Degradation of 2,4-dichlorophenol in aqueous solution by a hybrid oxidation process

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Abstract

A hybrid photo-electro-reaction system has been developed in this study, which consists of three functional electrodes: a TiO_2/Ti sheet as the anode, a steel (Fe) sheet as another anode in parallel, and a piece of graphite felt (GF) as the cathode. While an electrical current is applied between the Fe anode and GF cathode and UV light is irradiated on the surface of TiO_2/Ti anode, both of E-Fenton reaction and photoelectrocatalytic (PEC) reaction are involved simultaneously. The integration of E-Fenton and PEC reactions was evaluated in terms of 2,4-dichlorophenol (2,4-DCP) degradation in aqueous solution. In the meantime, the current distribution between two anodes and pH influence on the 2,4-DCP degradation were studied and optimized. Experimental results confirmed that 2,4-DCP in aqueous solution was successfully degraded by 93% and mineralized by 78% within 60 min in such a hybrid oxidation process. When a current intensity of 3.2 mA was applied, the current efficiency for H_2O_2 generation on the GF cathode was determined to be 61%. Furthermore, the experiments demonstrated that combination of E-Fenton reaction with photocatalytic reaction let the process be less pH sensitive and would be more favorable to water and wastewater treatment in practice.

Keywords: E-Fenton; H_2O_2; Photocatalysis; TiO_2; 2,4-DCP; Graphite felt

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1. Introduction

2,4-Dichlorophenol (2,4-DCP) is a chemical precursor for manufacture of a widely used herbicide 2,4-dichlorophenoxy acetic acid (2,4-D). After the herbicide have been applied on agricultural sites, 2,4-DCP is the major transformation product of 2,4-D by solarphotolysis and/or microbial activities in the nearby soil [1] or in natural water [2]. 2,4-DCP has also been found in disinfected water after chlorination, in the flue gas of municipal waste incineration [3], or in pulp and paper wastewater [4]. It has been realized that 2,4-DCP may cause some pathological symptoms and changes to endocrine systems of human [5,6].

Photocatalysis (PC) is a promising technique of advanced oxidation processes and has been proven to be successful in purification of water and wastewater [7-9]. However, the quick recombination between excited electrons and holes (e^-/h^+) from TiO2 catalyst results in a low quantum yield of below 5% only. Recently, photoelectrocatalysis (PEC) demonstrated great attraction in research to further accelerate PC reaction [10,11] by applying an external potential to drive away the conduction band electrons from TiO2 photoanode to a counter electrode as a cathode. This is an efficient way to eliminate the recombination of e^-/h^+ pairs and results in the extension of hole's lifetime [12,13].

On the other hand, Fenton reaction is also a well-proved technique to oxidize organic pollutants from water and wastewater effectively, in which hydrogen peroxide (H_2O_2) is catalyzed by ferrous ions (Fe^{2+}) to produce hydroxyl radicals (HO•). Recent development has been focused on the generation of $H2O2/Fe^{2+}$ by electrochemical means named the electro-Fenton (E-Fenton) process. In such a E-Fenton process, while Fe^{2+} can be electrically generated on a sacrificial anode via oxidation of iron, H_2O_2 is generated on a carbon cathode via the two-electron reduction of sparged oxygen [14,15]. Since the efficiency of H_2O_2 generation on the cathode is a key factor to affect the performance and operating cost in practical application, a variety of cathode materials such as mercury pool [16], carbon felt [17], reticulated vitreous carbon [18], graphite [19], activated carbon fiber [20], or carbon-PTFE [21] have been

studied. It should be noted that the Fenton reaction is not a universal solution and has two apparent limits of pH restriction and reaction selectivity, as an efficient reaction rate only occurs in a narrow pH range of 2-4 and many chemicals such as acetic acid, acetone, carbon tetrachloride, methylene chloride, *n*-paraffins, maleic acid, malonic acid, oxalic acid, and trichloroethane etc. are refractory towards Fenton reagent and [22].

