



Unusual catalytic effects of iron salts on phenol degradation by glow discharge plasma in aqueous solution

Lei Wang, Xuanzhen Jiang*

Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China

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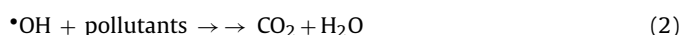
ABSTRACT

Catalytic effects of iron salts on phenol degradation induced by glow discharge plasma (GDP) were examined. It was found that ferric ions showed much better catalytic effect than that of ferrous ions. The reason was that GDP could produce hydroxyl radicals and hydrogen peroxide simultaneously; the hydroxyl radicals reacted with phenol to produce dihydroxycyclohexadienyl radicals which reduced the ferric ions to ferrous ions and the newly formed ferrous ions catalyzed the hydrogen peroxide to produce more hydroxyl radicals. Without iron salts, TOC of the solution gradually decreased with treatment time while COD of the solution increased due to the accumulation of the hydrogen peroxide. Without iron salts, catechol, hydroquinone, and hydroxyhydroquinone were major by-products. However, large amounts of catechol, hydroquinone and benzoquinone yielded in the presence of iron salts. The present study presents some new information related to Fenton's reaction.

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1. Introduction

Recently, various kinds of electrical processes are being developed to remove organic pollutants from water [1]. Glow discharge plasma (GDP) is a novel electrical process where the plasma is generated between a pointed electrode and an electrolytic solution in contact with it. It is called glow discharge because the critical voltage for the full discharge is 420V (invariant of the electrolyte's composition, concentration, temperature and surface tension) [2,3], which is close to the cathode-fall of glow discharge with water cathode [2]. Recently, GDP has shown to be efficient in the destruction of aqueous organic pollutants [4–8]. However, more recent studies indicated that a lot of H₂O₂ was formed in the course of pollutants removal [5]. As we know, water to be discharged should not contain too much H₂O₂ because it is hazardous for human and aquatic lives. The most desirable way is to add Fe²⁺ to convert the H₂O₂ to reactive hydroxyl radicals to enhance the pollutants removal through Fenton's reaction [9–11]:



Up to present, Fenton's reaction in GDP has not been systematically studied although some catalytic effects of Fe²⁺ were observed [5–8]. Therefore, the effects of iron salts on phenol removal were the focus of the present study.

2. Experimental

The experimental apparatus consisted of a dc high-voltage power supply and a reactor. The reactor is shown in Fig. 1. The reactor was made of Pyrex glass, with inner diameter of 7.0 cm and height of 17.0 cm. The anode was a pointed platinum wire ($\Phi = 0.6$ mm) sealed into a glass tube. The cathode was a stainless steel plate (area: 2.0 cm²) placed in another glass tube and separated from the anodic compartment by a glass frit of medium porosity. The reaction vessel was coated by a water jacket, where the solution was maintained at 298 ± 2 K by circulating water. Phenol was dissolved in a sodium sulfate solution (conductivity: 6.4 mS cm⁻¹, the initial pH was adjusted to the expected value by dilute sulfuric acid), and a 150 mL portion of it was poured into the reaction vessel for treatment. A dc voltage of 500 V was applied across electrodes to initiate the treatment. Depth of anode immersed in the solution (about 1.2 mm) was manually adjusted to average the current to 100 mA, with the current deviation less than ±4%.

During the treatment, the solution was magnetically stirred and a small portion was withdrawn for HPLC (Agilent 1100) analysis, where a Lichrospher C₁₈ reversed-phase column (Hanbon Sci. &

* Corresponding author. Tel.: +86 571 87951611; fax: +86 571 87951611.
E-mail address: chejiang@zju.edu.cn (X. Jiang).

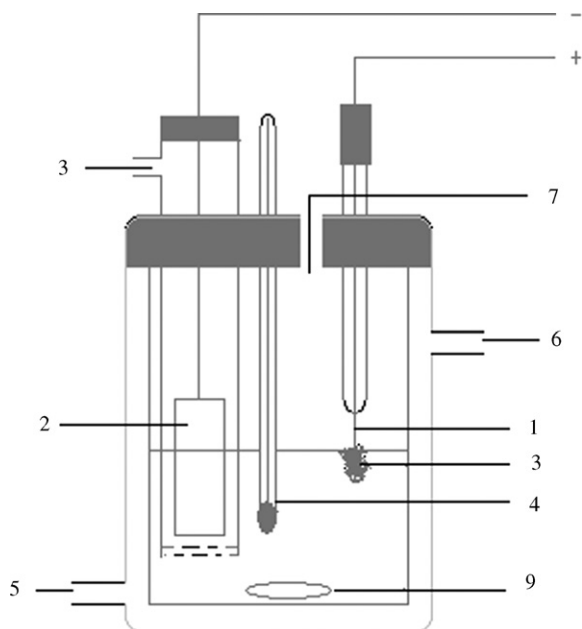


Fig. 1. Schematic of GDP reactor: (1) anode; (2) cathode; (3) glow discharge; (4) thermometer; (5) cooling water in; (6) cooling water out; (7) gas outlet and sampling port; (8) gas outlet for cathode compartment; (9) stirrer.

Tech.) and mobile phase of CH_3CN plus H_2O (40:60) were used at a flow rate of 0.8 mL/min. The detecting wavelength was 254 nm.

