

Formation of hydrogen peroxide and degradation of phenol in synergistic system of pulsed corona discharge combined with TiO₂ photocatalysis

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Abstract

In the present work, a synergistic system of pulsed corona discharge combined with TiO₂ photocatalysis has been developed to investigate the degradation rate of phenol solutions by varying experimental conditions of gas bubbling varieties (air, O₂, and Ar), solution pH values, and radical scavenger additives. The hydrogen peroxide (H₂O₂) concentration, which indicated the amount of hydroxyl radicals (•OH) in the reaction system under different conditions of gas bubbling varieties and scavenger species, was also reviewed. The obtained results revealed that degradation efficiency of phenol could be increased by the addition of TiO₂ in pulsed discharge system. The gas of Ar and O₂ bubbled into the reaction system was found to be favorable for phenol degradation and H₂O₂ formation. Both in air bubbling and in O₂ bubbling reaction system, the higher degradation rate of phenol occurred in the case of acidic solution. The addition of sodium carbonate or *n*-butanol in the solution displayed a negative effect for phenol removal, while the H₂O₂ concentration showed different changing trend by adding different radical scavengers. The most effective degradation of the three main intermediates of catechol, 1,4-hydroquinone, and 1,4-benzoquinone formed during phenol decomposition existed in the synergistic system of pulsed corona discharge and TiO₂ photocatalysis bubbled with O₂.

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1. Introduction

Electrical discharge technologies have attracted much attention for the degradation of organic compounds in aqueous solutions in the past decades. The corresponding processes reported include contact glow discharge electrolysis (CGDE) [1,2]; dielectric barrier discharges (DBD) [3–5], and pulsed corona discharges (PCD) [6–14]. As a high efficiency method, PCD is an alternative of advanced oxidation processes (AOPs) for removing biorefractory organic compounds in aqueous solutions. With a sharp rising time (a few nanoseconds) and short duration (nano to microseconds), PCD does not require an intense electric field to produce electrical discharge in water [15].

Many studies have been carried out using PCD for oxidizing organic pollutants, such as dyes [6,7], microorganisms [8,9], phenol [10–13], and aniline [14], in water. The needle-plate electrode configuration has often been employed among the used electrode geometries of needle-to-plate, wire-to-plate, or wire-to-cylinder electrode configuration. Furthermore, different discharge modes (streamer, spark, or stream-spark hybrid) occur by varying electrode distance. The major active species involved during the process of removing organic contaminants are hydroxyl radicals (•OH). Besides that, it has been concluded that hydrogen peroxide (H₂O₂), which is mainly formed by the recombination of •OH radicals, can be produced in pulsed corona discharge processes [16], and ozone is also found to be produced when oxygen was bubbled into the pulsed discharge system [6]. These reactive species are all responsible for the removal of organic pollutants in water.

Heterogeneous photocatalysis is also one of promising AOPs for wastewater treatment. As an economic and photosensitive semiconductor material, TiO₂ in anatase crystal form has been extensively used as photocatalyst in heterogeneous photocatal-

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ysis. In the process, a suspension or a supported layer of TiO_2 in polluted solutions can be excited by light of wavelength less than 385 nm, $\bullet\text{OH}$ radicals, which is able to oxidize a great variety of organic pollutants in wastewater following a series of chemical reactions, are then be produced by oxidation of OH^- or H_2O molecules on the surface of TiO_2 [17]. As ultra-violet (UV) is a main physical effect taking place during pulsed corona discharge process, especially in the spark or streamer–spark hybrid discharge modes, so it can also be used as lamp-house to induce the photocatalysis of TiO_2 photocatalyst. Wavelength of the detected UV light produced in pulsed discharge process is 313, 337, and 357 nm, which are all less than 385 nm [18] to excite photocatalysis of TiO_2 catalyst in pulsed corona discharge system. As a result, more $\bullet\text{OH}$ radicals could be produced by the combination of pulsed corona discharge and TiO_2 photocatalysis.

In the study, layer of TiO_2 supported on glasses beads prepared by traditional sol–gel technique was used as photocatalyst in the pulsed discharge system. Phenol, a priority pollutant, was chosen as a target pollutant to evaluate the effect of some operating parameters, such as solution pH values, gas bubbling varieties (air, O_2 , and Ar), and radical scavengers (sodium carbonate and *n*-butanol), on the degradation of phenol in the reaction system of pulsed corona discharge combined with TiO_2 photocatalysis. The amount of $\bullet\text{OH}$ radicals, which were indicated by the corresponding H_2O_2 concentration in reaction system, was investigated synchronously. Moreover, effect of the produced

ozone in the synergistic reaction system for removing phenol was evaluated. The intermediates as well as terminal removal rate of total organic carbon (TOC) of phenol oxidation in pulsed discharge system with TiO_2 and without TiO_2 were also analyzed in the paper.

2. Experimental

2.1. Chemicals and reagents

All chemicals were used as received without further purification. Phenol solutions were prepared by distilled water and the initial concentration was 100 mg/L. The supports for TiO_2 photocatalyst were soda lime glasses beads (5–6 mm diameter). HPLC-grade eluents were used for analytical experiment. Gas was purchased from Zhongyuan (China) gas supplying company.