Due to the similarity of reaction mechanism utilizing hydroxyl radicals to destroy organics in aqueous solution between the PEC reaction and E-Fenton reaction, it would be a good approach to combine them together to be a more efficient process. In the meantime, some of the drawbacks of each technique might be eliminated by some characteristics of another technique. The research work presented in this paper has developed a hybrid process by combination of PEC reaction and E-Fenton reaction in a three-electrode reaction system, in which 2,4-DCP was used as a model chemical in aqueous solution and its degradation under different reaction conditions was studied. Furthermore, the reaction mechanism relevant to the interaction between PEC reaction and E-Fenton reaction was also discussed based on the experimental results.

2. Experimental

2.1. Preparation of three electrodes

Titanium sheet (purity: 99.6%; thickness: 0.14 mm) from Goodfellow Cambridge Ltd. was used as a raw material to prepare a TiO_2/Ti film electrode. A piece of Ti sheet (10 mm × 50 mm) was ultrasonically cleaned in alcohol and acetone solutions, respectively and then washed with distilled water. The cleaned Ti sheet was submerged in 2 M HF solution for 2 min to polish its surface chemically. An anodic oxidation process at low voltage was conducted in a dual-electrode reaction chamber, in which the cleaned Ti sheet was used as the anode and a Pt foil with the same size was applied as the cathode. Two electrodes were submerged in aqueous electrolyte solution (1.5 M H_3PO_4 and 0.3 M HF) and an electroophoresis power supply (EPS 600 Pharmacia Biotech) was used to provide electrical potentials/currents between two electrodes. The anodic oxidation process was conducted in two stages for about

30 min. In the first stage, a constant current density of 10 mA cm^{-2} was fixed, until voltage gradually increased up to 30 V (galvanostatic anodization). In the second stage, the constant voltage of 30 V was kept to allow the current density was gradually reduced (potentiostatic anodization) until the oxidation reaction was complete. Then the anodized TiO_2/Ti sheet was calcinated at 723 K for 2 h for further phase transformation and crystallization. A piece of rectangle stainless steel sheet (10 mm × 50 mm × 1 mm) after surface passivation pretreatment was simply used as an iron (Fe) electrode. A piece of graphite fiber (GF) about 2 mm thick supplied by US National Electrical Carbon Products Inc. was cut into the same size (10 mm x 50 mm) as a GF electrode without any further treatment.

2.2. A three-electrode photoreactor and experimental procedure

A novel three-electrode (TiO_2-Fe-GF) photoreactor system used in this study consists of a cylindrical quartz glass reactor with a three-electrode configuration and an 8-W medium-pressure mercury lamp (LZC-UVA-365, Canada) with a main emission at 365 nm as an external UV-A light source. In this reactor, while the GF electrode was used as the cathode to generate H_2O_2, the TiO_2/Ti electrode was employed as the first anode to conduct PEC reaction under UV-A illumination and the Fe electrode was used as the second anode in parallel to release ferrous ion (Fe^{2+}) continuously for E-Fenton reaction. In addition, a saturated calomel electrode (SCE) was also placed in a separate chamber for potential control. In such a TiO_2-Fe-GF photoreactor, the working current and potential on the GF cathode were controlled by a potentiostat (ZF-9, Shanghai, China) and the current distribution between two anodes (TiO_2/Ti and Fe) was controlled by an external variable resistor.

[Fig. 1]

2,4-DCP chemical was purchased from Aldrich with analytical grade. Aqueous 2,4-DCP solution was prepared by dissolving 2,4-DCP into aqueous electrolyte solution (0.02 M Na_2SO_4). During each reaction, 50 mL of the 2,4-DCP solution was continuously aerated by oxygen and an electrical current was applied between the

anodes and cathode. Samples were taken from the reaction solution at different time intervals for analyses. Prior to HPLC analysis, all samples were filtered by a 0.45 μm Millipore filter to remove any particulates including the fiber desquamation from GF electrode. During the reaction, 50 mL reaction solution was continuously aerated by an oxygen gas flow at 40 mL min^{-1}, which was sufficient for oxygen supply and mixing.

2.3. Analytical methods

2,4-DCP concentration was determined by high performance liquid chromatograph (HPLC Finnigan P4000 Model) equipped with a UV detector (UV6000LP). The separation column is a reverse-phase column (RESTEK Pinnacle II, d-C18 4.6 mm × 250 mm, 5 μm) and a mobile phase consists of acetonitrile:water:acetic acid (69:30:1). H_2O_2 concentration was measured by a spectrophotometer (GENESYS 2 UV-VIS) at 400 nm wavelength, using $K_2Ti(C_2O_4)_3$ (analytical grade) as a colored indicator. Dissolved organic carbon (DOC) concentration was measured by a TOC analyzer (Shimadzu TOC-5000A) after sample filtration using the 0.45 (m Millipore filter.