H_2O_2 formed in the solution was determined colorimetrically using the reaction of H_2O_2 with titanil ions giving yellow-colored

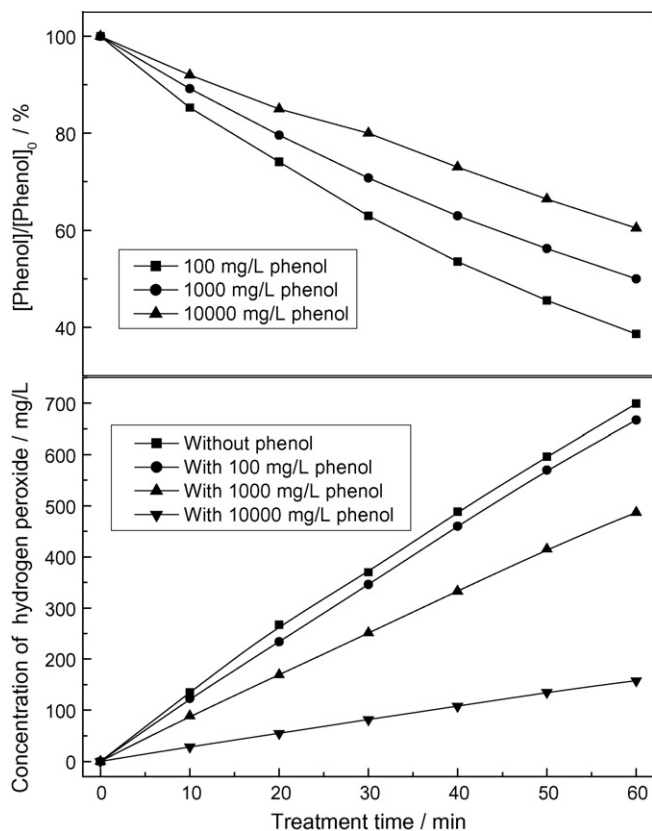


Fig. 2. Phenol removal and H_2O_2 formation during GDP treatment (voltage, 500 V; current, 100 mA; initial conductivity, 6.4 mS cm^{-1} ; initial pH, 6.5).

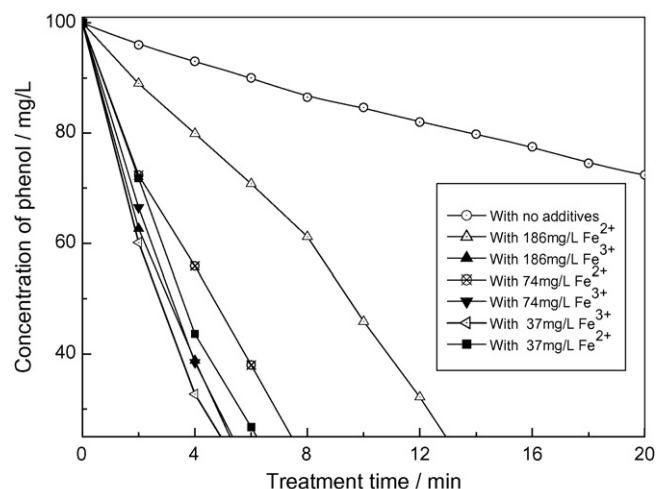
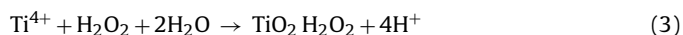


Fig. 3. Catalytic effects of iron salts on phenol removal (voltage, 500 V; current, 100 mA; initial conductivity, 6.4 mS cm^{-1} ; initial pH, 3.0).

complex of pertitanic acid [12]:



A 1.00 mL of the solution and 2.0 mL of titanium sulfate (12 g/L in 40% sulfuric acid) were mixed together and diluted to 10.00 mL with distilled water in a volumetric flask. The absorbance of the mixture was measured at 410 nm with a 5-mm colorimetric cuvette, where the concentration of H_2O_2 was calibrated with known standard stock H_2O_2 .

The concentration of Fe^{2+} was determined by a colorimetric method where 1,10-phenanthroline was used as the color reagent [13]. A 1.00 mL of sample, 1.0 mL of 0.4% 1,10-phenanthroline and 1.0 mL sodium acetate buffer (1 M, pH 4.75) were mixed together and 10 min later the absorbance of the resulting mixture was measured at 508 nm ($\epsilon = 1.12 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Total organic carbon (TOC) of the treated solution was determined by a TOC analyzer (TOC-V_{CSH}, Shimadzu) and the chemical oxygen demand (COD) was determined by a dichromate method.

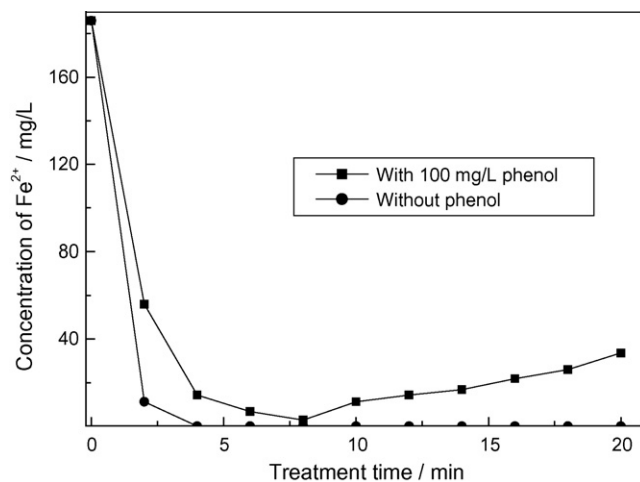


Fig. 4. Variation of Fe^{2+} concentration when 186 mg/L Fe^{2+} ions were initially added to the solution for GDP treatment (voltage, 500 V; current, 100 mA; volume of solution, 150 mL; initial conductivity, 6.4 mS cm^{-1} ; initial pH, 3.0).