2.2. Experimental and analytic procedure

The experimental apparatus consisted of a pulsed high-voltage power supply, which is consisted with what was mentioned in our former work [7], and a reactor, as Fig. 1 illustrates. The corona discharge voltage, pulse frequency, and storage capacitance C_p of the system were 0–50 kV adjustable, 0–200 Hz, and 4 nF, respectively. Experiments were carried out in a multi-needle-to-plate electrode geometry reactor. The reac-

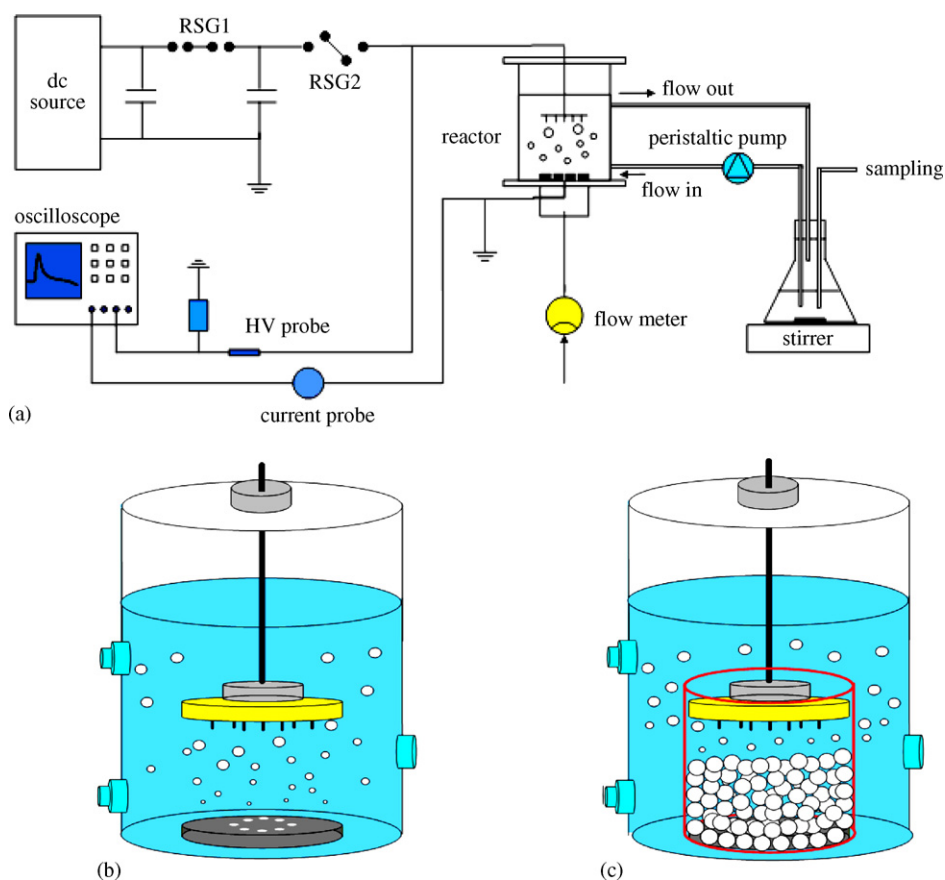


Fig. 1. Schematic representation of the experimental apparatus: (a) reaction system; (b) reactor; (c) reactor with TiO_2 photocatalyst deposited in it.

tor vessel was made from a Plexiglas™ cylinder (75 diameter and 100 mm length). The separation distance d between needle anodes and the plate cathode was 15 mm. The seven-needle stainless-steel anode, comprised of one needle in the center and the other six distributed uniformly around a circle of 7.5 mm radius, was secured within a resin disc. The ground plate electrode consisted of a 40 mm diameter stainless-steel disc (1.5 mm thickness) with eight 0.5 mm diameter finestrans on it. Gas was bubbled into the reactor through the finestrans by pump and the gas bubbling rate was controlled at 5 L/min in all experiments of the study.

In the investigation, the pulse width was less than 5 μ s, the corona discharge voltage was 21 kV, and pulse frequency was adjusted to 50 Hz. A Tektronix P6015A high-voltage probe, a Tektronix P6021 current probe, and a Tektronix TDS2024 digital oscilloscope are used together to monitor the waveforms of pulsed voltage and current in experimental process. Typical voltage and current waveforms from the experimental process with different gas bubbling varieties are shown in Fig. 2.

The traditional sol–gel method was used to prepare the immobilized TiO₂ films photocatalyst. The XRD pattern (not shown in the paper) revealed that the TiO₂ films on glasses beads exhibited anatase structure and the average crystal size calculated was 21.3 nm. As thickness is one of the important factors

influencing photocatalytic activity of TiO₂ films; the TiO₂ films photocatalyst used in the research was prepared by repeating 8 times of dip-withdrawing process. A plastic cylinder (40 mm inner diameter, 60 mm length), which was used as a fence to hold up the photocatalyst, was placed in the reactor. One hundred glasses beads immobilized TiO₂ films photocatalyst was deposited between anode and cathode and also within the plastic cylinder (as Fig. 1(c) shows).

