



Removal of phenol by activated alumina bed in pulsed high-voltage electric field

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Abstract

A new process for removing the pollutants in aqueous solution-activated alumina bed in pulsed high-voltage electric field was investigated for the removal of phenol under different conditions. The experimental results indicated the increase in removal rate with increasing applied voltage, increasing pH value of the solution, aeration, and adding Fe^{2+} . The removal rate of phenol could reach 72.1% when air aeration flow rate was 1200 ml/min, and 88.2% when 0.05 mmol/L Fe^{2+} was added into the solution under the conditions of applied voltage 25 kV, initial phenol concentration of 5 mg/L, and initial pH value 5.5. The addition of sodium carbonate reduced the phenol removal rate. In the pulsed high-voltage electric field, local discharge occurred at the surface of activated alumina, which promoted phenol degradation in the thin water film. At the same time, the space-time distribution of gas-liquid phases was more uniform and the contact areas of the activated species generated from the discharge and the pollutant molecules were much wider due to the effect of the activated alumina bed. The synthetical effects of the pulsed high-voltage electric field and the activated alumina particles accelerated phenol degradation.

Key words: pulsed high-voltage electric field; hybrid gas-liquid electrical discharge; activated alumina; phenol; Fenton's reaction; water treatment

Introduction

Phenol and its derivatives are widely distributed contaminants in groundwater and surface water, being generated from a number of industrial factories, such as refinery, textiles, pulp and paper, resin and plastics, pharmaceutical, petrochemical, and so on (Viraraghavan, 1998). Data from the National Pollutant Release Inventory indicated that in 2001, there were 47 facilities in Ontario releasing phenol and there was a substantial increase (>22%) in the release of phenol between 1995 and 2001. Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential toxicity to human and aquatic life, creating an oxygen demand in receiving waters, and imparting taste and odor to drinking water with even at parts-per-billion levels. Stringent US Environmental Protection Agency (USEPA) regulations call for lowering phenol content in the wastewater to less than 1 mg/L. Hence, its removal from industrial aqueous effluents is an important practical problem.

Advanced oxidation processes (AOPs) are considered to be promising methods to remove hazardous organic contaminants and kill bacteria in aqueous solution. Among these methods, pulsed high-voltage discharge process arouse many researchers' interest and attention (Joshi

et al., 1995; Sato *et al.*, 1996; Tezuka and Iwasaki, 1998; Chang, 2001). This method injects energy into an aqueous solution or atmosphere around the solution through a plasma channel formed by a high-voltage pulsed discharge between two electrodes. The strong electrical field produces high energetic electrons having energies of 5–20 eV. These electrons collide with the discharge medium (gas molecules or water molecules) unelastically. Through excitation, dissociation, and ionization processes, various chemically active species ($\cdot\text{OH}$, $\cdot\text{H}$, $\cdot\text{O}$, $^1\text{O}_2$, O_2^- , $\text{HO}_2\cdot$, H_2O_2 , O_3 , etc.) are generated (Sun *et al.*, 1997). In addition, depending upon the magnitude of the discharge energy and the character of discharge medium, processes such as thermal oxidation, vacuum UV photolysis, electrohydraulic cavitation, and supercritical oxidation occur (Sun *et al.*, 2000). These physical and chemical processes have a synergistic effect on the degradation of organic compounds and also on sterilization.

Hybrid gas-liquid discharge is an effective discharge mode for removing pollutants in aqueous solution. In this discharge mode, mist should be produced in the discharge region by certain means for increasing the contact areas of plasmas and pollutant molecules. When air, oxygen, or ozone is aerated through the electrodes, it forms hybrid gas-liquid two phases fluid, so simultaneous discharges in the liquid phase and in the gas phase above the liquid surface will take place. And the hybrid reactor may increase hydroxyl radical formation by the discharge at

the gas-liquid interface. In the previous study, it was often filled with pellets padding between the discharge electrodes of the reactor in gas pollution treatment, such as BaTiO₃ (Yamamoto *et al.*, 1996), activated alumina (Zhou and Zhang, 2005), and titanium dioxide (Yang *et al.*, 2004). Due to the effects of these catalysts, the removal efficiency of the deleterious gaseous compounds could be improved. In aqueous pollutants treatment, the addition of the padding into the reactor between the electrodes in hybrid gas-liquid electrical discharge will be effective for the cooperation of the electrical field and the padding, which has not been reported in previous published reports.

