Simultaneous oxidation of phenol and reduction of Cr(VI) induced by contact glow discharge electrolysis

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ABSTRACT

In this study, both phenol oxidation and Cr(VI) reduction induced by contact glow discharge electrolysis were investigated. Experimental results showed that the phenol oxidation increased markedly in the presence of Cr(VI) and the Cr(VI) reduction rose with the presence of phenol. The effect of Cr(VI) on phenol oxidation was hardly influenced by the solution pH, whereas the effect of phenol on Cr(VI) reduction at neutral pH was more evident than in acidic condition although the Cr(VI) reduction proceeded more rapidly in acid conditions. Possible mechanism of the synergistic effect was discussed based on the reaction kinetics. The findings would be helpful for removing organic and inorganic pollutants simultaneously in the complex wastewater.

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1. Introduction

Industrial wastewaters often contain a lot of inorganic and organic pollutants. The major inorganic pollutants are heavy metals. In most cases, heavy metals can be removed by electro-reduction. However, the electro-reduction is not proper for dilute Cr(VI) removal as it generally exists in the negatively charged forms: dichromate ($Cr_2O_7^{2-}$), hydrogen chromate ($HCrO_4^-$) and chromate (CrO_4^{2-}), which makes the transference of Cr(VI) to the cathode surface extremely difficult(against the electrical field). Current processes of treating Cr(VI) wastewater are by reduction with ferrous sulfate or sulfur dioxide to the less noxious Cr(III) in acidic condition followed by precipitation with alkali. However, the reduction methods create additional pollution due to the excessive use of reducing chemicals and the production of toxic by-products [1]. Phenols are present in many industrial wastewaters. Conventional processes such as bio-digestion, ozonation, Fenton oxidation and UV/H_2O_2 suffered either the slow kinetics or the high costs of oxidants.

In theory, Cr(VI) can be removed by reduction and phenols by oxidation. If the reduction-oxidation was coupled, the treatment costs will be mostly reduced. However, the Cr(VI) reduction by phenols at the normal conditions was difficult in the kinetic or dynamic aspects. Contact glow discharge electrolysis (CGDE) is a unique electrochemical process where plasma is sustained between a metal anode and an electrolytic surface [2,3]. During CGDE, various chemically active species such as hydrogen atoms, hydroxyl radicals and

hydrogen peroxide are formed with yields much higher than those stipulated by Faraday's law, which can induce a lot of redox reactions in the solution [2]. Recently, CGDE has been exhaustively investigated as a novel tool for the decontamination of aqueous pollutants [4–16]. Compared with other electrical processes, CGDE offers the advantages of instrumental simplicity and being able to treat highly conducting liquids. Previous studies showed that a variety of organic pollutants can be mineralized by CGDE through oxidation [4–15]. In addition, efficient reduction of aqueous acidic Cr(VI) to Cr^{3+} has also been achieved through CGDE [16]. These results seemed to imply that oxidation of organic pollutants and reduction of heavy metals can be simultaneously realized in CGDE. However, there seems no study on this point. Based on these considerations, Cr(VI) and phenol are chosen as the model pollutants in the present study to examine the synergistic effect between phenol oxidation and Cr(VI) reduction induced by CGDE.

2. Experimental

The reaction apparatus was very similar to that described elsewhere [13–16], which is illustrated in Fig. 1. The reactor was made of common 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 with ca. 10 mm exposed. The cathode was a stainless steel plate (surface area: 2.0 cm^2) placed in another glass tube and separated from the anodic compartment by a glass frit of medium porosity. The stock solution was prepared by dissolving a known amount of potassium dichromate or phenol in a sodium sulfate solution (conductivity: 6.4 mS/cm) and 150 mL portion was poured into the reaction vessel for treatment. The catholyte is the same as

