decreased its resistance to disease (Zhen et al. 2004). Moreover, studies have shown that asparagus root exudates and rhizome extracts could inhibit the growth of asparagus seedlings (Young 1984; Shafer and Garrison 1986).

The area of protected horticulture adopting soilless culture has increased worldwide in the past decade due to its advantages of decreasing the occurrence of soil-borne diseases, high productivity, and easy management (Van Os 1995; Jiang and Yu 2006). Soilless culture includes substrate cultivation and hydroponics. Apparently, phytotoxic substances can be released from organic substrates and roots. In terms of treatment method of waste nutrient solution, soilless cultivation is classified into two types, i.e., open and closed soilless culture. In recent years, soilless culture has gradually changed from open type to closed type globally, because closed soilless culture not only save water and fertilizer resources via nutrient solution recycle but also solve the water pollution and eutrophication problem through avoiding waste nutrient solution emission. Specially, Netherlands, the country with the largest areas of soilless cultivation, has changed the soilless cultivation from open to closed form through the legislation (Erik and Van 1999). However, closed soilless cultivation also gave rise to accumulation of phytotoxic substances from root secretion (Yu and Matsui 1994, 1999; Kitazawa et al. 2005; Lee et al. 2006) and organic substrate decomposition (Kato et al. 1977; Kong et al. 2006) during the long-term recycle of nutrient solution. In order to avoid the harmful impacts caused by the accumulation of phytotoxic substances in closed soilless cultivation, therefore, removing the phytotoxic substances in the nutrient solution is particularly important to gain high yields. Nowadays, the removal method of phytotoxic substances basically includes activated carbon adsorption (Yu et al. 1993; Yu and Matsui 1994; Lee et al. 2006) and nano-TiO₂ photocatalysis (Sunada et al.

2008; Miyama et al. 2009). Lee et al. (2006) found that activated carbon could effectively remove the phytotoxic substances accumulated in nutrient solution, and the inhibition on plant growth also reduced. However, its removal ability is limited since high-dose activated carbon treatment could not eliminate the harmful impact of these phytotoxic substances on plant growth (Lee et al. 2006).

Many studies on air purification and water pollutant removal by TiO₂ photocatalysis have been reported (Noguchi and Fujishima 1998; Ohko et al. 2001; Li et al. 2003; Shahmoradia et al. 2010; Slimen et al. 2012; Sánchez et al. 2012). Nano-TiO₂ photocatalysis refers to the oxidizing reaction when nano-TiO₂ absorbs UV light with a wavelength less than its band gap (approximately 385 nm), then organic matters that adsorb on the surface of nano-TiO₂ are oxidized and decomposed into inorganic small molecule such as CO₂ and H₂O (Gao et al. 2002). Nano-TiO₂ photocatalysis has the advantages of nontoxicity, no secondary pollution, long repeated use, complete decomposition, broad-spectrum of sterilization feature, etc. At present, there are only two reports about nano-TiO₂ photocatalysis elimination of the phytotoxic substances in nutrient solution (Sunada et al. 2008; Miyama et al. 2009). According to Sunada et al. (2008), the yield of hydroponic asparagus increased 1.6 times when nano-TiO₂ photocatalytic treatment was conducted in the hydroponic system. Miyama et al. (2009) showed that the growth and yield of tomato cultivated with rice hull substrate increased significantly when the nutrient solution was treated with nano-TiO₂ photocatalytic system, and the concentration of total organic carbon that came from rice hull substrate release and tomato roots secretion decreased. However, to our knowledge, the response of different constituents of phytotoxic substances in nutrient solution to nano-TiO₂ photocatalysis has not been reported.

In this experiment, six typical phytotoxic substances were selected, including benzoic acid, salicylic acid, ferulic acid, gallic acid, acetic acid, and tannic acid, and treated by immobilized nano-TiO₂ photocatalysis. The objectives of this research were to (1) study the photocatalytic degradation of phytotoxic substances by nano-TiO₂ photocatalysis, (2) examine the photocatalytic difference between two levels of immobilized nano-TiO₂, and (3) clarify the possible relationship between the structure of phytotoxic substances and their degradation degree by photocatalysis.