The experiment in this study was carried out by applying pulsed high voltage on the electrodes with the addition of activated alumina particles between the electrodes in hybrid gas-liquid electrical discharge mode. Phenol as target organic compound was sprinkled equably on the surface of the particles through a distribution tube, and then flowed along the particles thereby forming a thin layer of water film on the surface of the particles. Gas was aerated from the bottom of the reactor simultaneously. The specific objective of this study was to present the experimental data on the removal efficiency of phenol in hybrid gas-liquid electrical discharge mode with activated alumina particles and to probe the reaction mechanism.

1 Materials and methods

The discharge circuit used in the present study was self-designed and the pulse power supply with a rotating spark-gap switch was used to generate high-voltage pulse. The pulsed power supply parameters were as follows: peak voltage 0–50 kV (adjustable); pulse width 0–400 ns; pulse rise time 0–50 ns; and the repetition rate of pulse 0–250 pps (adjustable). The experimental set up is schematically shown in Fig.1. The reactor is made of plexiglas and the volume is 200 cm³. The plane electrodes are made of stainless steel with certain pointed protuberances on the surface. The separation distance of the electrodes is 20 mm, attached to the reactor wall with the dimension of 100.00 mm×100.00 mm. Phenol solution as the target organic compound was sprinkled equably on the surface of the particles through the distribution tube, and the flow rate was controlled by liquid flowmeter. Gas was aerated from the bottom of the reactor, and the gas flow rate was controlled by gas flowmeter. The experiment was

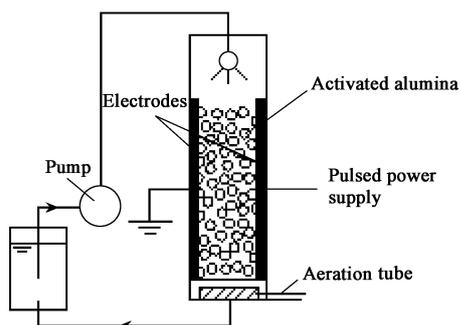


Fig. 1 Schematic diagram of experimental set up.

continuous running circularly for 90 min.

Spectrophotometer (UV-2500, Shimadzu, Japan) was used for measuring the concentration change of phenol. The removal rate (R) is calculated by the following equation:

$$R(\%) = \frac{A_0 - A}{A_0} \times 100\% \quad (1)$$

Where, A_0 is the absorbency of initial solution; A is the absorbency of treated solution. The temporal development of R factor was measured. Samples were analyzed immediately after being removed from the reactor.

The reactor was filled with activated alumina γ -Al₂O₃ particles with sphericity diameter ranging from 2 to 3 mm. The phenol solution was prepared by dissolving analytical grade phenol in distilled water. The solution pH was adjusted by adding a little amount of HCl or NaOH into the solution and was measured using the PHS-3C pH Meter (Shanghai Precision Scientific Instrument Co. Ltd, China). The initial phenol concentration was 5 mg/L in all the experiments and the initial pH of the solution was adjusted at 5.5 except for investigating the effect of the initial pH of the solution on the phenol removal. The flow rate of the phenol solution in reactor was 40 ml/min.

2 Results and discussion

2.1 Effect of applied voltage

As shown in Fig.2, the effect of applied voltage on the phenol removal rate, with increasing applied voltage the removal rate increases. When the initial concentration of phenol is 5 mg/L with pH 5.5, the removal rate can reach 4.0%, 19.5%, 46.33%, and 81.3%, respectively when the applied voltage is 0, 20, 25, and 30 kV.