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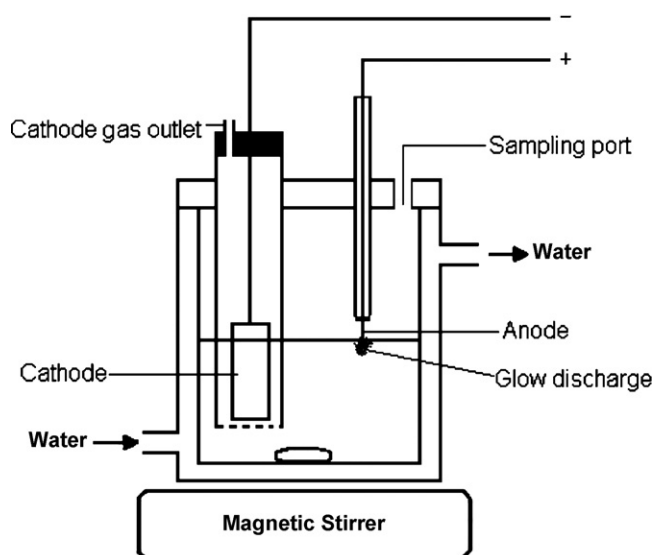E-mail address: lyjglow@sohu.com.

Fig. 1. Schematic diagram of the CGDE reactor.

Fig. 2. Phenol concentration variation in the presence of different concentration of Cr(VI) (voltage 500 V, current 100 mA, solution volume 150 mL, [phenol]$_0$ 100 mg/L, pH$_0$ 5.6).

anolyte. The solution in the jacketed reaction vessel was maintained at 298 ± 2 K by circulating cold water. Sulfuric acid or potassium hydroxide was utilized to adjust the solution pH to the expected value. DC voltage of 500 V was usually applied across the electrodes through a DC power supply to initiate the reaction. Depth of the anode immersed in the solution was carefully adjusted to average the current to 100 mA, with the current deviation less than $\pm 4\%$. The depth of the anode immersed was ca.1.2 mm.

During the treatment, the solution was gently stirred with a magnetic stirrer. Phenol and its degradation products were analyzed by HPLC [10]. Cr(VI) was determined by a colorimetrical method [16]. The gases produced from each compartment were analyzed by means of gas chromatography (HP 6890).
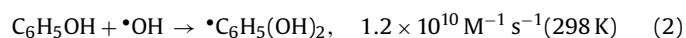
3. Results and discussion
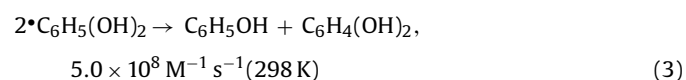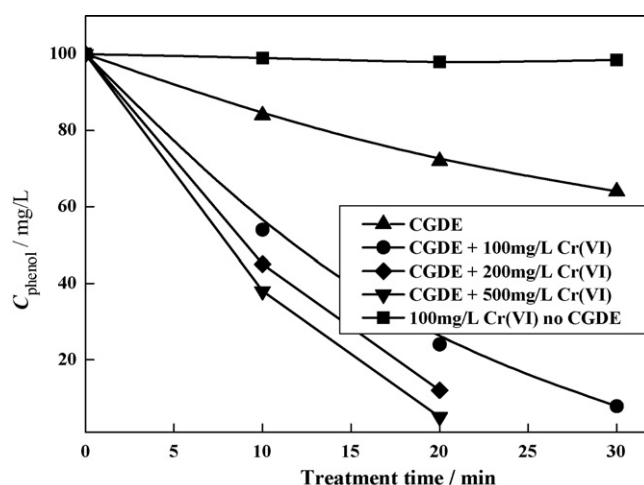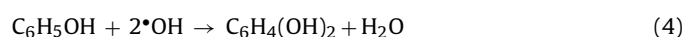
3.1. Phenol oxidation in the presence of Cr(VI)