3. Results and discussion

3.1. Effect of current intensity on H2O2 generation

The GF cathode used in this study is a carbon material with a microporous structure and high reduction potential, which can generate H_2O_2 on its surface with the following reaction:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E^0 = 0.695 \text{ V vs. NHE}$$

The rate of H_2O_2 generation on the GF cathode depends on several factors including electrolyte properties, applied current intensity, and dissolved oxygen concentration in the reaction solution. To study the rate of H_2O_2 generation affected by current intensity as a main parameter, a set of experiments in aqueous 0.02 M

Na_2SO_4 solution (without 2,4-DCP) was conducted by applying different current intensity from 0.5 mA to 5.0 mA between the Pt anode and the GF cathode. Each experiment lasted for 150 min and samples were taken at different time intervals to determine the accumulative H_2O_2 concentration in the solution. The experimental results are shown in Fig. 2.

[Fig. 2]

It can be seen that H_2O_2 concentration in the Na_2SO_4 solution gradually built up along with reaction time and eventually approached to its maximum levels. The experimental results showed that the higher current intensity was applied, the higher H_2O_2 concentration was achieved. For example, the accumulative H_2O_2 concentration at 60 min was increased from 0.125 mM at 0.5 mA to 0.728 mM at 3.2 mA significantly and was further increased up to 0.836 at 5.0 mA. To evaluate the current efficiency of H_2O_2 generation on the cathode, it is assumed that H_2O_2 is electrically generated from oxygen in aqueous solution with a theoretical amount determined by the following equation:

$$Q = I \times t = 2n \times N_A \times e = 2n \times (6.02 \times 10^{23}) \times (1.60 \times 10^{-19})$$

where Q is total quantity of electricity in coulombs (C); t is reaction time (s) and I is current intensity (A); n is the moles of electrogenerated H_2O_2 (M); N_A is Avogadro's constant (6.02×10^{23} molecules/mole); and e is electron charge (1.60×10^{-19} C).

According the above equation, the theoretical amount of H_2O_2 at different current intensity for the reaction time at 60 min was calculated and the current efficiency of H_2O_2 generation is evaluated as listed in Table 1. It can be seen that the efficiency of H_2O_2 generation on the GF cathode is decreased from 67% to 45% with the increased current intensity from 0.5 mA to 5.0 mA. Since the efficiency was quickly declined from 61% to 45% at the current intensity higher than 3.2 mA, the current intensity of 3.2 mA was employed in the following experiments as a cost-effective condition.

[Table 1]

3.2. Current distribution between two anodes

In this three-electrode photoreactor, two anodes (TiO_2/Ti and Fe) were applied in parallel. While a total current intensity of 3.2 mA was applied on the GF cathode to generate H_2O_2 sufficiently, the division of the current between two anodes was controlled by the external variable resistor. A set of experiments at different ratios of Fe:TiO_2/Ti (3.2:0, 3.1:0.1, 3.0:0.2, 2.6:0.6, and 1.8:1.4) was conducted in aqueous 2,4-DCP solution with an initial concentration of 15 mg L^{-1} under UV-A illumination for 60 min and the experimental results are shown in Fig. 3. The experiments demonstrated that the 2,4-DCP degradation reaction was affected by current distribution between two anodes significantly and the fastest degradation was achieved by nearly 90% at the ratio of 3.1:1.0 (3.1 mA on the Fe anode and 0.1 mA on the TiO_2/Ti anode). These results indicate that a small current on the TiO_2/Ti anode is sufficient to enhance the photocatalytic reaction and also avoid any electro-corrosion of the TiO_2/Ti electrode . On the other hand, a higher current on the Fe anode can release more ferrous ions into the reaction solution to enhance the E-Fenton reaction.