Table 1
Energy efficiencies of phenol decomposition and H₂O₂ formation during GDP treatment (voltage, 500 V; current, 100 mA; volume of solution, 150 mL; initial conductivity, 6.4 mS cm⁻¹)

| C ₀ (mg/L) | Fe ²⁺ added (mg/L) | Fe ³⁺ added (mg/L) | G _{phenol} (nmol/J) | G _{H₂O₂} (nmol/J) |
|-----------------------|-------------------------------|-------------------------------|------------------------------|--|
| 0 | 0 | 0 | | 19.6 |
| 100 | 0 | 0 | 0.60 | 16.9 |
| 100 | 18.7 | 0 | 6.6 | 1.7 |
| 100 | 0 | 18.7 | 8.4 | 0.0 |
| 100 | 37 | 0 | 7.4 | 0.0 |
| 100 | 0 | 37 | 9.5 | 0.0 |
| 100 | 74 | 0 | 5.7 | 3.5 |
| 100 | 0 | 74 | 8.6 | 0.0 |
| 1,000 | 0 | 0 | 4.4 | 12.5 |
| 10,000 | 0 | 0 | 29.4 | 3.9 |

3. Results and discussion

3.1. Phenol removal and H₂O₂ formation during GDP treatment

Fig. 2 shows the phenol removal and H₂O₂ formation in the solution during GDP treatment.

As shown in Fig. 2, the concentration of H₂O₂ in the solution almost increased linearly with the treatment time under certain phenol concentration; the formation rate of H₂O₂ decreased with the increase in phenol concentration. The formation rate of H₂O₂ was about 13.3 mg/(L min) without phenol, 11.5 mg/(L min) with 100 mg/L phenol, 8.5 mg/(L min) with 1000 mg/L phenol, and 2.7 mg/(L min) with 10,000 mg/L phenol.

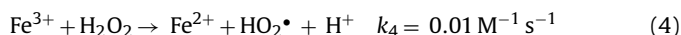
It is noted that the initial pH did not show appreciable effect on phenol removal and H₂O₂ formation (not shown). The above experimental results clearly indicated that a lot of H₂O₂ was formed even the phenol concentration was very high.

3.2. Phenol removal in the presence of iron salts

As shown in Fig. 2, there was a large quantity of H₂O₂ formed in addition to phenol removal during GDP treatment. Therefore, it is desirable to add Fe²⁺ ions to increase phenol removal through Fenton's reaction (Eq. (1)). Here, Fe²⁺ and Fe³⁺ ions were both under investigation and the experimental results are shown in Fig. 3.

It can be observed from Fig. 3 that both Fe²⁺ and Fe³⁺ ions showed remarkable catalytic effects on phenol removal; the catalytic activity of Fe³⁺ ions was much higher than observed from Fe²⁺ ions when their concentrations were high; the differences in catalytic behavior between Fe³⁺ and Fe²⁺ ions became less when their concentrations were low (the catalytic action of Fe³⁺ is still better). For example, the phenol removal was about 15% and increased to 55% in the presence of 186 mg/L Fe²⁺ within 10 min. However, the phenol removal reached 90% within the same time in the presence of 186 mg/L Fe³⁺. On the other hand, the phenol removal was 84% for Fe³⁺ and 75% for Fe²⁺ after 6 min of treatment when their concentrations were both at 37 mg/L. When the concentration of Fe²⁺ or Fe³⁺ was lower than 37 mg/L, the phenol depletion rate decreased (cf. Table 1).

The above results are not consistent with the mechanism of Fenton's reaction since rate constant of H₂O₂/Fe³⁺ is almost four orders of magnitude smaller than H₂O₂/Fe²⁺ (Eq. (4) and cf. Eq. (1)):



In order to better understand the mechanism, variation of Fe²⁺ ion concentration in the presence or absence of phenol where Fe²⁺ ions were initially added to the solution is shown in Fig. 4.