When the solutions were subjected to CGDE, water molecules near the plasma/solution interface dissociate to hydroxyl radicals and hydrogen atoms:

$$H_2O^+ + nH_2O \xrightarrow{CGDE} H_3O^+ + nOH + (n-1)H \tag{1}$$
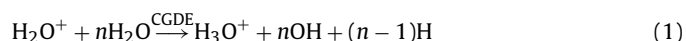
where n is the number of the water molecules decomposed per H_2O^+ ion from the plasma. Sengupta estimated the value of n could reach 12 by using cerous ion as the radical scavenger with an extrapolating method [3]. Hydroxyl radicals ($\cdot OH$) so produced are concentrated and reactive. When phenol is present, $\cdot OH$ radical behaves as an electrophile and immediately adds to the aromatic ring, forming the corresponding cyclohexydienyl radicals ($^\bullet C_6H_5(OH)_2$) [17]:

$$C_6H_5OH + {}^\bullet OH \rightarrow {}^\bullet C_6H_5(OH)_2, \quad 1.2 \times 10^{10} \text{ M}^{-1}\text{ s}^{-1}(298\text{ K}) \tag{2}$$

Without oxidants, the resulting radicals disproportionate to dihydroxybenzene and the starting material [17]:

$$2^\bullet C_6H_5(OH)_2 \rightarrow C_6H_5OH + C_6H_4(OH)_2,$$
$$5.0 \times 10^8 \text{ M}^{-1}\text{ s}^{-1}(298\text{ K}) \tag{3}$$

From reactions (2) and (3), the stoichiometry of phenol oxidation by $\cdot OH$ radical is

$$C_6H_5OH + 2^\bullet OH \rightarrow C_6H_4(OH)_2 + H_2O \tag{4}$$

It can be observed from reaction (4) that the oxidation of each phenol molecule needs two $^\bullet OH$ radicals. Generally, cyclohexydienyl radicals possess reducing nature [18] and can be oxidized by proper oxidants having more positive redox potentials such as oxygen [19] or transition metal ions (Fe^{3+} or Cu^{2+}) [20,21]. If so, oxidation of one phenol molecule only consumes one $^\bullet OH$ radical, which would be of practical importance in terms of energy costs. Oxygen can oxidize $^\bullet C_6H_5(OH)_2$ radical in the solution with a high rate constant [19]:

$$^\bullet C_6H_5(OH)_2 + O_2 \rightarrow C_6H_4(OH)_2 + HO_2{}^\bullet,$$
$$6.7 \times 10^8 \text{ M}^{-1}\text{ s}^{-1}(298\text{ K}) \tag{5}$$
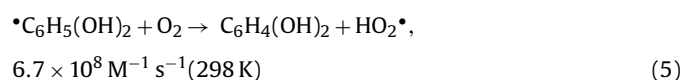
However, reaction (5) is inefficient due to the low solubility of oxygen. Consequently, the effect of aeration on phenol oxidation was limited.

Considering its oxidizing and toxic properties, Cr(VI) was selected to promote the phenol oxidation by CGDE. In Fig. 2 are shown the phenol concentration variations in the presence of different concentrations of Cr(VI).

It can be seen from Fig. 2 that Cr(VI) showed an apparent enhancing effect on the phenol oxidation. For example, the phenol removal efficiency after 20 min of CGDE treatment was less than 30% and increased to 76% and 95% in the presence of 100 and 500 mg/L of Cr(VI), respectively.

As Cr(VI) is a powerful oxidant, $^\bullet C_6H_5(OH)_2$ radicals can be readily oxidized by Cr(VI), possibly according to the following reactions:

$$^\bullet C_6H_5(OH)_2 + Cr(VI) \rightarrow {}^+C_6H_5(OH)_2 + Cr(V) \tag{6}$$

$$^+C_6H_5(OH)_2 \rightarrow C_6H_4(OH)_2 + H^+ \tag{7}$$

Reaction (6) is a rate-determining step, while its rate constant is unavailable to date. However, pulse radiolysis studies showed that the rate constants of $^\bullet C_6H_5(OH)_2$ oxidation by Fe(CN)$^{3-}$ and IrCl$_6{}^{2-}$ are both in the order of 10^9 M^{-1} s^{-1}. As the redox potential of Cr(VI)/Cr(V) (0.534 V) is in between Fe(CN)$_6{}^{3-}$/Fe(CN)$_6{}^{4-}$ (0.360 V) and IrCl$_6{}^{2-}$/IrCl$_6{}^{3-}$ (0.870 V), the rate constant of reaction (6) should be also in the order of 10^9 M^{-1} s^{-1} [21–23].