When degradation rate of phenol solution under different experimental conditions was reviewed, the volume of 250 mL phenol solution was circulated through the reactor by a peristaltic pump at a flow rate of 100 mL/min; while the same volume of distilled water was used for determining the total H₂O₂ concentration in every experimental system. Solutions of 0.01 mol/L KCl was employed to adjust solution conductivity. Solutions of 0.1 mmol/L H₂SO₄, 0.4 mmol/L Na₂SO₄, and 0.7 mmol/L NaOH were used to prepare initial solutions of phenol with different pH values. The corresponding solution pH is 3.6, 5.4, and 9.8, respectively. An Orion 828 pH meter was used to determine solution pH. Solution electrical conductivity was measured by a Hanna EC215 electrical conductivity meter. In the paper, the initial electrical conductivity of phenol solutions were all adjusted to 100 μ S/cm, but 200 μ S/cm when sodium carbonate was used as radical scavenger. The initial pH value of 100 mg/L phenol

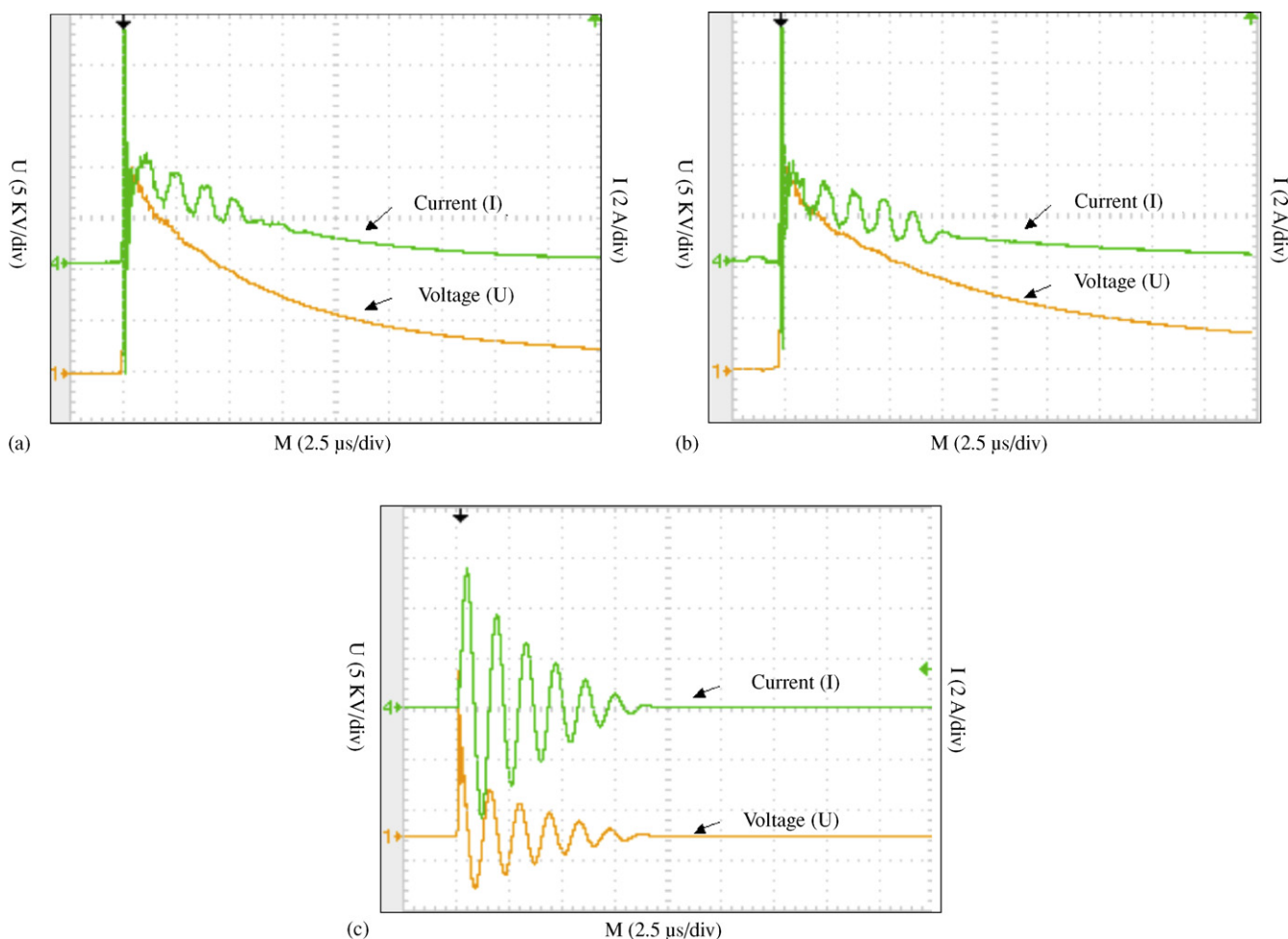


Fig. 2. Typical voltage and current waveforms with different gas addition: (a) air; (b) O₂; (c) Ar.

solution, with 100 $\mu\text{S}/\text{cm}$ solution conductivity was about 7.0. Solution pH was hardly affected by the addition of *n*-butanol with different concentration into experimental solutions. pH values of solutions were about 10.5 by adding sodium carbonate within 0.1–1.0 mmol/L concentration.