2 Materials and Methods

2.1 Preparation of Nano-TiO₂ Dispersion Solution and Its Immobilization on Tiles

Twenty grams of nano-TiO₂ powder (10-nm particle size), 11.25 mL colloidal silica (chemical purity), and 138.75 mL distilled water were mixed in a beaker. Then, the mixture solution was scattered for 30 min by ultrasound dispersing instrument (JY92-IIN, made in China), thus the nano-TiO₂ dispersion solution was made (nano-TiO₂ concentration was 0.133 g/mL). Two doses (1 and 2 mL) of nano-TiO₂ dispersion solution were coated uniformly on tiles (the size of one tile, 23.5 cm×5.2 cm), respectively, and the coated tiles were dried at room temperature. Then, they were roasted in muffle furnace at 120 °C for 0.5 h and 450 °C for 0.5 h continuously. After cooling, the tiles were taken out from the furnace. Tiles coated with two levels of nano-TiO₂, 11 and 22 g/m², were prepared.

2.2 Experimental Design

Three experiments were carried out to study the degradation effect of six selected typical phytotoxic substances by varied levels of immobilized nano-TiO₂. In the first experiment, the photocatalytic degradation of benzoic and salicylic acid by varied levels of immobilized nano-TiO₂ was tested. In the second experiment, the photocatalytic degradation of ferulic and gallic acid by varied levels of immobilized nano-TiO₂ was researched. In the third experiment, the photocatalytic degradation of acetic and tannic acid by varied levels of immobilized nano-TiO₂ was investigated. The phytotoxic substances used in the experiments are analytic purity reagents and were dissolved in distilled water.

There were six treatments in the first experiment, and each treatment repeated three times. Three tiles coated with or without nano-TiO₂ (total area 0.037 m²) was placed in one plastic box (27 cm×18 cm×9 cm) filled with 500 mL of 20 mg/L phytotoxic substance water solution for each replicate. Treatment 1 was benzoic acid water solution and tiles without nano-TiO₂; treatment 2 was benzoic acid water solution and tiles with 11 g/m² nano-TiO₂; and treatment 3 was benzoic acid water solution and tiles with 22 g/m² nano-TiO₂. Treatments 4, 5, and 6 were similar to

treatments 1, 2, and 3, just by replacing the benzoic acid water solution with salicylic acid water solution. Tiles without nano-TiO₂ were called *G0*, tiles coated with 11 g/m² nano-TiO₂ were called *G1*, and tiles coated with 22 g/m² nano-TiO₂ were called *G2*. For all treatments, the tiles were immersed in the phytotoxic substance water solution in the box, and the solution depth above the tiles was 6 mm. Six boxes were put along the longitudinal central axis of UV lamp randomly in each photocatalytic device and were below 15 cm from the UV lamp vertically.

The experiment was carried out in rectangle polyethylene plastic-closed photocatalytic device, and three photocatalytic devices were used in this study. Two UV lamps (30 W, 254 nm) are fixed on the inner surface of the cover of each device; the distance between the two lamps is 20 cm, and the length and irradiation intensity of the UV lamp are 90 cm and 1,100 μw/cm², respectively. The irradiation intensity of the UV lamp is measured at 15 cm from the lamp surface.

Similar treatments as the first experiment was designed in the second and third experiments, just by replacing the benzoic acid and salicylic acid with ferulic acid and gallic acid, acetic acid, and tannic acid, respectively.

2.3 Sampling and Determination Methods

All experiments lasted for 6 h. A 10-mL solution from each repeat was sampled after 2, 4, and 6 h, respectively. For the meantime, solution temperatures were recorded (Table 1). All the samples should be kept in the refrigerator at 4 °C for determining the concentration of phytotoxic substances.