As reaction (6) competes with reaction (3), the phenol removal could not be doubled except that all the $^\bullet C_6H_5(OH)_2$ radicals were oxidized by Cr(VI). Fig. 2 showed that the phenol removal in the presence of 500 mg/L Cr(VI) was about three times that without Cr(VI), indicating the reactions other than reaction (6) present. As is shown in Fig. 2, without CGDE, no phenol removal was observed in the presence of Cr(VI) suggests that the direct phenol oxidation
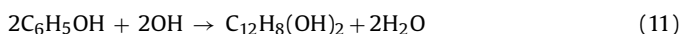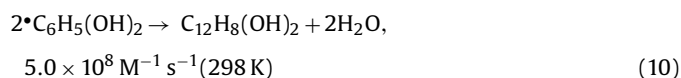
by Cr(VI) was negligible. The reason is that the $^\bullet$OH radicals and $^\bullet$H atoms are both produced in CGDE; they react mutually to form water again [2]:

$$^\bullet OH + {}^\bullet H \rightarrow H_2O, \qquad 2.0 \times 10^{10}\, M^{-1}\, s^{-1}(298\,K) \tag{8}$$
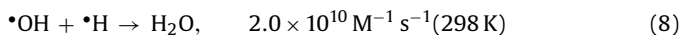
In the presence of Cr(VI), the $^\bullet$H atoms can also be rapidly oxidized by Cr(VI) according to the reaction [24]:

$$Cr(VI) + {}^\bullet H \rightarrow Cr(V) + H^+, \qquad 1.6 \times 10^{10}\, M^{-1}\, s^{-1}(298\,K) \tag{9}$$
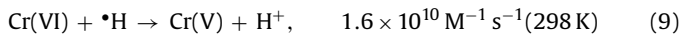
Reaction (9) suppressed the back reaction (8) and more $^\bullet$OH radicals are available for phenol oxidation. Cr(VI) reduction without phenol in basic medium supports the above assumptions [16]. It is noted that the dimerization of $^\bullet C_6H_5(OH)_2$ radicals can lead to one hydroxyl radical removing one phenol successful through reactions (10) and (11) [17]. However, HPLC analysis showed that the dimeric reaction was minor as little dimmer was detected, probably due to the relativity low phenol concentration utilized in the present experimental conditions.

$$2^\bullet C_6H_5(OH)_2 \rightarrow C_{12}H_8(OH)_2 + 2H_2O,$$
$$5.0 \times 10^8\, M^{-1}\, s^{-1}(298\,K) \tag{10}$$

$$2C_6H_5OH + 2OH \rightarrow C_{12}H_8(OH)_2 + 2H_2O \tag{11}$$

From the above discussions, the effects of Cr(VI) are two-fold: decrease the consumption of $^\bullet$OH radical for phenol oxidation and increase the concentration of $^\bullet$OH radical by scavenging the $^\bullet$H atoms. These two effects are all favorable for phenol oxidation.
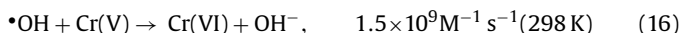
3.2. Effect of phenol on Cr(VI) reduction

Reaction (9) shows that the Cr(VI) can be reduced to Cr(V) by $^\bullet$H atoms produced by CGDE. Cr(V) can be further converted to Cr(III) by the following sequence [16]:

$$Cr(V) + Cr(V) \rightarrow Cr(IV) + Cr(VI) \tag{12}$$

$$Cr(V) + Cr(IV) \rightarrow Cr(III) + Cr(VI) \tag{13}$$
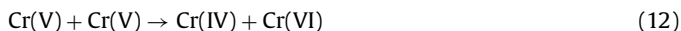
From reactions (9), (12) and (13), the stoichiometry of Cr(VI) reduction to Cr(III) by $^\bullet$H atoms is:

$$3^\bullet H + Cr(VI) \rightarrow Cr(III) + 3H^+ \tag{14}$$

At the same time, Cr(III) and Cr(V) can be oxidized back to Cr(IV) and Cr(VI) by the $^\bullet$OH radicals, respectively [24].

