Degradation of 4-chlorophenol in different gas–liquid electrical discharge reactors

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Abstract

In a pulsed high voltage discharge system, degradation of 4-CP, mineralization of TOC and energy efficiency in HDAW reactor were compared with those in HDBW and GD reactor at the same energy input and operation conditions. In HDAW reactor high voltage electrodes were submerged in the liquid phase and ground electrode was placed in the gas phase above water surface to form hybrid gas–liquid discharge. The HDBW reactor employed both high voltage electrodes and ground electrode in liquid phase and the GD reactor employed high voltage electrodes above water level. It was found that degradation efficiency of 4-CP, mineralization of TOC and energy efficiency in HDAW reactor were all higher than those in other reactors, indicating that HDAW reactor was the most favourable configuration for pollutant removal. The combination of both discharge in gas phase and liquid phase enhanced the formation of ozone and hydrogen peroxide, which in turn resulted in the promotion on 4-CP degradation in HDAW reactor. In addition, ozone, hydrogen peroxide and active radicals all acted on pollutant degradation but radical oxidation was proved as a main degradation mechanism in these three reactors by adding *tert*-butyl alcohol. The further extent of oxidation of intermediates proceed was caused in HDAW reactor than that in other two reactors.
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Keywords: Spark discharge; HDAW reactor; Ozone; Hydrogen peroxide; 4-CP degradation

1. Introduction

Due to the ubiquitous presence of chlorophenols in the natural environment and their toxic properties, the decomposition of chlorophenols is therefore of great importance and has been examined extensively by several advanced oxidation technologies (AOTs) [1–3]. More recently, among the AOTs, the pulsed high voltage discharge process is seemed a novel method for removal of chlorophenols in wastewater [4]. This method injects energy into an aqueous solution through a plasma channel formed by a pulsed high voltage discharge between two electrodes. Pulsed high voltage discharges generated directly in water initiate a variety of physical and chemical processes [5–7]. These include intense ultraviolet radiation, overpressure shock waves, and, especially, the formation of various active chemical species, such as radicals ($H^\bullet$, $O^\bullet$, $^\bullet OH$) and molecular specials (H_2O_2, O_3).

Several different discharge modes, such as streamer corona discharge, spark discharge, and arc discharge, have been studied with a variety of electrode geometries (e.g., point–point, needle–plate and wire–cylinder) for degradation of phenolic compounds by pulsed high voltage discharge. Recently, needle–plate electrode geometry reactor, which utilizes electrodes submerged into the liquid phase to form corona-like discharge [5,8], is a familiar liquid discharge (LD) reactor. LD reactor can also be configured to produce ozone by injection of oxygen (or air) through a high voltage hollow electrode immersed in water. This reactor is classified as a type of hybrid gas–liquid discharge (HD) reactors. Another HD reactor, which combines ground electrode above the water with oxygen flowing and high voltage electrode submerged in liquid without bubbling, has been observed non-thermal plasma discharge formed in gas phase with corona-like discharge in liquid phase [9–11]. Except for removal of pollutants in LD and HD reactors, gas discharge (GD) reactor, with pulsed high voltage electrodes in the gas phase above water level and the ground electrode submerged into liquid, has been used as well [12,13].

In LD reactor, the effect of conductivity is critical to the formation of discharge in water [6]. Compared with no gas

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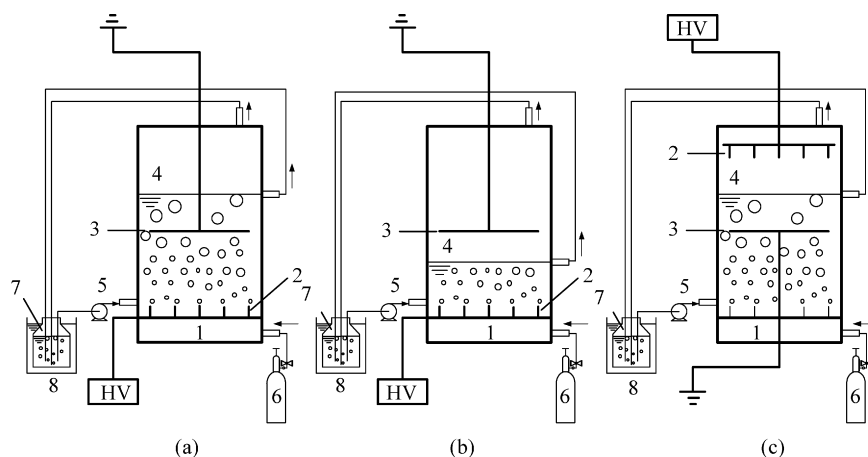 *E-mail address:* lclei@zju.edu.cn (L. Lei).