The concentration of benzoic and salicylic acid was measured by ultraviolet spectrophotometry (Duan 2009). First, 25 mL benzoic acid solutions of 0, 4, 8,

Table 1 Reaction temperature of the photocatalytic degradation of phytotoxic substances by immobilized nano-TiO₂ during experiments (in degree Celsius)

Experiments	Before UV irradiation	Experimental stages		
		2 h	4 h	6 h
The 1st experiment	27	31	30	25
The 2nd experiment	18	25	27	23
The 3rd experiment	11	22	24	22

12, 16, and 20 mg/L were prepared. The absorbency of benzoic acid solution at each concentration at 227 nm were determined, and the standard curve was drawn. Second, the absorbencies of benzoic acid solution samples were determined at 227 nm according to the absorbency and standard curve to calculate the concentration of benzoic acid in the samples. The concentrations of salicylic acid solution samples were measured similarly to benzoic acid, but the determination wavelength for salicylic acid solution was at 230 nm.

Acetic acid concentration was measured by titration method (He 2009). In this method, phenolphthalein was used as indicator, and NaOH solution (0.001 mol/L) was used to determine the concentration of acetic acid in the sample. The concentrations of ferulic acid, gallic acid, and tannic acid were measured by $\text{FeCl}_3\text{-K}_3[\text{Fe}(\text{CN})_6]$ colorimetry (Fu et al. 2006; Jiang et al. 2010). First, 0, 0.5, 1, 1.5, 2.0, and 2.5 mL of ferulic acid solution at the concentration of 20 mg/L were put in the corresponding test tubes, and then the solution in each test tube of up to 2.5 mL with distilled water was made. Second, 2.5 mL of 99 % ethanol, 2 mL of 0.3 % sodium dodecyl sulfate, and 1 mL of 0.6 % $\text{FeCl}_3\text{-0.9 %K}_3[\text{Fe}(\text{CN})_6]$ (volume ratio 1:0.9) mixture were added into every tube, and then the tubes were placed in the dark for 5 min. Third, 17 mL HCl (0.1 mol/L) was added into each test tube, the tubes were shaken to allow complete reaction of the solution, and then the absorbencies of the solution was measured by spectrophotometry at 720 nm 20 min later. The standard curve was drawn according to the absorbencies and corresponding ferulic acid concentrations. The absorbencies of ferulic acid solution samples (2.5 mL taken from each repeat) were also measured following the above second and third steps, and the concentrations of ferulic acid solution samples were calculated according to the standard curve.

In this study, cumulative degradation rate and photocatalytic degradation efficiency were calculated. The cumulative degradation rate means the degradation percentage of phytotoxic substance after 2, 4, and 6 h of treatment. The photocatalytic degradation efficiency refers to the degradation amount of a phytotoxic substance per hour and per square meter for the first 2 h, the second 2 h, and the last 2 h during experiments. The formula of cumulative degradation rate

and the photocatalytic degradation efficiency were as follows:

$$D_c = \frac{C_0 - C_x}{20} \times 100\%.$$

D_c represents the cumulative degradation rate of a phytotoxic substance. C_0 represents the concentration of a phytotoxic substance treated with G0 after 2, 4, or 6 h. C_x represents the concentration of a phytotoxic substance treated with G1 or G2 after 2, 4, or 6 h.

$$D_p (\text{mg}/\text{m}^2/\text{h}) = \frac{(\Delta C_x - \Delta C_0) \times V}{2 \times 0.037}.$$

D_p represents the photocatalytic degradation efficiency for the first 2 h, the second 2 h, or the last 2 h during experiments. ΔC_x represents the reduced concentration of a phytotoxic substance treated with G1 or G2 for the first 2 h, the second 2 h, or the last 2 h during experiments. ΔC_0 represents the reduced concentration of a phytotoxic substance treated with G0 for the first 2 h, the second 2 h, or the last 2 h during experiments. V stands for the volume of phytotoxic substance water solution: 500 mL for the first 2 h, 490 mL for the second 2 h, and 480 mL for the last 2 h.

2.4 Data Analysis

The experimental data were analyzed by SAS 8.2 software, and the multiple comparisons between the treatments were conducted by the least significant difference method.