$$^\bullet OH + Cr(III) \rightarrow Cr(IV) + OH^-, \qquad 3.8 \times 10^8\, M^{-1}\, s^{-1}(298\,K) \tag{15}$$

$$^\bullet OH + Cr(V) \rightarrow Cr(VI) + OH^-, \qquad 1.5 \times 10^9\, M^{-1}\, s^{-1}(298\,K) \tag{16}$$

Although the rate constants of the reactions (15) and (16) are small compared with that of reaction (9), they cannot be overlooked since the concentration of $^\bullet$OH radicals near the plasma-solution interface are higher than $^\bullet$H atoms (see reaction (1)). In order to inhibit the reaction of $^\bullet$OH with the Cr(V) and Cr(III), phenol was used as an $^\bullet$OH scavenger (reaction (2)). In Fig. 3 are shown the effects of phenol on Cr(VI) reduction.

As can be observed from Fig. 3, phenol also showed a positive effect on Cr(VI) reduction. For example, the Cr(VI) removal is about 32% without phenol, 50% with 100 mg/L phenol and 62% with 500 mg/L phenol, with 5 min of CGDE treatment.

The reaction rate constant of $^\bullet$OH with phenol is $1.2 \times 10^{10}\, M^{-1}\, s^{-1}$, which is about ten times the rate constant for the reaction of $^\bullet$OH with Cr(V). More $^\bullet$OH radicals were trapped with higher concentration of phenol present, which inhibits the re-oxidation of Cr(III) and Cr(V). In addition, the $^\bullet C_6H_5(OH)_2$ radicals can reduce Cr(VI). The net reaction is that each $^\bullet$OH radical is converted to an $^\bullet C_6H_5(OH)_2$ radical which reduces one equivalent of Cr(VI) to Cr(V) or one third that of Cr(VI) to Cr(III).
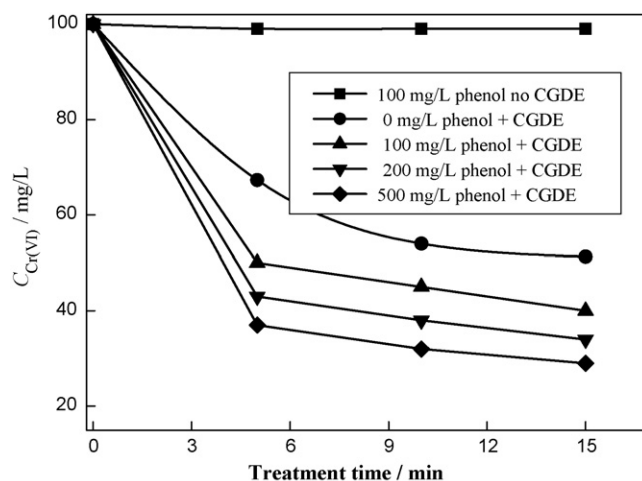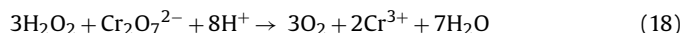

Fig. 3. Cr(VI) concentration variation in the presence of different concentrations of phenol (voltage 500 V, current 100 mA, solution volume 150 mL, [Cr(VI)]$_0$ 100 mg/L, pH$_0$ 5.6).