[Fig. 3]

3.3. Interaction of individual reactions

In such a hybrid reaction system, several reactions could contribute to the 2,4-DCP degradation in aqueous solution, including (1) direct photolysis by UV-A illumination, (2) direct electro-chemical oxidation on the TiO_2/Ti anode or Fe anode, (3) PEC reaction and H_2O_2-assisted PEC reaction on the TiO_2/Ti electrode, and (4) E-Fenton reaction and photo-assisted E-Fenton reaction in the solution. Since the photolysis of 2,4-DCP under UV-A irradiation is insignificant due to low adsorption band of below 286 nm by 2,4-DCP [23] and the direct electro-chemical oxidation on both anodes is also weak due to a low current intensity of 3.2 mA only. Comparatively both the H_2O_2-assisted PEC reaction and photo-assisted E-Fenton reaction may play

more important roles. To study the interaction of individual reactions, three experiments were conducted. The first experiment was carried out using two electrodes only (TiO_2/Ti anode and GF cathode). The experiment was performed in the 2,4-DCP solution (initial concentration = 15 mg L^{-1}) under UV-A illumination by applying a weak current at 0.1 mA as a H_2O_2-assisted PEC oxidation reaction. The second experiment was conducted using two electrodes (Fe anode and GF cathode) and a high current at 3.1 mA was applied with and without UV-A illumination as photo-assisted E-Fenton and E-Fenton reactions. The third experiment was conducted using three electrodes together (TiO_2/Ti anode, Fe anode and GF cathode) and a total current intensity of 3.2 mA with a distribution ratio of 3.1:0.1 was applied. The experiment was performed under UV-A illumination to represent an integrative oxidation reaction. All the above experiments with an initial pH 5.8 lasted for 60 min. and the experimental results are compared in Fig. 4.

[Fig. 4]

The experimental results showed that the 32% of 2,4-DCP reduction was achieved by the E-Fenton reaction after 60 min; 45% by the photo-assisted E-Fenton reaction; and 46% by the H_2O_2-assisted TiO_2 PEC reaction. These results confirmed that both the TiO_2 PEC reaction and E-Fenton reaction played significant roles in the 2,4-DCP degradation. These results also confirmed that the 2,4-DCP degradation by E-Fenton reaction was really enhanced by UV-A illumination. Furthermore, much higher percent of 2,4-DCP reduction up to 93% was achieved by the integrative reaction, in which the proper current distribution with the ratio of 3.1:0.1 can well balance both reactions in such a three-electrode reaction system. In such a reaction system, while the existence of H_2O_2 in the solution could enhance the TiO_2 PEC reaction as the H_2O_2-assisted TiO_2 PEC reaction and UV-A illumination could also enhance the E-Fenton reaction as the photo-assisted E-Fenton reaction, where some interactive reactions may occur as well. It has been reported that $Fe(OH)^{2+}$ has an absorption band between 290 and 400 nm and can produce hydroxyl radicals and Fe(II) ions. The

primary reactions in the case of photo–Fenton reaction using the near-UV and even visible light can be given as follows [24]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + HO\bullet$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO\bullet$$

To further compare the rates of 2,4-DCP reduction in the above experiments, all experimental data were fitted by the simple first-order kinetic model, the values of kinetic constant, k, for all reactions were calculated and are presented in Table 2. It can be noted that both constants of H_2O_2-assisted PEC reaction and photo-assisted E-Fenton reaction are 1.01 and 1.11, respectively, while the constant of the integrative reaction is 4.23. These results demonstrated that the H_2O_2-assisted PEC reaction and photo-assisted E-Fenton reaction were two main reactions dominating in such a three-electrode reaction system. However, the rate of integrative reaction was even higher than the sum of H_2O_2-assisted PEC reaction and photo-assisted E-Fenton reaction. It should be indicated that any extra benefits obtained from the combination of photochemical reaction and electrochemical reaction would be more attractive rather than the simple summation only. However, the exact mechanism of individual reactions involved in such a three-electrode reaction system is quite sophisticated and needs to be further explored in the following studies.

[Table 2]

3.4. Effect of pH on 2,4-DCP degradation

Since E-Fenton reaction is a pH-sensitive approach, the effect of pH on 2,4-DCP degradation is studied by conducting three experiments for the H_2O_2-assisted TiO_2 PEC reaction, the E-Fenton reaction, and the integrative reaction, respectively in a wide pH range of 1-9. The reaction at pH 1 was controlled with H_2SO_4-H_3PO_4 buffer solution and the reactions at pH 3-9 are controlled with H_3PO_4-NaH_2PO_4-Na_2HPO_4

buffer solution. The experimental results are shown in Fig. 5.