3 Results and Discussion

3.1 Photocatalytic Degradation of Phytotoxic Substances by Varied Levels of Immobilized Nano-TiO₂

3.1.1 Photocatalytic Degradation of Benzoic and Salicylic Acid

The concentrations of benzoic acid solution treated with G1 and G2 were significantly lower than that treated with G0. There was no significant difference between G1 and G2 on the photocatalytic degradation

Table 2 Concentrations of benzoic and salicylic acid after photocatalysis by varied levels of immobilized nano-TiO₂ (in milligram per liter)

Levels of immobilized nano-TiO ₂	Benzoic acid			Salicylic acid		
	2 h	4 h	6 h	2 h	4 h	6 h
G0	15.80 a	14.75 a	13.47 a	19.73 a	19.34 a	18.81 a
G1	12.65 b	9.66 b	7.24 b	14.50 b	11.22 b	8.45 b
G2	12.31 b	9.31 b	6.75 b	13.94 b	10.30 c	7.43 c

Letters in same column mean significant difference at 5 % level

of benzoic acid. The concentrations of salicylic acid solution treated with G1 and G2 were also significantly lower than that treated with G0. However, significant difference was found between G1 and G2 on the photocatalytic degradation of salicylic acid after the 4 and 6-h treatments (Table 2).

3.1.2 Photocatalytic Degradation of Ferulic and Gallic Acid

The concentration of ferulic acid solution treated with G0 was significantly higher than that treated with G1 and G2. There was no significant difference between G1 and G2 on the photocatalytic degradation of ferulic acid. The concentration of gallic acid solution treated with G0 was 1.7–7.9 times higher than that treated with G1 and G2. It appeared that there is a significant difference between G1 and G2 on the photocatalytic degradation of gallic acid after the 6-h treatment, and the concentration of gallic acid solution treated with G1 was 1.04 mg/L higher than that treated with G2 (Table 3).

3.1.3 Photocatalytic Degradation of Acetic and Tannic Acid

The concentrations of acetic acid solution and tannic acid solution treated with G0 were significantly higher than that treated with G1 and G2. With time change, it

appeared that there is significant difference between G1 and G2 on the photocatalytic degradation of acetic and tannic acid (Table 4).

The above results (Tables 2, 3, and 4) showed that there was no significant difference between G1 and G2 on the photocatalytic degradation of benzoic and ferulic acid, while G1 and G2 made significant difference on the photocatalytic degradation of salicylic, gallic, acetic, and tannic acid with time change. These results meant that the significant difference of the photocatalytic effect between two levels of immobilized nano-TiO₂ might be related to the concentrations of phytotoxic substances and their traits.

3.2 Cumulative Degradation Rates of Phytotoxic Substances by Immobilized Nano-TiO₂ Photocatalysis

3.2.1 Cumulative Degradation Rates of Benzoic and Salicylic Acid

The benzoic acid and salicylic acid were degraded by immobilized nano-TiO₂ photocatalysis, and, after 6 h of treatment, the cumulative degradation rate of benzoic acid reached 33.1 % by G1 and 33.6 % by G2, while that of salicylic acid reached 51.8 % by G1 and 56.9 % by G2. There was significant difference between the cumulative degradation rate of benzoic acid and that of salicylic acid by immobilized nano-TiO₂ (Fig. 1a).

Table 3 Concentrations of ferulic and gallic acid after photocatalysis by varied levels of immobilized nano-TiO₂ (in milligram per liter)

Levels of immobilized nano-TiO ₂	Ferulic acid			Gallic acid		
	2 h	4 h	6 h	2 h	4 h	6 h
G0	18.57 a	16.93 a	17.12 a	15.98 a	13.39 a	11.03 a
G1	16.48 b	14.33 b	13.52 b	9.31 b	4.76 b	2.43 b
G2	16.15 b	14.88 b	12.68 b	8.30 b	4.00 b	1.39 c

Letters in same column mean significant difference at 5 % level

Table 4 Concentrations of acetic and tannic acid after photocatalysis by varied levels of immobilized nano-TiO₂ (in milligram per liter)

Levels of immobilized nano-TiO ₂	Acetic acid			Tannic acid		
	2 h	4 h	6 h	2 h	4 h	6 h
G0	17.07 a	17.12 a	19.07 a	18.08 a	16.24 a	15.04 a
G1	8.8 b	7.73 b	4.8 b	12.55 b	7.29 b	4.55 b
G2	8.03 b	5.6 c	3.87 c	12.33 b	7.06 b	3.54 c