Concentration of phenol and its main intermediates formed during phenol oxidation were analyzed by means of high performance liquid chromatography (HPLC: Shimadzu LC-10Avp equipped with an UV-Vis detector and a Shim-pack VP-ODS column). A mixture of methanol:water in the ratio 70:30 at a flow rate of 1.0 mL/min ($\lambda = 280 \text{ nm}$) and 55:45 at 0.5 mL/min flow rate ($\lambda = 277 \text{ nm}$) was used, respectively, to determine phenol decay and main by-products formation. TOC of phenol solution was monitored with a Shimadzu TOC-V_{CPH} total organic carbon analyzer. Ozone concentration in solution was determined by a CX-100II ozone detector (EBARA Corporation). A colorimetric method developed by Ghormley and co-workers [19] was used to measure H_2O_2 concentration in reaction system. The hydrogen peroxide concentration was calculated by the absorbance of I^{3-} measured at 350 nm using a Unico UV-2102C spectrophotometer.

3. Results and discussion

3.1. Effect of gas bubbling varieties in the two discharge system with and without TiO_2

As reported in the literature [20], the amount and the role of different radicals formed in the pulsed corona system were influenced by gas bubbling varieties. Besides $\bullet\text{OH}$, $\bullet\text{O}$, and $\bullet\text{H}$ radicals, other active species, such as ozone might partially answer for the removal of organic compounds in the reaction system. Based on such a conclusion, degradation rate of phenol under the three gas bubbling varieties of air, O_2 , and Ar were investigated (Fig. 3(a)). Furthermore, the synergistic effect of pulsed corona discharge and TiO_2 photocatalysis was reviewed synchronously. H_2O_2 concentration in each experimental condition was also measured (Fig. 3(b)).

Fig. 3 indicates that degradation efficiency of phenol solutions could be increased by adding TiO_2 films photocatalyst in the pulsed discharge system in the case of air and O_2 used as bubbling gas, while the effect of photocatalysis was not obvious when Ar was bubbled into the pulsed discharge system. Degradation rate of phenol could be increased 10.6% and 18.1%, respectively, under the condition of air and O_2 bubbling reaction system. Similarly, same changing trend could be achieved for H_2O_2 formation under different gas bubbling varieties in the two reaction system. Since removal rate of phenol and H_2O_2 concentration was higher in the sole pulsed corona discharge system when Ar was the bubbling gas, photocatalysis of TiO_2 films was more distinct in air and O_2 bubbling system.

On the other hand, the obtained results show that the degradation rate of phenol was close when O_2 and Ar was bubbled into the pulsed corona discharge system combined with TiO_2 photocatalyst, especially after 60 min treatment. However, H_2O_2 concentration in the synergistic reaction system with Ar bubbling was almost double than that with O_2 bubbling after 60 min

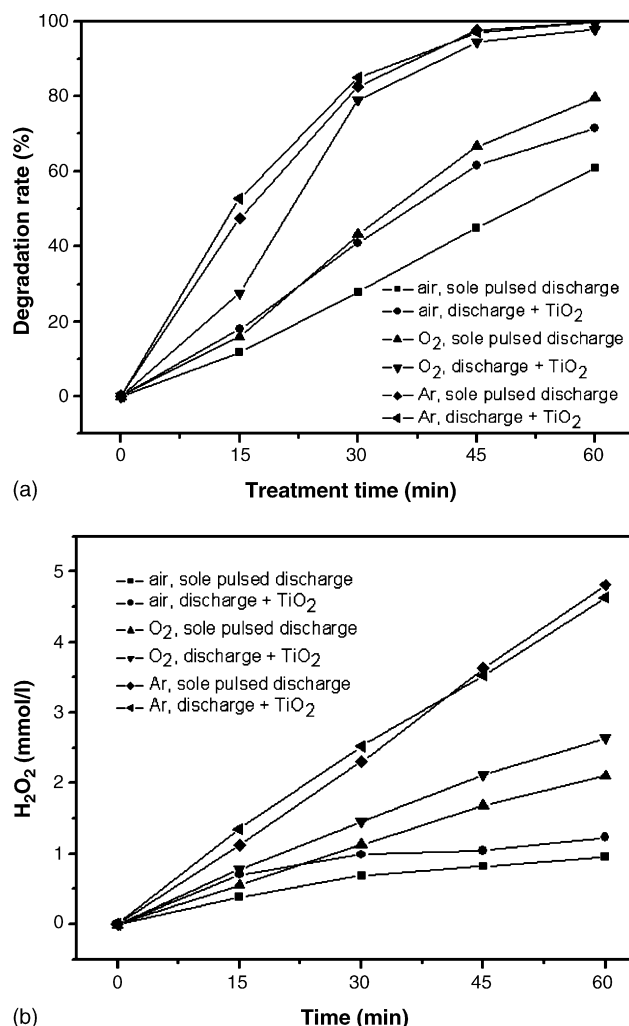


Fig. 3. Effect of gas bubbling varieties on phenol degradation and H_2O_2 formation in two discharge systems with and without TiO_2 (pH \approx 7.0): (a) degradation rate of phenol; (b) H_2O_2 concentration.

discharge. Both degradation rate of phenol and H_2O_2 concentration was lower when air was used as bubbling gas. Such a result might be due to the following reasons: first, the electron collisions are essentially elastic in reaction system with Ar bubbling, which is due to its monatomic structure, more intense discharge can come into being in the reaction region, and the radicals densities is increased accordingly. Thus, degradation rate of phenol and H_2O_2 amount was higher when Ar was bubbled into the discharge system. The strong discharge in the Ar bubbling system could be confirmed from the typical voltage and current waveforms with different bubbling gas shown in Fig. 2. Secondly, when oxygen was bubbled into the reaction system, 0.5 mg/L ozone was detected after 60 min discharge; while there was no detectable amount of ozone produced after the same discharge time in the case of Ar bubbling due to the absence of O_2 in its composition. Therefore, ozone had some responsibilities for the removal of phenol in the reaction system with O_2 bubbling. For the degradation of phenol in air bubbling system, the produced ozone concentration was too little to be detected by the ozone detector on account of relative smaller amount of O_2 in

air, but the formed ozone in the reaction system must be favor for removing phenol in aqueous solutions.