3.3. Effect of initial pH on the phenol oxidation and the Cr(VI) reduction

Fig. 4 shows the phenol and the Cr(VI) removals after 5 min of CGDE treatment. It can be observed from Fig. 4 that the difference in phenol removal in the presence and absence of Cr(VI) are almost kept constant in the pH range from 1.5 to 8.5. However, the effect of phenol on the Cr(VI) removal were more evident in neutral solution than in acidic solution, although the Cr(VI) reduction proceeded faster in acid condition. The above phenomena can be explained by the fact that the presence of phenol decreased the concentration of hydroxyl radicals. Consequently, the formation of H$_2$O$_2$ was inhibited [17]:

$$\cdot OH + {}^\bullet OH \rightarrow H_2O_2, \qquad 5.3 \times 10^9\, M^{-1}\, s^{-1}(298\,K) \tag{17}$$
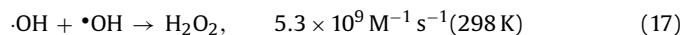
H$_2$O$_2$ can directly reduce Cr(VI) in acidic medium [16]:

$$3H_2O_2 + Cr_2O_7{}^{2-} + 8H^+ \rightarrow 3O_2 + 2Cr^{3+} + 7H_2O \tag{18}$$

Each $\cdot$OH radical can be converted to one reducing radical by phenol, and this means that three hydroxyl radicals can reduce one Cr(VI) to Cr(III). According to reactions (18) and (19), three hydroxyl radicals can also reduce on Cr(VI) to Cr(III) through coupling to the
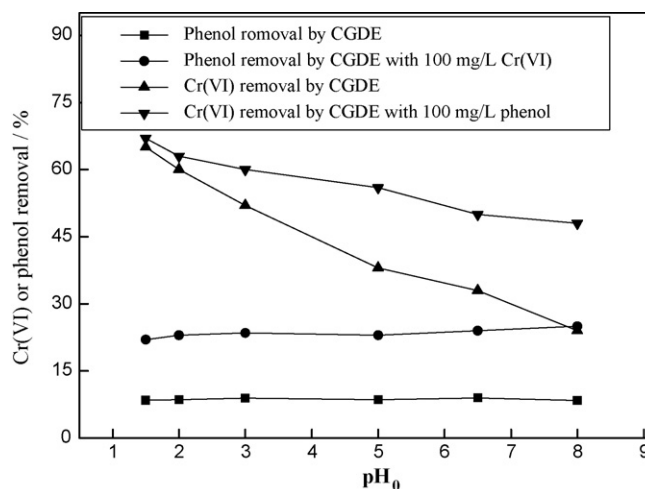

Fig. 4. Effect of initial pH on phenol and Cr(VI) removal with 5 min of treatment(voltage 500 V, current 100 mA, solution volume 150 mL, [phenol]$_0$ 100 mg/L, [Cr(VI)]$_0$ 100 mg/L).

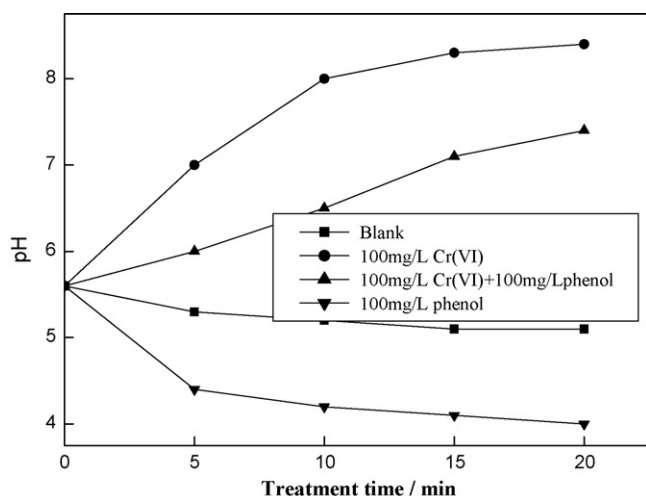**Fig. 5.** pH variations in different solutions with treatment time (voltage 500 V, current 100 mA, solution volume 150 mL).

Fig. 6. Effects of phenol concentration(a) Cr(VI) concentration, (b) on O_2 and H_2 formation in the anodic compartment (voltage 500 V, current 100 mA, solution volume 150 mL, treatment time 5 min. pH_0 5.6).