Letters in same column mean significant difference at 5 % level

3.2.2 Cumulative Degradation Rates of Ferulic and Gallic Acid by Immobilized Nano-TiO₂ Photocatalysis

Ferulic acid and gallic acid were all effectively decomposed by immobilized nano-TiO₂ photocatalysis, and, after 6 h of treatment, the cumulative degradation rates of 1F, 2F, 1G, and 2G were 17.9, 22.2, 43.0, and 48.2 %, respectively. The cumulative degradation rate of gallic acid was higher than that of ferulic acid by immobilized nano-TiO₂ photocatalysis, and there was a significant difference between the cumulative degradation rate of gallic acid and that of ferulic acid (Fig. 1b).

3.2.3 Cumulative Degradation Rates of Tannic and Acetic Acid by Immobilized Nano-TiO₂ Photocatalysis

The tannic and acetic acid were well degraded by immobilized nano-TiO₂ photocatalysis, and, after 6 h of treatment, the cumulative degradation rates of 1T,

2T, 1A, and 2A reached 52.5, 57.5, 71.3, and 76.0 %, respectively. The cumulative degradation rate of acetic acid was higher than that of tannic acid, and the difference between the cumulative degradation rate of acetic acid and that of tannic acid was significant (Fig. 1c).

The cumulative degradation rates of six phytotoxic substances were different, and we concluded that the photocatalytic degradability of six phytotoxic substances depends on their structures, the pH of each phytotoxic substance water solution, and so on. Research had shown that the quantity and type of substituents in benzene ring affected nano-TiO₂ photocatalytic oxidation degradation of the aromatic compounds. Chlorobenzene and aniline were those mono-substituted aryl ring compounds that could be more easily degraded by nano-TiO₂ photocatalysis than nitrochlorobenzene and *p*-nitroaniline which were bis-substituted aryl ring compounds. Compared to chlorobenzene with aniline, amino replacement was more easily degraded than chlorine replacement (Ye and Li 2000). The photocatalytic degradation of organic matters by nano-TiO₂ photocatalysis was a complex process,

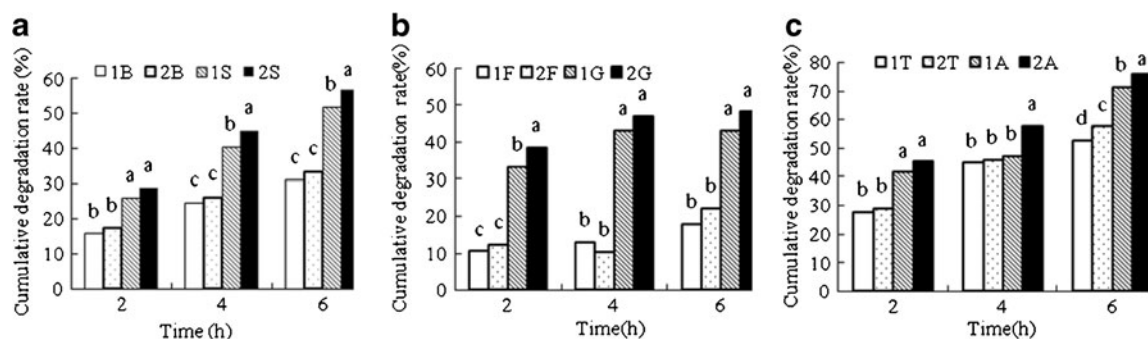


Fig. 1 Cumulative degradation rates of benzoic acid and salicylic acid (a), ferulic acid and gallic acid (b), and tannic acid and acetic acid (c) by immobilized nano-TiO₂ photocatalysis. 1B, benzoic acid was photocatalyzed by G1; 2B, benzoic acid was photocatalyzed by G2; 1S, salicylic acid was photocatalyzed by G1; 2S, salicylic acid was photocatalyzed by G2; 1F, ferulic acid was

photocatalyzed by G1; 2F, ferulic acid was photocatalyzed by G2; 1G, gallic acid was photocatalyzed by G1; 2G, gallic acid was photocatalyzed by G2; 1T, tannins was photocatalyzed by G1; 2T, tannins was photocatalyzed by G2; 1A, acetic acid was photocatalyzed by G1; 2A, acetic acid was photocatalyzed by G2. The letters on the bar chart mean significant difference at 5 % level