It is believed that the reaction mechanism of pulsed discharge process may be similar to those in radiolytic processes, such as γ -radiation, electron beam radiation, pulsed radiolysis, and photochemistry process (He *et al.*, 2005), which produce radicals and molecular species (\cdot OH, \cdot H, \cdot O, HO₂ \cdot , H₂O₂, etc.). These radicals and active species attack the contaminant molecules to be treated through excitation, dissociation, and ionization of the medium material with energy injection. In the bulk-phase corona-

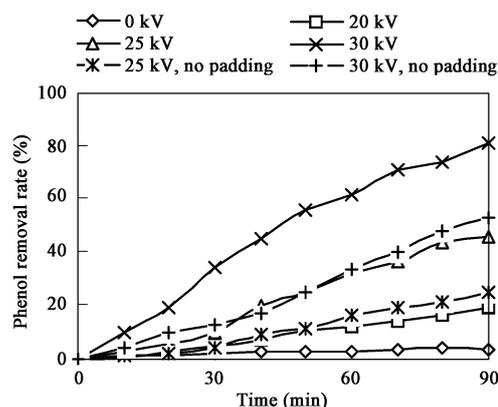
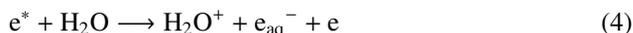
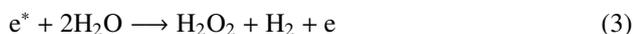


Fig. 2 Effect of applied voltage on the phenol removal rate.

induced chemical reactions, it has been found that the pulsed corona discharge leads to the formation of hydrogen peroxide, hydroxyl radicals, and aqueous electrons, and the high energetic electron e^* transforms to low energetic electron e . The main reactions are assumed to be (Joshi *et al.*, 1995):



Eqs. (2), (3), and (4) are assumed to be initiated by the pulsed streamer corona and will therefore be directly affected by the characteristics of the discharge. From these primary reactions, the propagation reactions can be gained to produce $HO_2\cdot$ radical (Joshi *et al.*, 1995). Under ultraviolet radiation produced from the discharge region, $\cdot OH$ can be obtained by Eq. (5) (Sun *et al.*, 2000).



Due to the thin water film on the surfaces of the particles, discharge will easily take place, and the activated species can oxidize the phenol molecules effectively. Therefore, due to the formation of active species, such as $\cdot OH$, $\cdot H$, $\cdot O$, $HO_2\cdot$ and H_2O_2 in the discharge, the hazardous organic compounds can be removed effectively.

When the gap between the discharge electrodes is unchanged, it is found that with increasing voltage the electric field intensity increases, and then the quantity and energy of the high energetic electrons can be increased, which will lead to more collision opportunities of high energetic electrons with the gas and water molecules. With excitation, dissociation, and ionization of these molecules, more radicals and active species can be produced, and the intensity of UV radiation is enhanced simultaneously (Clements *et al.*, 1987). The synthetical effects of the active species and UV radiation accelerate the degradation of phenol.

The activated alumina particles will be polarized when the pulsed high voltage is applied on the electrodes, and then a strong electrical field will be formed around every particle, which induces the formation of the local discharge (Zhou *et al.*, 2005). So the local strong electrical field is exerted on the thin water film at the surface of activated alumina particles, which makes the contact areas of the plasmas generate from the gas-liquid discharge and the pollutant molecules wider. At the same time, the space-time distribution of discharge will be more uniform due to the activated alumina particles bed. The local corona discharge near the holes of the particles enhances the kinetic energy of the electrons nearby, and then increases the collision frequency with the contamination molecules, which accelerates the degradation of phenol. In addition, the active particles, such as ions, electrons, excited levels of neutral molecules, and metastable radicals in plasmas produced by discharge conduce secondary electrons emission and induce certain chemical reactions on the activated alumina surface. This is when they bombard the particles surface, thereby modifying the particle surface, and

then the activated alumina particles adsorb contaminations more easily.

Accordingly, the synthetical effects between the pulsed electrical field and activated alumina particles accelerate the degradation of phenol and the removal efficiency increases with increasing voltage.

2.2 Effect of initial pH

The effect of pH on the phenol removal rate is shown in Fig.3. With decreasing pH the whole removal rate is reduced.