[Fig. 5]

The first experiment demonstrated that pH had a moderate influence on the H_2O_2-assisted TiO_2 PEC reaction, in which 2,4-DCP degradation was increased with increased pH from 1 to 7 gradually and then decreased beyond pH 7 slightly. The second experiment confirmed that pH had a sharp influence on the E-Fenton reaction with a maximum reaction rate at pH 2.5-3 as a common nature of most Fenton reactions. Furthermore, the third experiment showed that the 2,4-DCP degradation in the integrative reaction was increased quickly at the lower pH range from 1 to 3 and then gradually decreased at the higher pH range from pH 3 to 9. However, the reduction of 2,4-DCP degradation from its maximum value at pH 3 to the lowest value at pH 9 was only 10% difference. From these results, it is believed that the combination of E-Fenton reaction with photocatalytic reaction may gain a benefit to overcome its pH-sensitive character and it becomes less necessary to adjust pH of water and wastewater with a neutral pH condition prior to the treatment.

To further study the pH change during the integrative reaction, one more experiment was conducted without pH control under UV-A illumination for 60 min with an initial 2,4-DCP concentration of 15 mg l^{-1} and initial pH 5.8. The 2,4-DCP concentration and pH were monitored simultaneously during the reaction. The experimental results in Fig. 6 demonstrated that when 2,4-DCP degradation was achieved by more than 90% at 60 min, pH of reaction solution was only slightly decreased from 5.8 to 4.8. Although several factors may affect the pH in the reaction solution, it was confirmed in our previous work that the H_2O_2 generation on the cathode can increase pH by consuming H^+, while the degradation of some organics such as 2,4,6-TCP can decrease pH due to release of acidic intermediate products such as organic acids [25]. Some researchers also reported that degradation of 2,4-DCP produced weak acids by photo-Fenton-like oxidation [26]. This pH neutralization function in the TiO_2/Ti-Fe-GF reaction system might have one more benefit to

maintain pH for any acid-releasing reactions in practical water and wastewater treatment.

[Fig. 6]

3.5. Accumulation of H_2O_2 concentration

The H_2O_2 concentration in the reaction solution plays a critical role, depending on both rates of its generation and consumption. To study the H_2O_2 accumulation in the integrative reaction system, 4 experiments were carried out by applying the same current intensity of 3.2 mA on the GF cathode under different reaction conditions, which included two experiments in aqueous 0.02 M Na_2SO_4 only solution with and without UV-A illumination and other two experiments in aqueous 2,4-DCP + 0.02 M Na_2SO_4 solution with and without UV-A illumination. The experimental results are summarized in Fig. 7. The results demonstrated that the accumulative H_2O_2 concentration in the aqueous 0.02 M Na_2SO_4 only solution were significantly higher than those in the 2,4-DCP+0.02 M Na_2SO_4 solution, due to no H_2O_2 consumption resulted from the reaction with 2,4-DCP. On the other hand, the accumulative H_2O_2 concentration under UV-A illumination built up slightly slower than those without UV-A illumination, due to more H_2O_2 consumption under UV-A illumination.

[Fig. 7]

3.6. Mineralization of 2,4-DCP

To study the 2,4-DCP mineralization in the integrative reaction, DOC at different time intervals was also determined and the experimental results are shown in Fig. 8. The results showed that the degree of 2,4-DCP mineralization in the integrative reaction was higher than both the H_2O_2-assisted-TiO_2 PEC and photo-assisted E-Fenton reactions, significantly. It should be noted that 78% of 2,4-DCP mineralization was achieved by the integrative reaction, which was even higher than 57% as the sum of H_2O_2-assisted-TiO_2 PEC and photo-assisted E-Fenton reactions. Sabhi and Kiwi [23]

carried out a similar photo-assisted E-Fenton reaction and found that mineralization of 2,4-DCP was only 21% after 60 min reaction time when added H_2O_2 concentration was 1.25mM. Similar to the pattern of 2,4-DCP degradation, the experiments further confrimed that some interactive reactions might occur in such a TiO_2/Ti-Fe-GF reaction system beyond the PEC reaction and E-Fenton reaction, which provided extra benefits to develop an efficiency treatment process.