It can be seen from Fig. 4 that, without phenol, the concentration of Fe²⁺ ions dropped to zero within 4 min of treatment, indicating that the Fe²⁺ ions were oxidized by the oxidative species from GDP

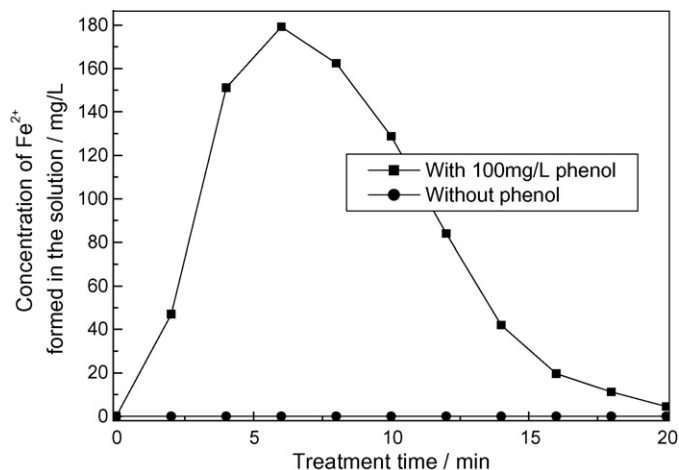


Fig. 5. Fe²⁺ formation during GDP treatment when 186 mg/L Fe³⁺ ions were initially added to the solution (voltage, 500 V; current, 100 mA; volume of solution, 150 mL; initial conductivity, 6.4 mS cm⁻¹; initial pH, 3.0).

[2]. On the other hand, the ferrous ion concentration dropped to about 3 mg/L within the first 8 min, and thereafter increased slowly, implying that the ferrous ions were regenerated.

The formation of Fe²⁺ ions when Fe³⁺ ions were initially added to the solution is shown in Fig. 5.

From Fig. 5, it can be observed that over 95% of Fe³⁺ ions were converted to Fe²⁺ ions in the presence of phenol and no Fe²⁺ ions

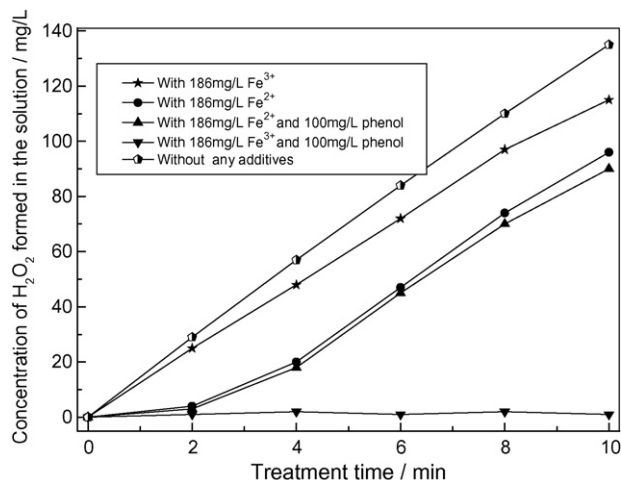
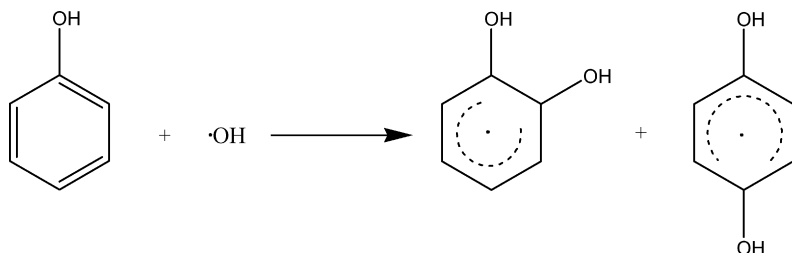


Fig. 6. Effects of iron salts and phenol on H₂O₂ formation during GDP treatment (voltage, 500 V; current, 100 mA; volume of solution, 150 mL; initial conductivity, 6.4 mS cm⁻¹; initial pH, 3.0).

were detected without phenol. This phenomenon demonstrated that the possible reduction by hydrogen peroxide (Eq. (4)) and cathode reduction (Eq. (5)) were negligible.

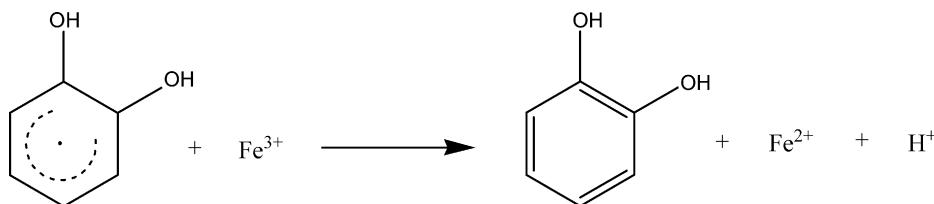


Therefore, the conversion of Fe^{3+} ions to Fe^{2+} ions must be from other pathways, and one most probable way was by dihydroxycyclohexadienyl radicals, which were resulted from the attack of the hydroxyl radicals on phenol (Eq. (6)) [14]:

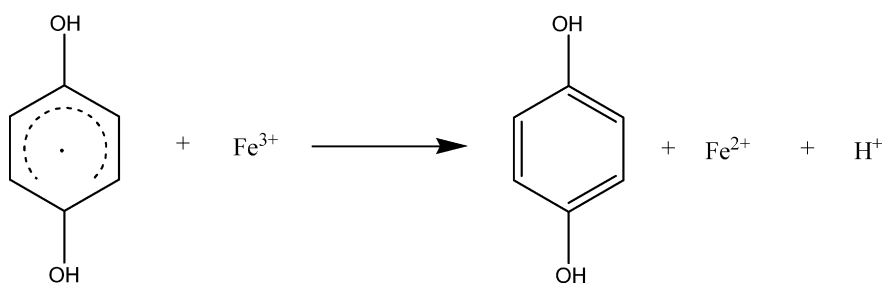


(6)

The above dihydroxycyclohexadienyl radicals possess reducing nature and can rapidly reduce Fe^{3+} ions to Fe^{2+} ions because they are prone to aromatise (Eqs. (7) and (8)).