3.2. Effect of solution pH in the synergistic system

As solution pH is one of the most important factors, which influence degradation rate of organic compounds in pulsed corona discharge, heterogeneous photocatalysis as well as ozone oxidation process, effect of solution pH on phenol degradation in the synergistic system of pulsed corona discharge and TiO₂ photocatalysis was studied in our research Fig. 4 illustrates change of degradation rate of phenol with treatment time at different solution pH values (3.6, 5.4, and 9.8) in the case of air bubbling and O₂ bubbling, respectively.

As it is apparent in Fig. 4, the amount of phenol removal was observed higher in the case of the lower solution pH than the other two solution pH values; such a changing trend was more distinct when O₂ was bubbled into the reaction system. At the same time, degradation rate of phenol solution was lower at basic solution under the two gas bubbling condition of air and O₂ bubbling. As carbonates could be generated during the oxidation

processes of organic compounds in aqueous solutions, while it has been concluded that •OH radicals would become unselective and react readily with carbonate ions, which substantially reduce the oxidation efficiency of phenol [21]. This reaction process might partly explain the reason of the above experimental results. On the other hand, research has concluded that basic condition was propitious to organic compounds removal in ozone oxidation processes [22]. However, though ozone could be produced when O₂ was bubbled into the synergistic reaction system, the obvious result of a worse degradation rate of phenol occurred when O₂ used as bubbling gas. For the decomposition of organic compounds by ozone oxidation, different reaction route would take place under dissimilar solution pH values. The direct ozonation pathway would dominate under acidic or neutral solution conditions. But in basic solution, the radical-type chain reaction of ozone would be promoted, which accelerates the transformation of ozone into •OH radicals, hence hydroxyl radical reactions dominate to oxidize contaminants [23]. Equally, with the same explanation for inhibition of •OH radicals in basic solution condition carbonate ions by provided above and a little amount of ozone produced in the reaction system, a lower oxidation efficiency of phenol might exist at a higher solution pH. This reaction process might be another reason to interpret the higher degradation rate of phenol at acidic solution when O₂ was bubbled into reaction system, in which ozone was produced.

3.3. Effect of radical scavengers in the synergistic system

Carbonate ions and *n*-butanol are the suitable •OH scavengers, so their effect on phenol decomposition as well as H₂O₂ formation in the synergistic system of pulsed corona discharge and TiO₂ photocatalysis, as shown in Figs. 5 and 6. Air was used as gas bubbling source.

It is obvious from the figures that the degradation rate of phenol decreased with the increase of additive amount of scavengers. At the same time, the decreasing amount of phenol removal was more notable when sodium carbonate was added into the reaction system. On the other hand, though the degradation rate of phenol was decreased in the case of sodium carbonate used as scavenger, the concentration of H₂O₂ in the reaction system increased but not decreased. On the contrary, in the case of adding *n*-butanol in solution, the formed amount of H₂O₂ decreased as the decrease of removal rate of phenol under the same condition. Such an adverse result might be due to the other formation mechanism of H₂O₂ in solutions. It is well known that H₂O₂ could be formed by the recombination of •OH radicals, but the electrolytic reaction of dissolved O₂ on the negative electrode in alkaline solution would also lead to the formation of H₂O₂. As sodium carbonate is belonging to alkaline electrolyte, hence electrolysis reaction route to form H₂O₂ would take effect in the reaction system. Accordingly, H₂O₂ concentration presented an augment trend with the increase of additive amount of sodium carbonate in solution.

In order to depict the effect of radical scavengers in the synergistic reaction system more particularly, experiments were carried out to review the degradation rate of phenol and corresponding amount of H₂O₂ by adding sodium car-