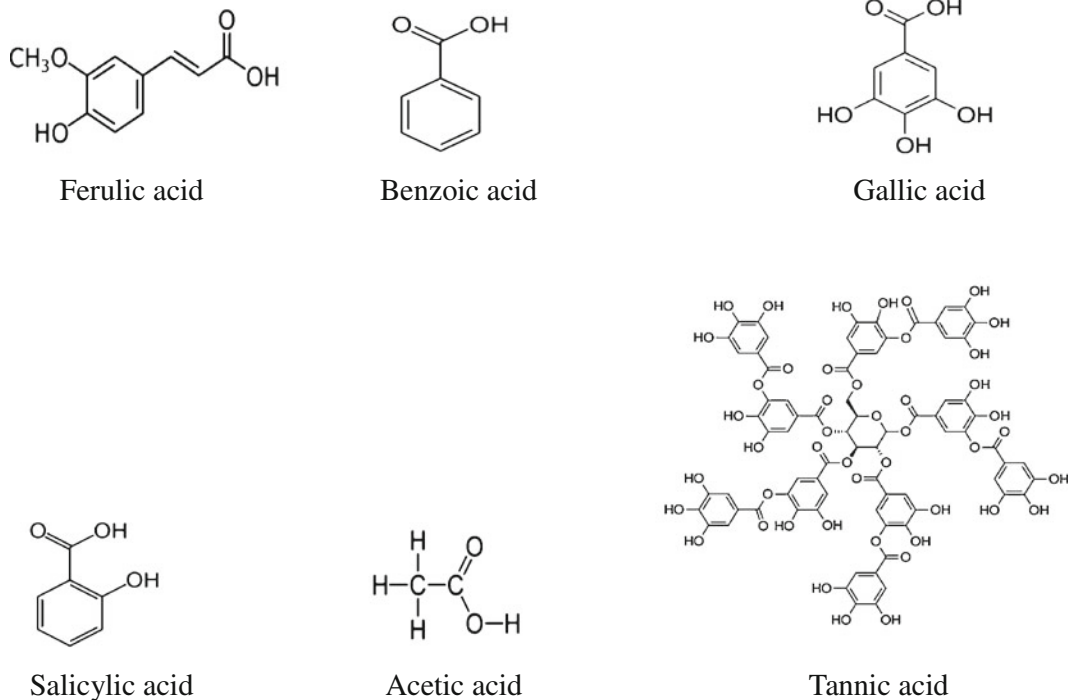


Fig. 2 Structures of the six selected phytotoxic substances

including the formation of intermediates and eventual degradation to CO_2 , H_2O , and other small inorganic molecules. Konstantinou and Albannis (2003) studied the mineralization of several pesticides by nano- TiO_2 photocatalysis. The results suggested that the main intermediates of pesticide degradation included (1) hydroxylated products and derivatives usually after dehalogenation of the parent pesticide, if halogen substituents are present; (2) products of oxidation of the side chain, if present; (3) ring opening products for aromatic pesticides; and (4) decarboxylation products. Thus, the characteristics of organic structure and functional group had important influence on the degradation process by nano- TiO_2 photocatalysis (Zhou et al. 2004).

In our research, the molecular weight, substituent type and quantity of six phytotoxic substances were different, which may affect their cumulative degradation rate by immobilized nano- TiO_2 photocatalysis. The pH of solution was also an important factor to affect the degradation of six phytotoxic substances by nano- TiO_2 photocatalysis. It had revealed that the photocatalytic degradation of benzoic acid at $\text{pH}=3.5$ by nano- TiO_2 was better than at $\text{pH}=8$. When the initial pH rose, benzoic acid reaction rate constant first increased and then decreased by nano- TiO_2 photocatalysis (Yu et al. 2008). The effect of nano- TiO_2 photocatalytic oxidation of TNT in neutral and alkaline conditions was better than in acidic conditions (Son et al. 2004). In our