(7)



(8)

As a result, a lot of Fe^{2+} ions were formed in the solution under the action of GDP and the newly formed Fe^{2+} ions further react with H_2O_2 in the solution to produce more hydroxyl radicals (Eq. (1)). If this assumption establishes, the amount of H_2O_2 accumulated in the solution with Fe^{2+} would be different from that with Fe^{3+} during phenol degradation. The effects iron salts on H_2O_2 formation during phenol degradation are shown in Fig. 6.

It can be observed from Fig. 6 that there was a lot of H_2O_2 remained in the solution in the presence of Fe^{2+} only, Fe^{3+} only, Fe^{2+} plus phenol. However, there was no H_2O_2 accumulated in the presence of Fe^{3+} plus phenol.

When the concentration of the added Fe^{2+} ions was low, they could be rapidly oxidized to Fe^{3+} ions and the difference in catalytic effects between Fe^{3+} and Fe^{2+} became less. However, the Fe^{3+} still showed better catalytic effect than Fe^{2+} .

3.3. Degradation by-products and mechanism

HPLC analysis was performed to explore the possible degradation mechanism. Without iron salts, three isomeric dihydroxybenzenes and hydroxyhydroquinone were identified during the GDP treatment, and the information of these by-products is shown in Fig. 7. It can be found that the distribution of dihydroxybenzene intermediates was catechol > hydroquinone \gg resorcinol.

These results can be explained on the basis of *ortho*- and *para*-directing nature of hydroxyl group, which is because of the donation of lone pair of electrons on hydroxyl group to the *ortho*- and *para*-positions of the benzene ring by conjugation. The hydroxyl radicals attacking the benzene ring are electrophilic and prefer to react at *ortho*- and *para*-position. Hydroxyhydroquinone was resulted from the hydroxylation of hydroquinone and catechol [16]. Pyrogallol was also detected, but its concentration was too low to be precisely determined. No benzoquinone was detected without iron salts.

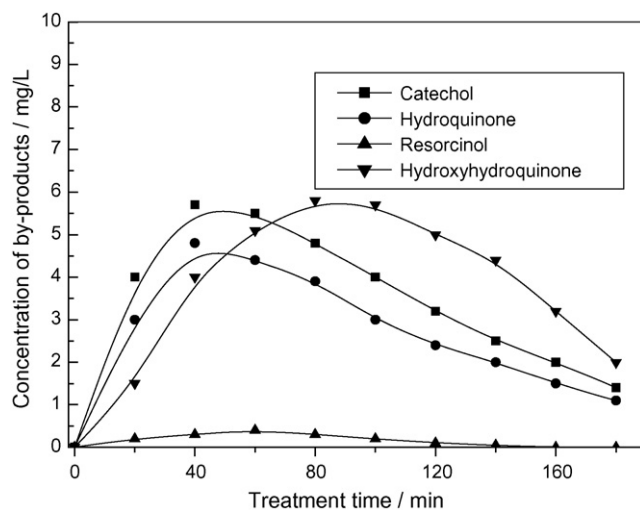


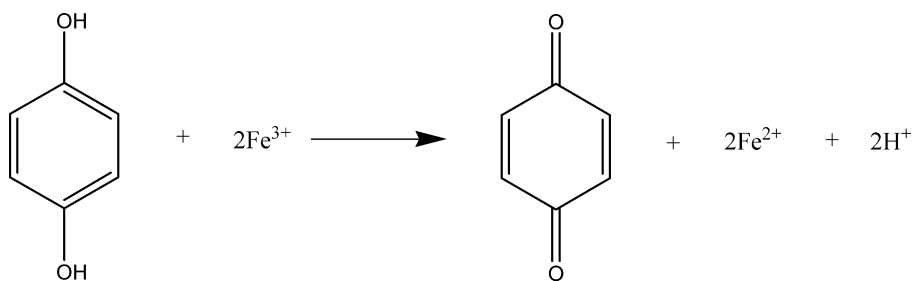
Fig. 7. Major by-product concentrations during GDP treatment without iron salts (voltage, 500 V; current, 100 mA; volume of solution, 150 mL; initial conductivity, 6.4 mS cm^{-1} ; initial pH, 6.5).

It can also be seen from Fig. 7 that the concentrations of the intermediate products were always one order of magnitude lower than that of phenol. This may be that the phenol decomposition only takes place near the plasma surface, where the by-products undergo further decomposition before going to the bulk solution. The pH and conductivity changes during GDP treatment are shown in Fig. 8.

It can be observed from Fig. 8 that the pH of the solution dropped rapidly in the presence of phenol, indicating that some of the organic acids were produced. The conductivity in the presence of phenol increased more rapidly in the presence of phenol also shows that organic acids were produced [16].

It is noted that large amounts of degradation by-products were formed in the presence of iron salts. They were hydroquinone, catechol and benzoquinone. Their distributions in the presence of 37 mg/L Fe^{3+} were shown in Fig. 9.