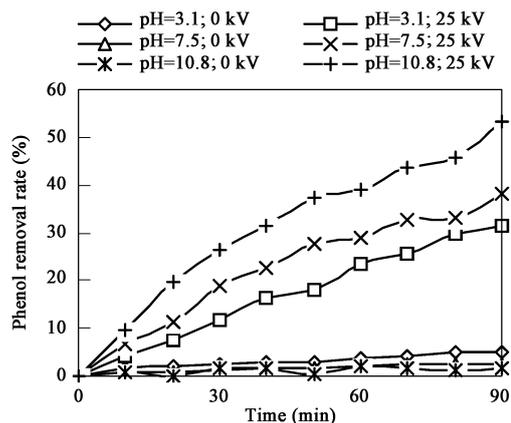
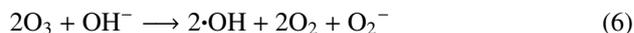


Fig. 3 Effect of pH on the phenol removal rate.

As stated in above paragraphs, ozone could be formed when oxygen existed. Then ozone would transfer into the solution and participate in the degradation of phenol. In the aqueous solution, ozone can also react with water molecules to form hydrogen peroxide, which then decomposes to form hydroxyl radicals. It is well known that the hydroxyl radical plays a crucial role in the removal of pollutants from aqueous solutions which is a very powerful and nonselective oxidant with a high reaction rate constant (10^8 – 10^{11} L/(mol·s)) (Haag and Yao, 1992). At a lower pH, ozone is fairly stable and the direct reaction of ozone is in dominance, which restrains the formation of $\cdot OH$ radical. While at a higher pH, the concentration of OH^- is higher in aqueous solution which catalyzes ozone to decompose rapidly to form $\cdot OH$ (Staehelin and Hoigne, 1982) (Eq. (6)).



Therefore, more $\cdot OH$ radicals are formed at higher pH that explains the higher phenol removal rate. For instance, the removal rate is 31.4%, 38.0%, and 53.3%, respectively under the solution pH 3.1, 7.5, and 10.8 when the initial concentration of phenol is 5 mg/L.

Since the pH changes with time, the variations of solution pH value after discharge at different initial pH and voltage were investigated and the result is shown in Fig.4.

As shown in Fig.4, at the same initial pH with increasing voltage, there is further decrease in pH. This is because the pH value not only affects the redox potential of oxidants, such as H_2O_2 , O_3 , $\cdot OH$, and so on, but also affects the chemical reactions processes. When discharge occurs in

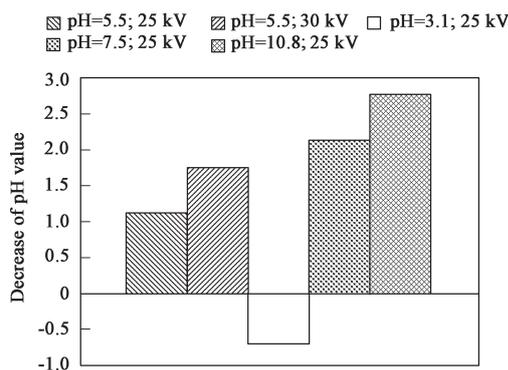


Fig. 4 Decrease in solution pH value after discharge at different initial pH and voltage.

the aqueous solution, the change in pH is due to hydrogen peroxide production, and in the case of the treated phenol solution, other organic acids may be produced. On the other hand, due to N_2 existing in air, certain nitric acid will form in aqueous solution. With increasing voltage, the production of hydrogen peroxide, organic acid, and nitric acid increases, and so there is further pH decrease.

2.3 Effect of air aeration

The effect of air aeration on the removal rate is shown in Fig.5. The removal rate increases with the increase of the air aeration flow rate. For example, under the condition of applied voltage 25 kV, the removal rate is 56.7% and 72.1%, respectively, when the air aeration flow rate is 800 ml/min and 1200 ml/min.