Table 5 Photocatalytic degradation efficiencies of phytotoxic substances by immobilized nano- TiO_2 photocatalysis during time change (in milligram per square meter per hour)

Experimental stages (h)	Benzoic acid		Salicylic acid		Ferulic acid		Gallic acid		Tannic acid		Acetic acid	
	G1	G2	G1	G2	G1	G2	G1	G2	G1	G2	G1	G2
0–2	21.4 a	23.7 a	35.6 a	39.4 a	14.2 a	16.5 a	45.4 a	52.3 a	37.6 a	39.2 a	56.3 a	61.6 a
2–4	11.7 b	11.8 b	19.3 b	21.8 b	3.4 b	–2.5 b	13.1 b	11.4 b	22.9 b	22.9 b	7.5 c	16.6 b
4–6	8.6 b	9.5 b	14.6 c	15.3 b	6.5 b	15.7 a	–0.3 c	1.6 c	10.1 c	15.2 c	31.9 b	24.1 b

Letters in same column mean significant difference at 5 % level

experiments, the six selected phytotoxic substances are all weak organic acids, and the pH of their water solution might cause the variation in cumulative degradation rate by immobilized nano-TiO₂ photocatalysis.

Current data suggested that nano-TiO₂ photocatalytic degradation of selected phytotoxic substances with benzene ring was more difficultly than that of phytotoxic substances without benzene ring. The phytotoxic substance with more types of substituent on the benzene ring was more difficultly degraded by nano-TiO₂ photocatalysis than that with the less one. The phytotoxic substances with hydroxyl and carboxyl on the ortho of the benzene ring were more easily photocatalytically decomposed than those on other positions. The phytotoxic substances contained more hydroxyl substituents, and their degradation rates were higher. The structures of six selected phytotoxic substances are listed in Fig. 2.

3.3 Photocatalytic Degradation Efficiencies of Phytotoxic Substances by Immobilized Nano-TiO₂ Photocatalysis

The photocatalytic degradation efficiencies of all phytotoxic substances by immobilized nano-TiO₂ photocatalysis in 0–2 h were significantly higher than those of in 2–4 and 4–6 h, and the photocatalytic degradation efficiencies of all phytotoxic substances decreased gradually during time change (Table 5). This phenomenon was in line with the photocatalytic degradation rates of phytotoxic substances by immobilized nano-TiO₂ photocatalysis. Many studies had shown that the photocatalytic degradation rate by nano-TiO₂ decreased with the concentration reduction of the degraded substances. And at the high concentration, the photocatalytic degradation rate had little relationship with the solute concentration (Sabate et al. 1991; Lu et al. 1993; Kim and Hong 2002). In this study, the photocatalytic degradation efficiencies of all phytotoxic substances decreased gradually, which might account for the reduction of the concentration of each phytotoxic substances.

4 Conclusions

In our experiment, the two levels of immobilized nano-TiO₂ are effective on the photocatalytic degradation of selected phytotoxic substance. In practical

application, it is recommended that immobilized 11 g/m² nano-TiO₂ on tiles is an optimal in terms of reducing costs and resources.

After the 6-h treatment by immobilized nano-TiO₂ photocatalysis, the cumulative degradation rates of the six typical phytotoxic substances range from 22.2 to 76.0 %. The cumulative degradation rate of acetic acid is the greatest, while that of ferulic acid is the lowest. In the three experiments, the six phytotoxic substances are substantially degraded by immobilized nano-TiO₂ photocatalysis. The cumulative degradation rates of selected phytotoxic substances are different, i.e., salicylic acid > benzoic acid, gallic acid > ferulic acid, acetic acid > tannic acid. The photocatalytic degradation efficiency of each phytotoxic substance is greatest in 0–2 h, and the photocatalytic degradation efficiencies of all phytotoxic substances decrease during the 6-h treatment. In this study, the six typical phytotoxic substances can be effectively degraded by nano-TiO₂ photocatalysis. Therefore, it can be a viable method for waste nutrient solution treatment in closed soilless horticulture. In view of the nano-TiO₂ superior photocatalytic oxidation performance, it has broad application prospects in waste nutrient solution treatment.

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