When catechol was subjected to GDP, no benzoquinone was formed in the presence or absence of iron salts. When hydroquinone was subjected to GDP, no benzoquinone was produced without iron salts and a lot of benzoquinone yielded in the presence of iron salts. Therefore, benzoquinone was resulted from oxidation of hydroquinone by Fe^{3+} ions as described by the following reaction (Eq. (9)):



Based on the above discussions, the phenol degradation pathway in the presence of iron salts is proposed in Fig. 10.

From Fig. 10, it can be seen that the hydroxyl radicals initially attack phenol to form *para*- and *ortho*-dihydroxycyclohexadienyl radicals, and then the dihydroxycyclohexadienyl radicals reduce Fe^{3+} ions to Fe^{2+} ions. The newly formed Fe^{2+} ions react with H_2O_2 to produce more hydroxyl radicals to enhance phenol degradation. Although the proposed mechanism seems to be similar to that in Fenton's reaction, it is different in nature.

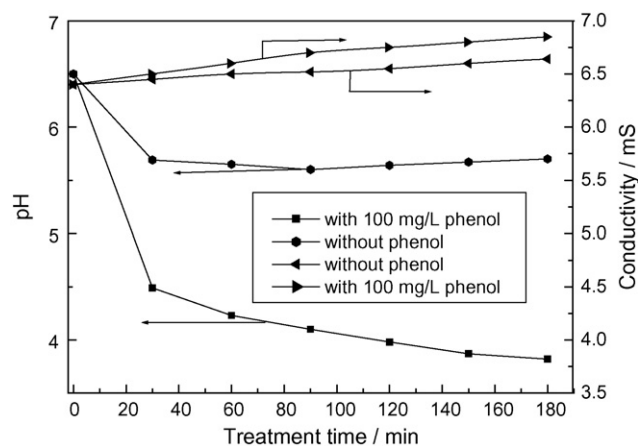
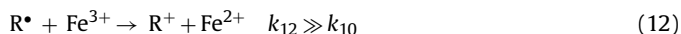
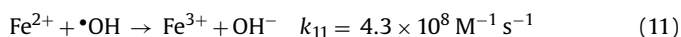
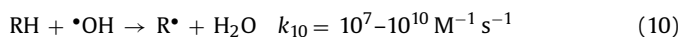


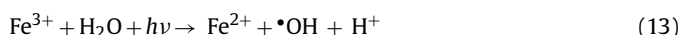
Fig. 8. pH and conductivity changes during GDP treatment (voltage, 500 V; current, 100 mA; volume of solution, 150 mL; initial conductivity, 6.4 mS cm^{-1} ; initial pH, 6.5).

In classical Fenton's reaction, it is generally considered that the reactions between H_2O_2 and Fe^{2+} in acidic condition involved the following major reactions besides the reactions (1) and (4) [15]:



The hydroxyl radicals produced in reaction (1) (1 mol hydroxyl radicals consumes 1 mol Fe^{2+} ions) can both react with RH to produce $\text{R}\cdot$ radicals (Eq. (10)) and with Fe^{2+} ions to produce Fe^{3+} ions (Eq. (11)). As $k_{12} \gg k_{10}$, the Fe^{2+} ions consumed in reaction (1) can be regenerated through reaction (12). On the other hand, as reaction (11) exists, the Fe^{2+} ions can not be fully regenerated and the overall Fe^{2+} ions would be gradually consumed and finally the reactions go to a Fenton-like one ($\text{Fe}^{3+} + \text{H}_2\text{O}_2$). Although the Fe^{3+} ions can be reduced to Fe^{2+} ions by H_2O_2 through reaction (4), the Fe^{2+} ions would be rapidly oxidized to Fe^{3+} ions (Eqs. (1) and (11)). Therefore, the degradation rate in conventional Fenton system often became lower at later stage as the overall rate is determined by reaction (4), the slowest one. Generally, ultraviolet light

was employed (UV/Fenton) to regenerate Fe^{2+} ions to accelerate the reaction [17]:



However, the UV/Fenton method has two major shortcomings. It is energy consuming since the above reaction (Eq. (13)) has a very low quantum yield [18]. It is only useful when the water to be treated or being treated has good transmittance for UV light (if the water has no good transmittance for UV light, the UV light will not be effectively absorbed by Fe^{3+} ions Eq. (13)).

As GDP can produce both hydroxyl radicals and H_2O_2 ; when the hydroxyl radicals (not produced through Fenton's reaction) were introduced to the solution, the extra hydroxyl radicals will be converted to $\text{R}\cdot$ radicals (Eq. (10)), which can effectively reduce Fe^{3+} ions to Fe^{2+} ions. That is to say, the hydroxyl radicals act as strong reducing agents (in fact it is very oxidizing). As a result, the Fenton's reaction was accelerated. As GDP can produce reducing agents just through electrical energy, the GDP can overcome the shortcomings of UV/Fenton reaction.

3.4. COD and TOC changes

COD and TOC are important indicators of water contamination. The COD and TOC changes during phenol degradation are presented in Figs. 11 and 12, respectively.