[Fig. 8]

4. Conclusion

In this study, it has been confirmed that 2,4-DCP in aqueous solution is successfully degraded by 93% and mineralized by 78% within 60 min in a hybrid oxidation process by integrating the E-Fenton and photocatalytic reactions. When a current intensity of 3.2 mA was applied on the GF cathode, the current efficiency for H_2O_2 generation was determined to be 61%. Although the E-Fenton reaction is a pH-sensitive process, the experiments demonstrated that combination of E-Fenton reaction with photocatalytic reaction let the process become less pH sensitive and can be applied under a more neutralized pH condition, which would be favorable to water and wastewater treatment in practice.

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429 pathway of 2,4-dichlorophenol transformation by photo-Fenton-like oxidation,
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435 Table 1. Accumulative Amount of H_2O_2 (C_{H2O2}) in Experiments and Theoretical
436 Values at 60 min.

Applied current intensity (mA)	C_{H2O2} (mM)	Theoretical value (mM)	Generation efficiency (%)
0.5	0.125	0.187	67
1.5	0.349	0.56	62
3.2	0.728	1.19	61
5.0	0.836	1.87	45

437

438 Table 2. Kinetic Constant (k_R) for 2,4-DCP Degradation in Aqueous Solution

Reaction system	k_R ($\times 100$ / min^{-1})	R^2	Degradation (%)
Anodic oxidation on TiO_2 electrode	0.04	0.9982	2.9
Anodic oxidation on Fe electrode	0.12	0.9929	6.2
Photolysis under UV-A illumination	0.07	0.9971	3.6
E-Fenton reaction	0.62	0.9378	32
TiO_2 PEC reaction	0.81	0.9825	36
H_2O_2-assisted TiO_2 PEC reaction	1.01	0.9783	45
Photo-assisted E-Fenton reaction	1.11	0.9779	46
Integrative reaction	4.23	0.9956	93

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Fig.1. Sketch of the photo-electro-reaction system.

Fig. 2. Effect of current on H_2O_2 generation (O_2 flow rate = 40 ml min^{-1} nearby GF cathode).

Fig. 3. Effect of current distribution on 2,4-DCP degradation (Anodes: TiO_2/Ti and Fe; cathode: GF; total current intensity = 3.2 mA; O_2 flow rate = 40 ml min^{-1}; initial 2,4-DCP concentration = 15mg l^{-1} under UV-A irradiation).

Fig. 4. 2,4-DCP degradation in aqueous solution by different reactions without pH control

Fig. 5. Effect of pH on 2,4-DCP degradation by different reactions with pH control.

Fig. 6. pH change during 2,4-DCP degradation in aqueous solution by integrative reaction without pH control.

Fig. 7. H_2O_2 accumulation under different experimental conditions without pH control.

Fig. 8. Mineralization of 2,4-DCP in aqueous solution in different reactions.

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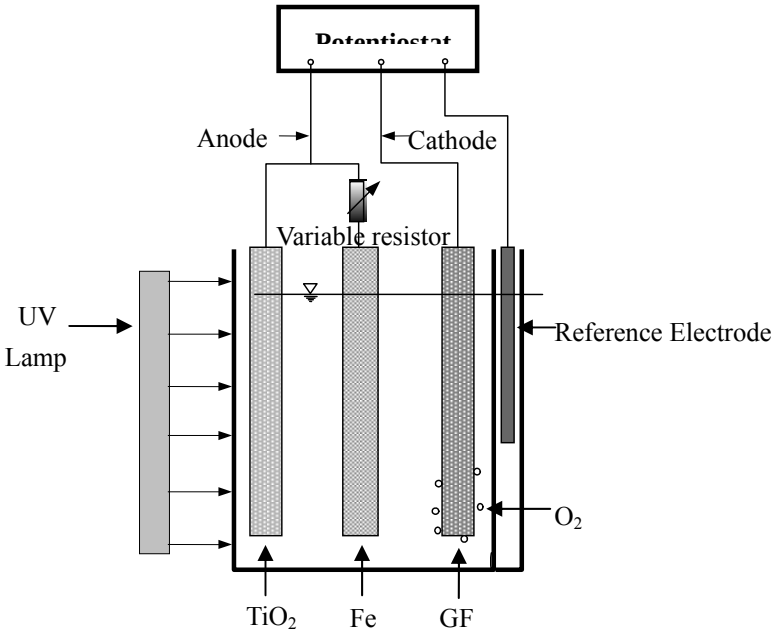

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482 Fig. 1.