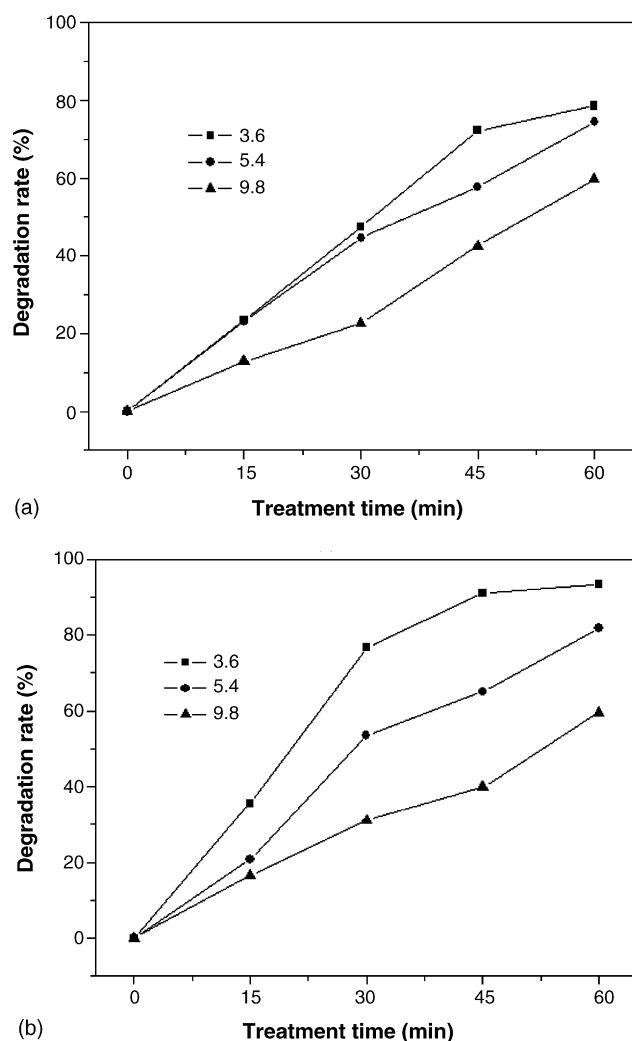
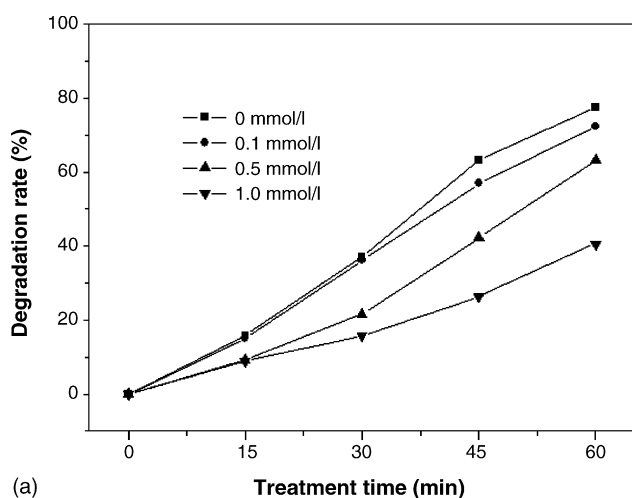
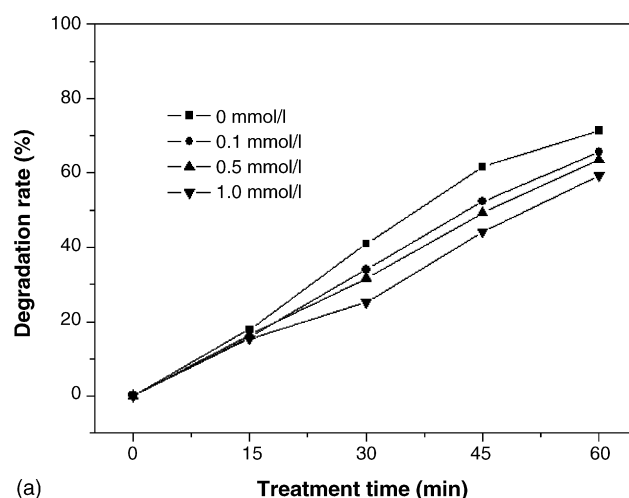


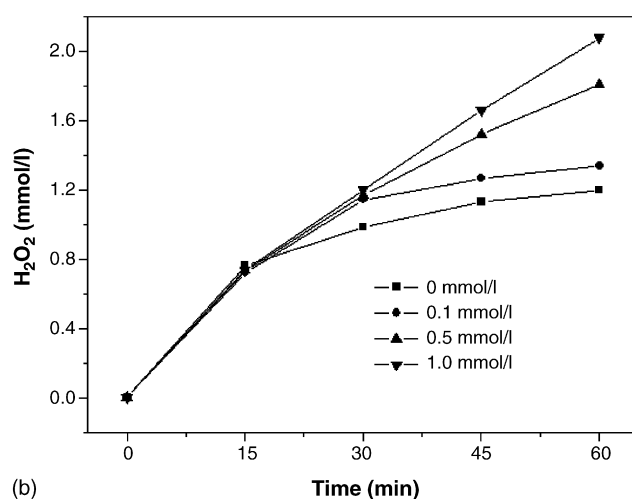
Fig. 4. Effect of solution pH on phenol degradation with different gas bubbling varieties: (a) air; (b) O₂.



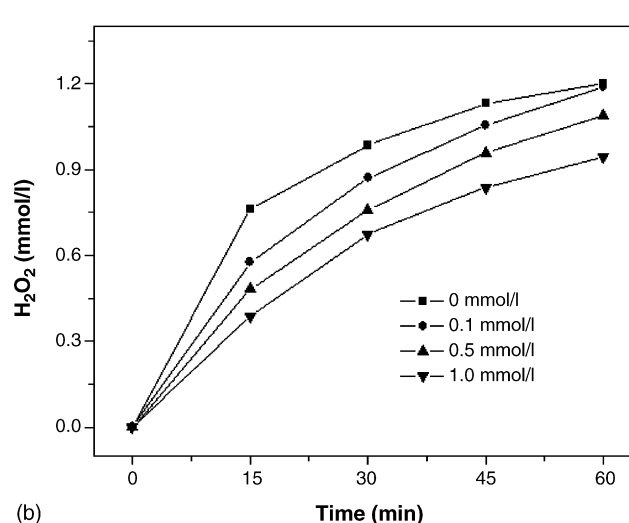
(a)



(a)



(b)



(b)

Fig. 5. Effect of Na_2CO_3 addition on phenol degradation and H_2O_2 formation ($\text{pH} \approx 10.5$): (a) degradation rate of phenol; (b) H_2O_2 concentration.