H_2O_2. Presence of phenol converts the hydroxyl radicals to reducing ones but suppresses the formation of H_2O_2. Their effects are offset mutually in acidic media. However, the presence of phenol increases the concentration of hydrogen atoms through scavenging hydroxyl radicals, which favors the reaction (8). The ultimate result is that the Cr(VI) reduction is still increased by phenol in acid condition.

In order to better elucidate the process, pH variations in different solutions were recorded and the results are shown in Fig. 5.

It can be indicated from Fig. 5 that the pH increases with treatment time in the solution only contain Cr(VI) whereas the pH decreases when the solution only contain phenol. This is due to the fact Cr(VI) exists in the metalate form; its reduction needs the participation of H$^+$ ions. Giving $Cr_2O_7^{2-}$ as an example, the reaction is:

$$Cr_2O_7^{2-} + 6^{\bullet}H + 8H^+ \rightarrow 2Cr^{3+} + 7H_2O \qquad (19)$$
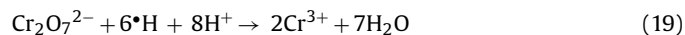
In the case of phenol, the pH decreases with treatment time is due to the generation of organic acids, which is the subsequent oxidation of the intermediate products. The organic acids dissociate to give H$^+$ ion and the pH decreases [7].

Previous investigations showed that the Cr(VI) reduction proceeded faster in acid condition than in neutral or basic ones [16]. As shown in Fig. 5, when the solution contains both phenol and Cr(VI), the pH increase was not apparent. This means that the acid can be saved in Cr(VI) removal. When the blank solution was subjected to CGDE, a little pH decrease was also observed, presumably due to some nitric acid was formed under the action of CGDE on the dissolved nitrogen gas in water, which is also favorable for Cr(VI) reduction. The overall reaction can be described as [25]:

$$4N_2 + 9H_2O \xrightarrow{CGDE} 5NH_4NO_3 + 3HNO_3 \qquad (20)$$

3.4. By-products formation and nature of the reactions

Several phenol degradation products were detected by HPLC in low yields. Without Cr(VI), the by-products were chiefly catechol and hydroquinone at the early stage of treatment and some hydroxyhydroquinone [$C_6H_3(OH)_3$] was also detected in trace amounts. With further increase of treatment time, carboxylic acids were appreciably detected because of the ring opening. Finally the resulting carboxylic acids slowly decomposed to carbon dioxide and water. The phenol degradation byproducts in the presence of Cr(VI) are similar to those observed without Cr(VI) [7]. Cr(VI) reduction
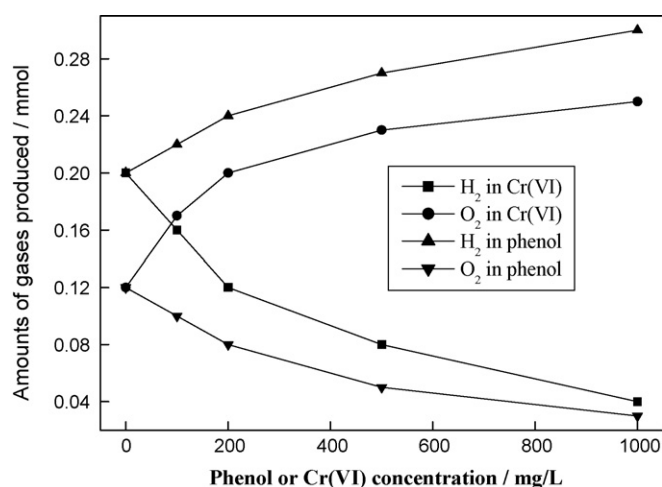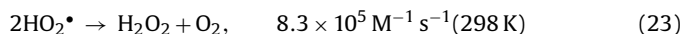
leads to a series of unstable intermediates according the reactions (12) and (13). However, these intermediates are short-lived and cannot be detected by the normal methods. The amount of Cr(III) formed is equal to that Cr(VI) depleted, indicating these intermediate products only exists in water instantaneously [9].