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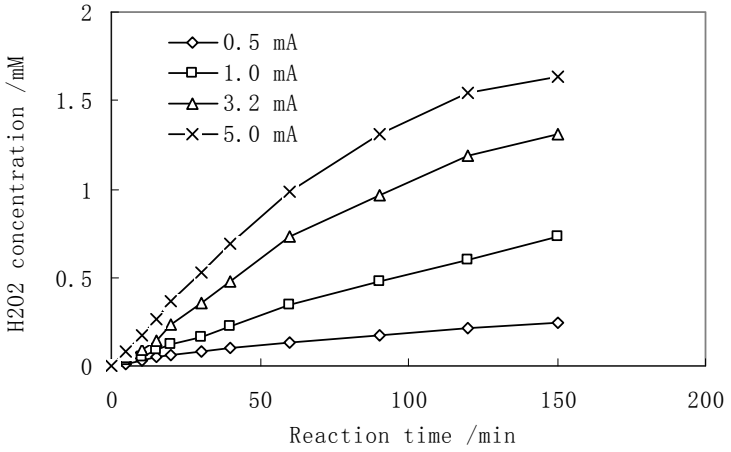

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489 Fig. 2.

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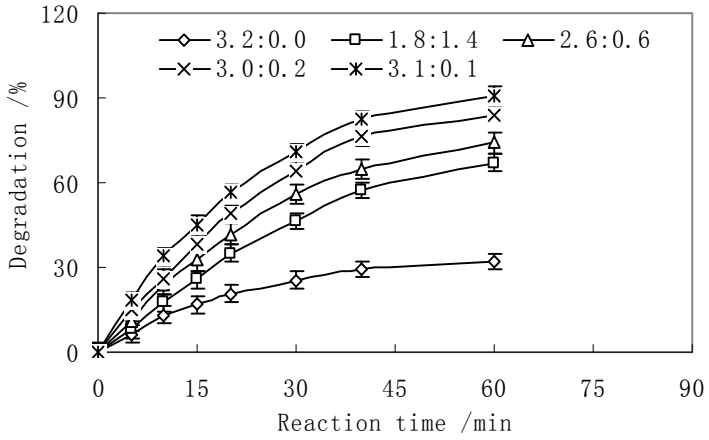

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495 Fig. 3.

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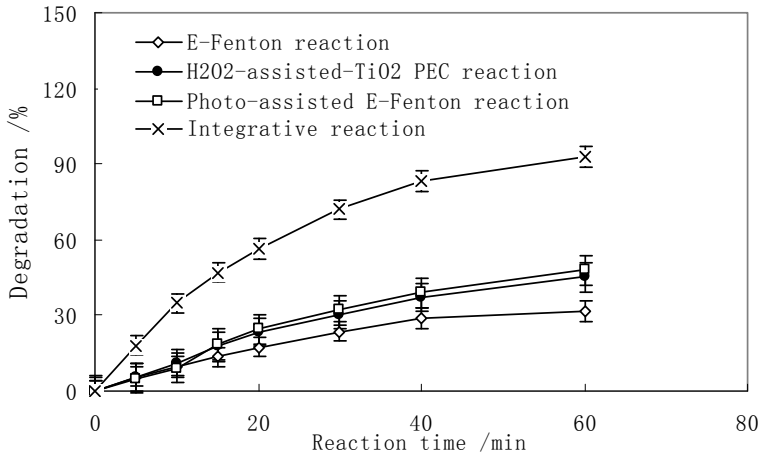

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500 Fig. 4.