In the case of air aeration, the space-time distribution of gas and liquid is more uniform and stable due to the existing of the activated alumina particles bed. The opposite flow of liquid and gas brings the disturbed flow at the boundary surface of gas-liquid phases, which is beneficial to the mass transfer and diffusion of activated species generated in the discharge region to the water film. In addition, with aeration, enough oxygen is supplied in good time in the reaction region and with the discharge, more ozone is formed which has strong oxidation potential. As stated above, the high energetic electrons produced by the electrical field could collide with the

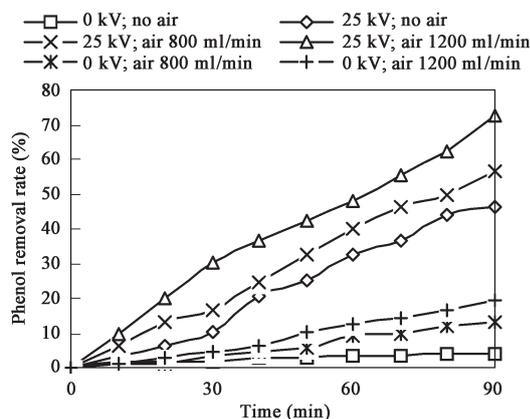
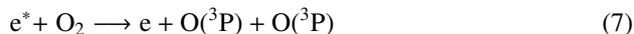


Fig. 5 Effect of air aeration on the phenol removal rate.

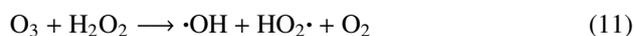
oxygen molecules to form ozone through reaction 7–9 (M serves as a third particle, representing any other gas molecules in the discharge region) (Miichi *et al.*, 2000).



Furthermore, $\cdot OH$ radical formation is more effective through the reaction of atomic oxygen (which is generated by collision reaction of electrons with O_2 in the above-mentioned reactions) with water molecule (Eq. (10)) (Miichi *et al.*, 2000).



Additionally, in the aqueous solution, ozone can react with H_2O_2 produced in the discharge course to form $HO_2\cdot$ and $\cdot OH$, which accelerate the phenol degradation (Eqs (11) and (12)) (Wen *et al.*, 2002).



With increasing air aeration flow rate, the O_2 content in the discharge region increases, so more ozone and $\cdot OH$ radical can form to oxidize the pollutants, which promotes the degradation of phenol. In addition, with air aeration in the electric field, more radicals can be produced through the excitation, dissociation, and ionization processes of other molecules, such as N_2 . The N_2 molecule decomposes to atomic N or excited state N_2 and a small quantity of N_2^+ or N^+ (Zhu *et al.*, 2005). These activated species can also take part in the phenol degradation course.

On the other hand, as shown in Fig.5, the process of air aeration also affects the removal rate of phenol under the conditions that no voltage is applied, airflow rate is 800 and 1200 ml/min, and the removal rate is 13.12% and 19.48%, respectively. The reason may be that during the aeration process, certain parts of phenol may volatilize. Otherwise, due to the air aeration, the particles in the padding bed are disturbed, which leads to the formation of more space between the particles. So the adsorption areas of the particles enlarge, and more phenol will be absorbed on the surface of the particles, which increases the phenol removal rate.

2.4 Effect of radical scavenger

During the discharge course, hydroxyl can be produced which is a very powerful and nonselective oxidant that has the redox potential of 2.80 V. It reacts with the organic pollutants with a high reaction rate constant. Carbonate is a typical buffer, and the anion of which is well known as a radical scavenger. The effect of radical scavenger sodium carbonate on the phenol removal rate is shown in Fig.6.

As shown in Fig.6, due to the effect of sodium carbonate in the solution in the pulsed high-voltage discharge course, the phenol removal rate reduces dramatically. Carbonate is a radical scavenger, and it can react with $\cdot OH$ rapidly to form certain non active products and terminate the whole

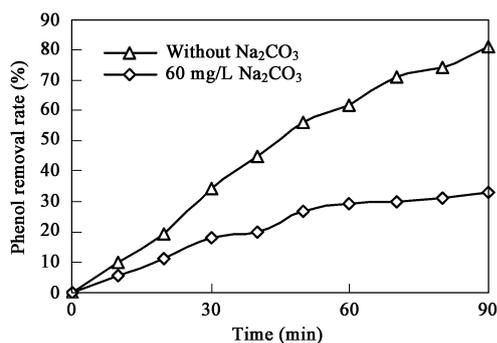


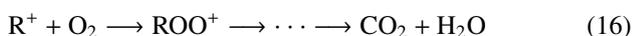
Fig. 6 Effect of radical scavenger on the phenol removal rate (applied voltage 30 kV).

radicals reaction course. The decrease of $\cdot\text{OH}$ leads to the reduction of the phenol removal rate, which indicates that $\cdot\text{OH}$ produced in the discharge plays a crucial role in the phenol degradation course.