It is observed from Fig. 11 that the solution COD increased with treatment time without iron salts and sharply decreased in the presence of iron salts. Possible reason is that H_2O_2 formed in the solution was oxidized by dichromate during COD

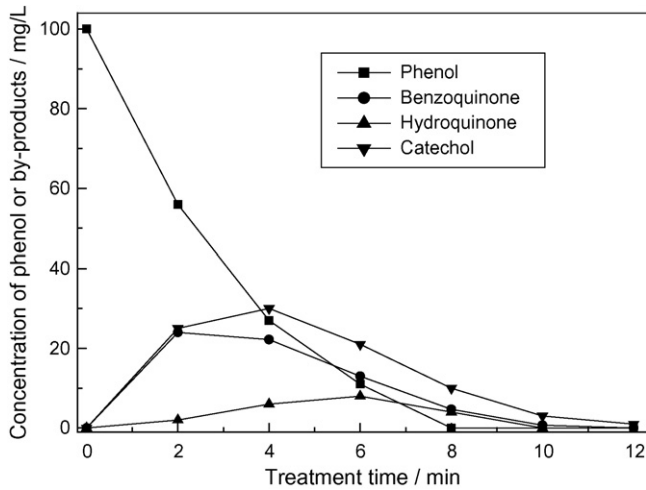


Fig. 9. Formation of intermediate products during GDP treatment when 37 mg/L Fe^{3+} were initially added to the solution (voltage, 500 V; current, 100 mA; volume of solution, 150 mL; initial conductivity, 6.4 mS cm^{-1} ; initial pH, 3.0).

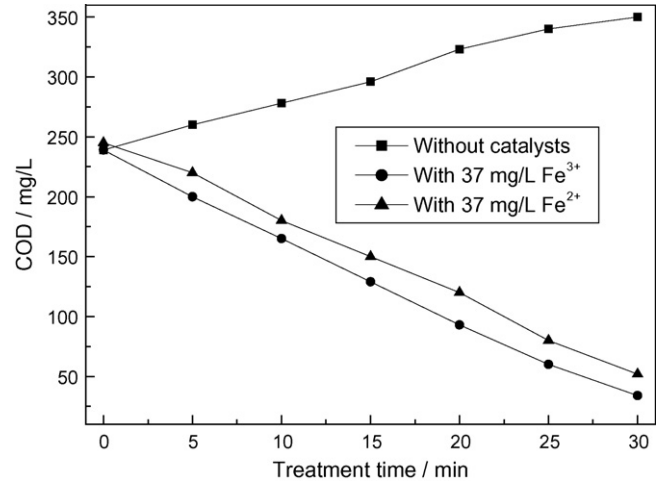
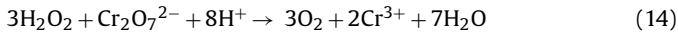


Fig. 11. COD changes during GDP treatment (voltage, 500 V; current, 100 mA; volume of solution, 150 mL; initial conductivity, 6.4 mS cm^{-1} ; initial pH, 3.0).

measurement:



As H_2O_2 consumes the dichromate, the value of solution COD is larger than the actual value. It can be observed from Fig. 12

that TOC of the solution gradually reduced with treatment time without catalysts. However, the reduction rate of TOC is lower than the disappearance rate of phenol (ref. Fig. 2), indicating some by-products formed in the solution. TOC and COD changes indicated the mineralization rate of phenol is higher with Fe^{3+} than with Fe^{2+} .

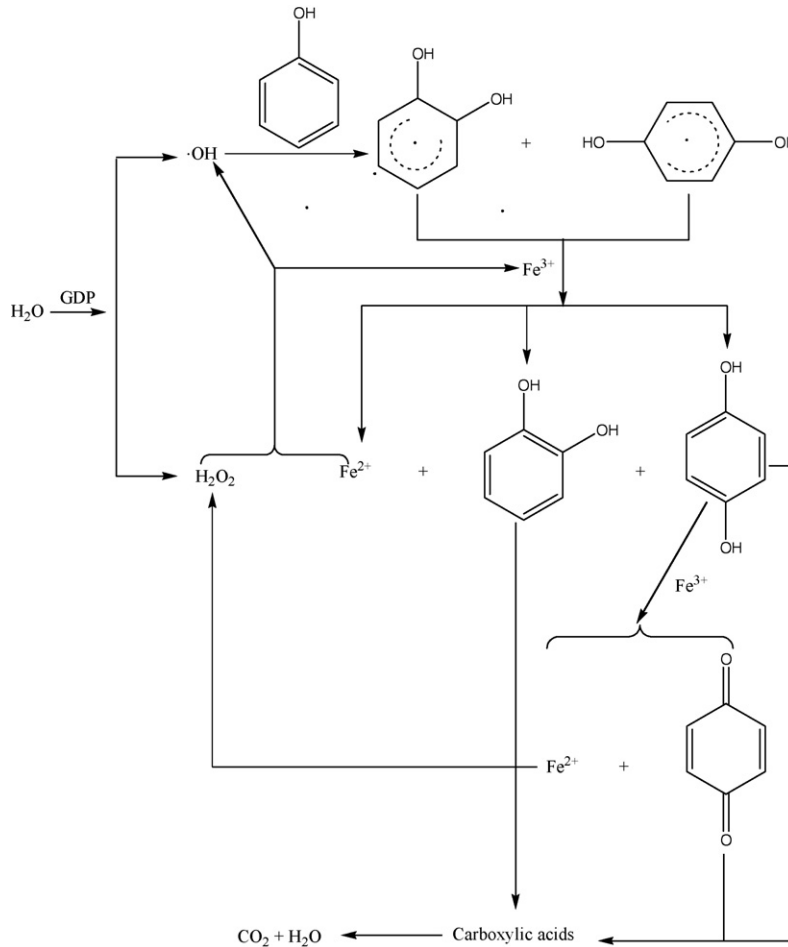


Fig. 10. Proposed phenol degradation pathway in the presence of iron salts induced by GDP.