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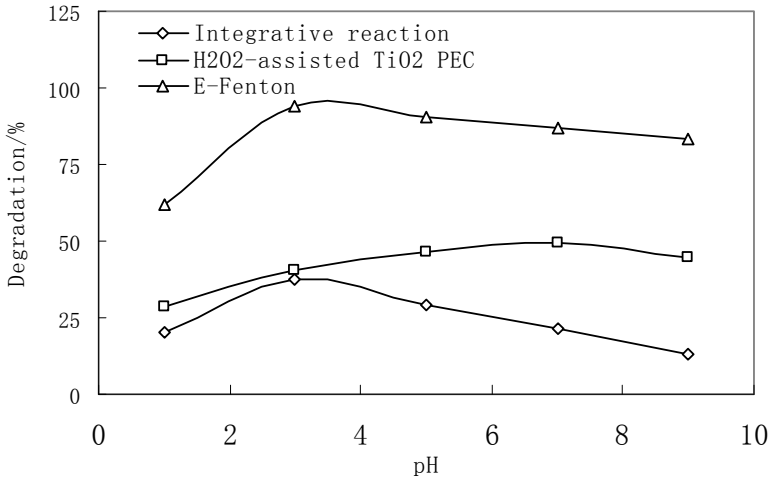

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506 Fig. 5.

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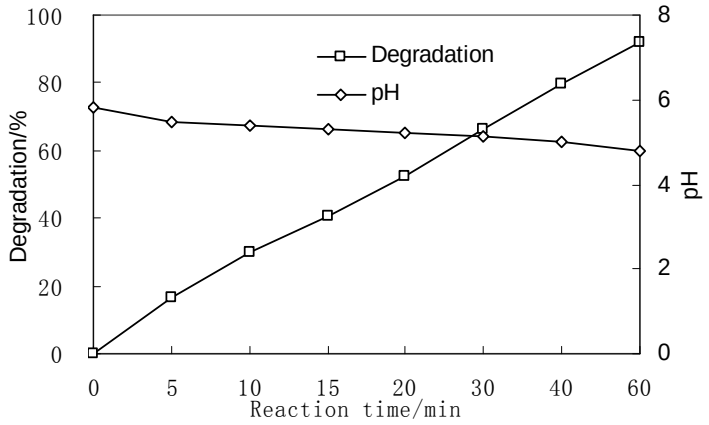

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512 Fig. 6.

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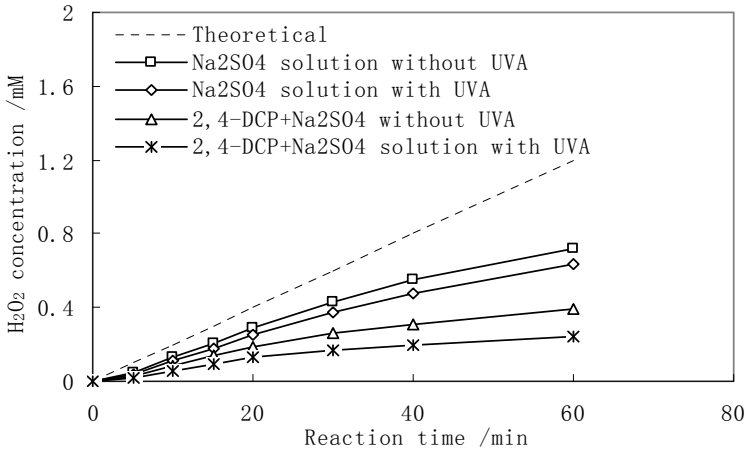

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517 Fig. 7.

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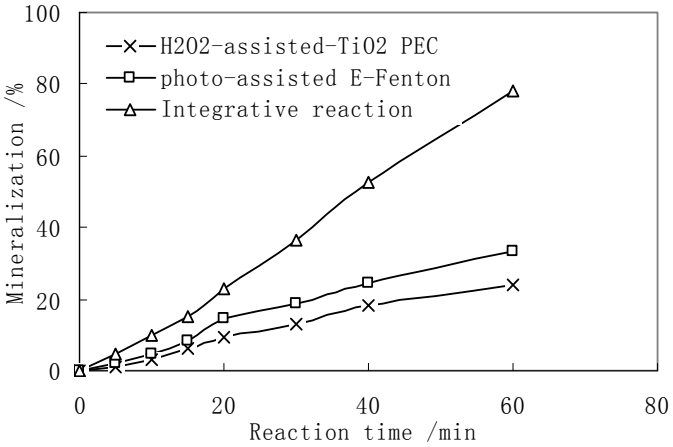

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529 Fig. 8.

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