Special attention is paid on the formation of H_2 and O_2 in the gas phase. H_2 and O_2 were produced in the anodic compartment whereas only H_2 was formed in the cathodic compartment during CGDE treatment. The amount of H_2 yielded in the cathodic compartment in phenol or Cr(VI) solution is the same, was stipulated by the Faraday's law [16]. This indicated that the cathode action contributes little to the phenol oxidation or Cr(VI) reduction in CGDE. The amounts of H_2 and O_2 produced in different solutions with 5 min of CGDE treatment in the anodic compartment are shown in Fig. 6a and b.

It can be seen from Fig. 6a that the amounts of H_2 in the anodic compartment decrease whereas that of O_2 increases with increasing initial Cr(VI) concentration. H_2 was the result of $\cdot$H atoms coupling:

$$^{\bullet}H + {}^{\bullet}H \rightarrow H_2, \qquad 1.3 \times 10^{10}\,M^{-1}\,s^{-1}(298\,K) \qquad (21)$$
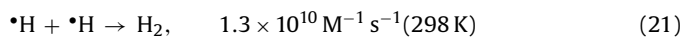
As more hydrogen atoms were consumed by Cr(VI) at the higher Cr(VI) concentrations, the amounts of H_2 reduced. The following reactions should be considered accounting for the formation of oxygen:

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}, \qquad 4.5 \times 10^7\,M^{-1}\,s^{-1}(298\,K) \quad (22)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2, \qquad 8.3 \times 10^5\,M^{-1}\,s^{-1}(298\,K) \qquad (23)$$

Presence of Cr(VI) consumes hydrogen atoms and increases the concentration of hydroxyl radicals. The increasing concentration of hydroxyl radicals ultimately increases the reactions (22) and (23). It can be seen from Fig. 6b that the amounts of H_2 increases whereas the oxygen decreases with increasing initial phenol concentration. This is because the presence of phenol consumes hydroxyl radicals, suppressing the back reaction (reaction (8)) and ultimately favors the reaction (21).

From the above experimental results, the phenol oxidation in inert solution can be written as (at the initial stage as the example):

$$C_6H_5OH + H_2O \rightarrow C_6H_4(OH)_2 + H_2 \qquad (24)$$
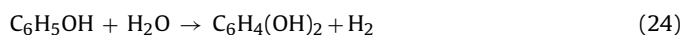
High concentration of Cr(VI) reduction induced by CGDE was [16]:

$$4Cr(VI) + 6H_2O \rightarrow 4Cr(III) + 3O_2 + 12H^+ \qquad (25)$$
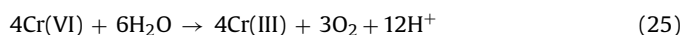
According to Fig. 6, in solutions with high concentration of phenol and Cr(VI), the overall reaction can be described:

$$3C_6H_5OH + 2Cr(VI) + 3H_2O \rightarrow 3C_6H_4(OH)_2 + 2Cr(III) + 6H^+ \tag{26}$$
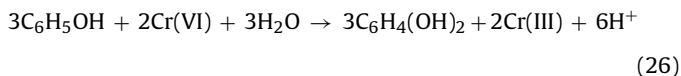
Reaction (26) was not favorable in normal conditions. However, the reaction can be successfully effected under the action of CGDE. Generally electric field in the magnitude of MV/cm has to be applied in water to form corona discharge [26]. However, 500 V is enough for operation in CGDE, which is favorable for industrial applications in terms of operation safety.

4. Conclusions

CGDE can induce phenol oxidation and Cr(VI) reduction simultaneously. The removal efficiency of the both pollutants can be enhanced in the presence of each other. The result not only be restricted to CGDE, but also throws an enlightenment to employ other electrical processes to efficiently degrade organic pollutants for actual wastewater containing both organic and inorganic species.

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