2.5 Effect of Fe^{2+}

For achieving more phenol removal, the effect of Fe^{2+} addition into the solution was investigated. As shown in Fig. 7, the removal rate increases with the addition of Fe^{2+} . It can receive 88.2% of removal rate when Fe^{2+} is 0.05 mmol/L.

The increased removal of phenol in the presence of ferrous iron is due to the well-known Fenton's reaction whereby hydrogen peroxide which is formed in the discharge course reacts with ferrous iron to produce hydroxyl radical. $\cdot\text{OH}$ then attacks organic pollutant molecules which causes the radical chain induction, propagation, and termination reactions. These reactions cause the carbon chain in the organic pollutant structure to rupture, and finally result in yielding CO_2 , H_2O , and other inorganic substances (Eqs. (13)–(16)) (Grymonpré *et al.*, 2001).



On the other hand, Fe^{2+} will turn into a $\cdot\text{OH}$ scavenger with increasing concentration, and $\cdot\text{OH}$ will be consumed partially, which decreases the phenol removal rate (Eq.

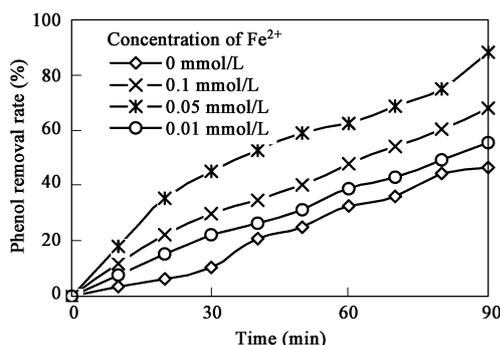
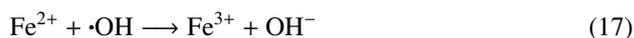


Fig. 7 Effect of Fe^{2+} on phenol removal rate (applied voltage 25 kV).

(17)) (Neyens and Baeyens, 2003).



Otherwise, the solution conductivity will increase when the Fe^{2+} concentration increases, which decreases the formation of the activated species, such as H_2O_2 , and so the phenol removal rate is reduced. At higher Fe^{2+} concentration, the ferrous salt will flocculate, which will cut down the Fe^{2+} amount to react with H_2O_2 . Consequently, the phenol removal rate increases first and then decreases with increasing Fe^{2+} concentration. During the reaction course, part of Fe^{2+} will be oxidized to Fe^{3+} and form $\text{Fe}(\text{OH})_3$, which will deposit on the surface of activated alumina particles. Therefore, the Fe^{2+} quantity reduces in the solution so as to reduce the phenol removal rate.

2.6 Analysis of the phenol degradation course

The hybrid gas-liquid electrical discharge on the surface of activated alumina can induce the large-scale radical chain reactions in the thin water film. The reactants produced in the discharge region with high oxidation potentials, such as $\cdot\text{OH}$, $\cdot\text{O}$, O_3 , and H_2O_2 , are the most effective for oxidizing organic pollutants, in which the most powerful oxidant species are the hydroxyl radicals followed by atomic oxygen and ozone. These produced radicals can attack the pollutants and accelerate its degradation.

Treated sample solutions were analyzed and benzoquinone could be detected in the products. It was also found that pH decreased gradually with the reaction holding on, which predicted that certain acidic products were formed in the reaction system. In addition, the TOC content decreased with increasing reaction time, which explained that phenol was mineralized partially. The decomposition pathway assumed for the degradation process of phenol is shown in Fig. 8. The main intermediate products are pyrocatechol, hydroquinone, resorcinol, benzoquinone, and certain other unidentified products. Phenol and intermediate products will be removed if the discharge time is long enough, then CO_2 and H_2O can be gained.