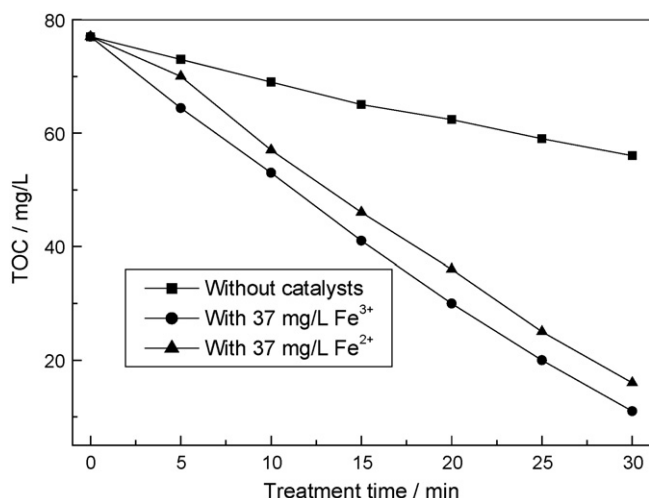


Fig. 12. TOC changes during GDP treatment (voltage, 500 V; current, 100 mA; volume of solution, 150 mL; initial conductivity, 6.4 mS cm⁻¹; initial pH, 3.0).

3.5. Energy efficiency

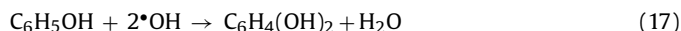
Energy efficiency is an important parameter in practice. In this work, the energy efficiency for phenol degradation (G_{phenol}) and for H_2O_2 formation ($G_{\text{H}_2\text{O}_2}$) [19,20] can be defined as follows:

$$G_{\text{phenol}} = \frac{(1/2)C_0 \text{ Vol}}{Pt_{1/2}} \quad (15)$$

$$G_{\text{H}_2\text{O}_2} = \frac{C_{\text{H}_2\text{O}_2} \text{ Vol}}{Pt_{1/2}} \quad (16)$$

where C_0 is the initial phenol concentration, Vol the solution volume, $t_{1/2}$ the time for half of phenol removal, P the electrical power and $C_{\text{H}_2\text{O}_2}$ is the H_2O_2 concentration at $t_{1/2}$. The values of G_{phenol} and $G_{\text{H}_2\text{O}_2}$ are shown in Table 1.

As indicated from Table 1 that G_{phenol} increases while $G_{\text{H}_2\text{O}_2}$ decreases with the increase of C_0 without iron salts. For example, G_{phenol} increases from 0.6 nmol/J to 29.4 nmol/J while $G_{\text{H}_2\text{O}_2}$ decreases from 19.6 nmol/J to 3.9 nmol/J as C_0 increases from 100 mg/L to 10,000 mg/L. The above phenomena can be explained on the basis that hydroxyl radicals are the key active species for phenol decomposition. Hydroxyl radicals are consumed for phenol oxidation and the coupling to H_2O_2 is suppressed as C_0 increases. However, as the amount of hydroxyl radicals required for phenol removal are equal to those for H_2O_2 formation (hydroxyl radicals for by-products degradation are not considered):



Therefore, the ultimate phenol decomposition yield should not be higher than 19.6 nmol/J. Table 1 indicated that G_{phenol} reached 29.4 nmol/J as C_0 was 10,000 mg/L, indicating that phenol pyrolysis took place as C_0 was high [21]. It is noted that the present energy costs for phenol removal is close to those reported in pulsed corona reactor [22]. However, the energy cost for H_2O_2 formation in the present study is about twofold to those in pulsed corona discharge (about 8.0 nmol/J) [19,20]. Therefore, the investigation of Fenton's reaction is of great importance in GDP. The optimum concentrations of Fe^{3+} and Fe^{2+} for phenol degradation are 37 mg/L. It can be found that the difference of G_{phenol} between Fe^{3+} and Fe^{2+} at 37 mg/L is 2.1 nmol/J, much higher than observed in GDP treatment without catalysts (0.6 nmol/J).

4. Conclusions

The catalytic effects of iron salts on phenol degradation by GDP were systematically investigated since there was a lot of H_2O_2 produced in the solution. Fe^{3+} ions unusually exhibited a better catalytic ability than Fe^{2+} ions, which has not been reported in other literature [9–11]. A lot of Fe^{2+} ions were formed only in Fe^{3+} /phenol/GDP system showed that the reduction of Fe^{3+} by cathode or H_2O_2 were negligible. Without iron salts, the intermediate products of hydroxylated phenols (catechol, hydroquinone, and hydroxylhydroquinone) were trace in comparison with that of parent phenol. In the presence of iron salts, a lot of hydroquinone, catechol and bezoquinone were detected. TOC and COD changes during treatment also demonstrated that Fe^{3+} ions had better catalytic action than that of Fe^{2+} ions. The present results present a new method in the acceleration of Fenton's reaction where the UV light was not effective.

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