Fig. 6. Effect of *n*-butanol addition on phenol degradation and H_2O_2 formation ($\text{pH} \approx 7.0$): (a) degradation rate of phenol; (b) H_2O_2 concentration.

bonate and *n*-butanol under the condition of air bubbling and O_2 bubbling. The results are recorded in Table 1. The degradation rate and H_2O_2 concentration showed in the table are values obtained after 60 min treatment in the reaction system.

From Table 1, it can be seen that the degradation rate of phenol decreased both in air bubbling and in O_2 bubbling system by using sodium carbonate as radical scavenger. H_2O_2 concentration was also declined by the addition of sodium

carbonate under the condition of O_2 bubbling, which was different from the changing rule in air bubbling reaction system. Such result might be attributed to the more feasibility to form ozone but not H_2O_2 when O_2 was bubbled into the reaction system. As for adding *n*-butanol in phenol solution, removal of phenol was decreased. H_2O_2 concentration in experimental system was also a little declined under the condition of the addition of *n*-butanol due to the reaction of *n*-butanol with $\cdot\text{OH}$.

Table 1

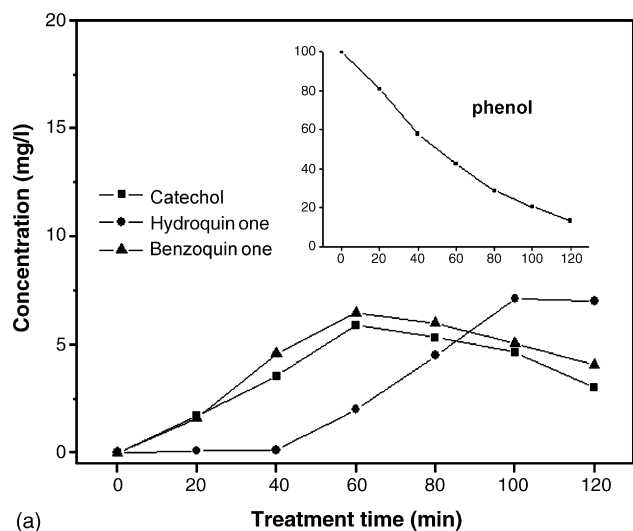
Comparison of phenol degradation and H_2O_2 formation by adding different scavengers under the condition of air and O_2 bubbling

Experimental condition	Solution condition	Degradation rate of phenol solution (%)	H_2O_2 concentration (mmol/L)
Air		77.5	1.20
Air, addition of 0.5 mmol/L Na_2CO_3	200 $\mu\text{S}/\text{cm}$	63.2	1.81
O_2	$\text{pH} \approx 10.5$	98.1	2.61
O_2 , addition of 0.5 mmol/L Na_2CO_3		76.4	2.06
Air		71.4	1.23
Air, addition of 0.5 mmol/L <i>n</i> -butanol	100 $\mu\text{S}/\text{cm}$	63.5	1.08
O_2	$\text{pH} \approx 7$	97.9	2.64
O_2 , addition of 0.5 mmol/L <i>n</i> -butanol		88.6	2.57

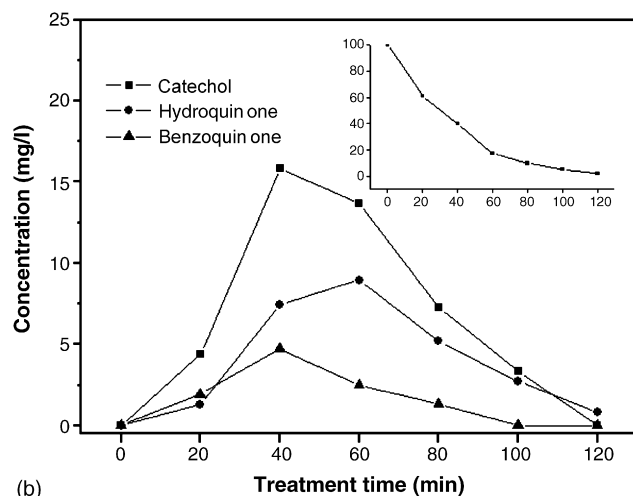
3.4. By-products formation and TOC removal in the two discharge system with and without TiO₂

The major intermediates of phenol degradation and the degradation route have always been paid much attention by many chemists in the past two decades [24–27]. The main intermediates detected in the phenol oxidation were ring compounds and short chain acids. The ring intermediates mainly included catechol, hydroquinone and benzoquinone. For acquiring the synergistic effect of pulsed corona discharge and TiO₂ photocatalysis, the by-products from phenol oxidation in the two discharge system with and without TiO₂ photocatalyst under the condition of air and O₂ bubbling were identified during the 120 min degradation process, as depicted in Fig. 7 (sole pulsed corona discharge system) and Fig. 8 (pulsed corona discharge system combined with TiO₂ photocatalyst). Removal rate of TOC of the 100 mg/L phenol solution after 120 min treatment in each reaction system was also reviewed in the experiment.