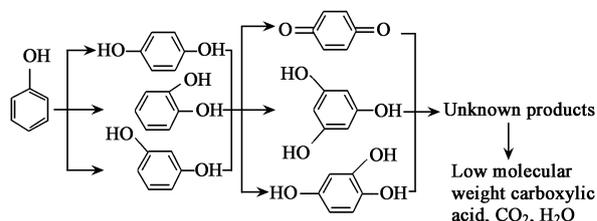
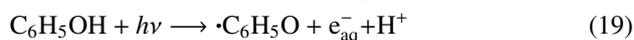


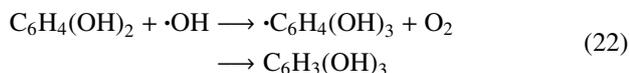
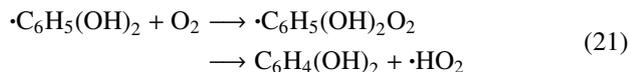
Fig. 8 Decomposition pathway assumed for the degradation process of phenol.

The main reactions of phenol with the oxidants can be summarized as follows:



In the presence of oxygen, $\cdot\text{C}_6\text{H}_5(\text{OH})_2$ also reacts easily

with oxygen to form $\cdot\text{C}_6\text{H}_5(\text{OH})_2\text{O}_2$, then decays to form $\text{C}_6\text{H}_4(\text{OH})_2$ and sequentially form $\text{C}_6\text{H}_3(\text{OH})_3$.



Molecular ozone selectively reacts with contaminants through cycloaddition and electrophilic reactions with unsaturated aromatic and aliphatic species. In the oxidation process of phenol by molecular ozone, it has been proposed that electrophilic attack by ozone leads to formation of hydroxylated products, catechol, and hydroquinone, which are the major intermediates (Sun *et al.*, 1999).



Phenol and its intermediate products pyrocatechol, hydroquinone, resorcinol, and benzoquinone are toxic. The toxicity of phenols depends on the type and positions of the substituents in the aromatic ring. The toxic effect of phenols and their derivatives is directly related to the formation of free radicals, known as semiquinone, in the reaction of oxidation and reduction. The fundamental precursors of semiquinones are quinones, catechols, and catecholamines. It is known that in physiological conditions, semiquinone radicals quickly react with oxygen generating superoxide anion radicals being precursors of other toxic species of oxygen. Phenols, undergoing biotransformation to catechols, can be precursors of semiquinone. The toxicity of catechol is manifested during the formation of semiquinones and their effect on the spatial structure of proteins, while no changes in lipids have been reported (Bozena and Sylwiak, 2003). Since the intermediate products are toxic, and with the discharge going on, the aromatic ring can be opened and the toxicity can be dramatically decreased.

3 Conclusions

A new process for removing the pollutants in aqueous solution-activated alumina bed in pulsed high-voltage electric field was investigated for the removal of phenol. The phenol removal rate increased with increasing applied voltage, increasing pH value of the solution, air aeration, and adding Fe^{2+} . The addition of sodium carbonate reduced the phenol removal rate because it was a radical scavenger. The additive of Fe^{2+} could promote the phenol degradation mainly due to the formation of $\cdot\text{OH}$. With the discharge progressing, phenol could be mineralized to form CO_2 and H_2O . In the pulsed high-voltage electric field, the activated alumina particles could be polarized when the pulsed high voltage was applied on the electrodes, which induced the formation of the local discharge and increased the phenol removal in the thin water film. At the same time, the space-time distribution of gas-liquid phases was more uniform and stable and the contact areas of activated species generated from the discharge and the

pollutant molecules were much wider due to the effect of the activated alumina bed. The contrary flow of liquid and gas brought the disturbed flow at the boundary surface of gas-liquid phases, which was beneficial to the mass transfer and diffusion of activated particles generated in the discharge region to the water film.

Although this method needs some energy consumption, its advantage is obvious. It can produce many active species, such as $\cdot\text{OH}$, O_3 , H_2O_2 , and so on synchronously, which has high oxidation potential and can oxidize organic pollutions effectively. And it can be used for the water deep oxidation for drinking at lower concentration. The microorganisms' degradation method is limited for the lower nutrient concentration. But the reaction system should be studied continuously and optimized for obtaining higher energy efficiency.

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