Comparing Figs. 7(a) and 8(a), and Figs. 7(b) and 8(b), respectively, it can easily concluded that the maximum amount

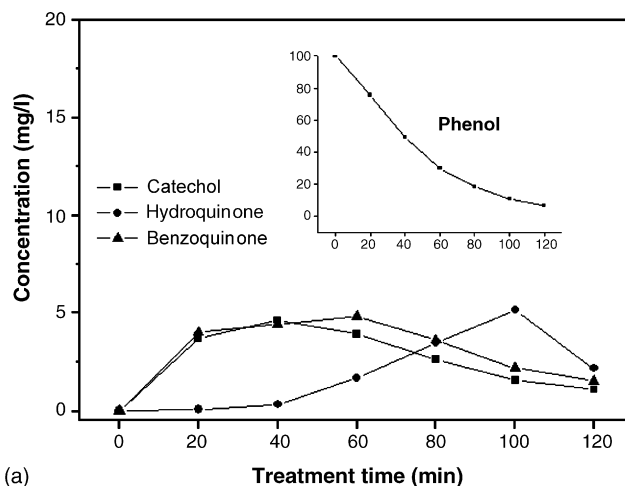


(a)

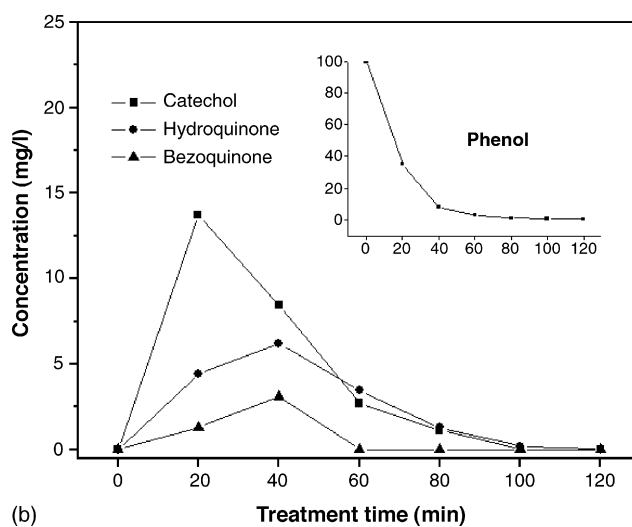


(b)

Fig. 7. Phenol degradation and by-products formation in discharge system without TiO₂ (pH ≈ 7.0): (a) air; (b) O₂.



(a)



(b)

Fig. 8. Phenol degradation and by-products formation in discharge system with TiO₂ (pH ≈ 7.0): (a) air; (b) O₂.

of ring intermediates produced in sole pulsed discharge system was higher than that in the combined system of pulsed discharge and TiO₂ photocatalyst. Such a result indicated that the higher degradation efficiency occurred in the synergistic system. This conclusion could also be confirmed from the increase of removal rate of TOC 2.7% from 26% to 28.7% in air bubbling system, and 10.9% from 55.2% to 66.1% in O₂ bubbling system. Besides that, the amount of intermediates formed in each reaction system all presented descend trend after 120 min treatment.

Considering effect of gas bubbling varieties on by-products formation and TOC removal during phenol degradation in the two pulsed discharge system with and without TiO₂, it is obvious to see by comparing (a) and (b) of Figs. 7 and 8 that thorough degradation of intermediates produced during phenol decomposition was appeared in the reaction system with O₂ bubbling. After 100 min treatment, the three main ring intermediates of catechol, hydroquinone, and benzoquinone formed during phenol degradation was almost out of the synergistic system. The results indicated that higher degradation and mineralization efficiency of phenol in reaction system with O₂ bubbling than that in system with air bubbling. Moreover, the maximum concentration of catechol and 1,4-hydroquinone was higher in O₂ bubbling

system. Therefore, ozone would like to take much responsibility for the higher decomposition of phenol in the reaction system.

4. Conclusions

Mineralization of phenol could be increased in the synergistic system of pulsed corona discharge and TiO₂ photocatalysis. •OH was considered to be the most significant active species for phenol removal in the synergistic reaction system. In the experimental system, gas bubbling varieties, solution pH and radical scavenger additives were all important factors for affecting phenol degradation. When Ar was bubbled into the reaction system, it had highest degradation rate of phenol and H₂O₂ concentration of the three gas bubbling system, which was ascribed to the more intense electric field formed in the reaction system. As more ozone could be formed to react with phenol in the reaction system with O₂ bubbling, the degradation rate of phenol in O₂ bubbling system went near to that in Ar bubbling system, while hydrogen peroxide concentration has much distinguish in the two reaction system. Due to the inhibition of radicals by carbonate ions in the basic solution, the condition of acidic solution would benefit for phenol removal. Sodium carbonate and *n*-butanol could react immediately with •OH, hence the addition of sodium carbonate and *n*-butanol in reaction solution would decrease the removal efficiency of phenol. The higher phenol mineralization (66.1%) achieved when O₂ was bubbled into the synergistic reaction system than in sole pulsed discharge system (55.2%). Furthermore, three main by-products of catechol, 1,4-hydroquinone, and 1,4-benzoquinone formed during phenol oxidation were almost degraded thoroughly in the synergistic system bubbled with O₂.

Acknowledgements

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