Fig. 1. Schematic diagram of HDBW reactor (a), HDAW reactor (b) and GD reactor (c). (1) Oxygen room, (2) high voltage electrode, (3) ground electrode, (4) liquid surface, (5) peristaltic pump, (6) cylinder, (7) solution tank, (8) cooling water.

bubbling, the addition of gas clearly enhances the degradation efficiency [14–16] because the mean-free-path length of the electron is increased to produce spark discharge in water [14]. In the case of GD reactor, ozone could be produced in an air or oxygen environment to diffuse into the liquid phase. However, only a part of active species plenty, such as $H^\bullet$, $O^\bullet$, $^\bullet OH$ and H_2O_2, produced at the gas–liquid interface can dissolve into the water and destroy the pollutants [11–13], so that the utilization of active species in gas discharge is limited. In order to investigate the synthesis effect of spark discharge in liquid phase and non-thermal plasma discharge in gas phase immediately, a novel HD reactor is explored, with oxygen bubbled through high voltage hollow electrode immersed in water whereas the ground electrode placed over water, defined as HDAW reactor. In addition, efficient degradation of contamination and maximal utilization of electric energy are investigated in this novel HDAW reactor in comparison to those in HDBW reactor and GD reactor. HDBW reactor, as described above, with both electrodes submerged into liquid phase and gas bubbling through a high voltage hollow electrode, only could produce spark discharge in liquid. GD reactor with gas bubbling through the bottom of reactor into liquid phase then into gas phase only could produce discharge in gas phase.

In this study, degradation of 4-CP, mineralization of TOC and energy efficiency utilization in HDAW reactor was investigated in comparison to the results in HDBW and GD reactor. And the concentration of ozone, hydrogen peroxide and intermediates of 4-CP degradation were measured to explore the differences between HDAW reactor and other two reactors.

2. Experimental

2.1. Setup

The experimental apparatus consists of a pulsed high voltage power supply and an electrical discharge reactor. The power supply is identical to that in previous work [17,18]. Electrical energy is formed from a large pulse-forming capacitance (4000 pF) and is released as a pulsed electrical discharge using a double rotat-

ing spark gap. In this study, the applied voltage is 16 kV and the pulse repetition rate is 100 Hz.

The electrical discharge reactors used in the present study are depicted in Fig. 1. The reactor vessel made of Plexiglas contains a needle–plate geometry electrode system (Ø 90 mm). The high voltage electrodes are seven hollow stainless steel injection needles (Ø 0.7 mm). The ground plate electrode is a stainless steel disk of 85 mm in diameter. Fig. 1 depicts the schematic diagram of HDBW reactor (a), HDAW reactor (b) and GD reactor (c). The distance between high voltage electrodes and ground electrode is 20 mm. For HDAW reactor and GD reactor, the distance between ground electrode and water level is 10 mm. Oxygen is bubbled through needles in both HD reactors or through the bottom of GD reactor. The flow rate of oxygen bubbled into the liquid is all about $0.2\,m^3/h$. The gas overflows from the top of reactor and then is circulated into the solution tank in order to increase efficient contacting of gaseous ozone with the solution. The solution of 4-CP (500 mL) is stored in the solution tank and circulated into reactor by a peristaltic pump. The solution tank is cooled by cooling water in order to maintain the total solution at 25 °C. In our study, the experiments were all conducted three times and gave reproducibility within 5%.

2.2. Reagent and measurement

4-CP was dissolved in distilled water at initial concentration of 50 ppm (389 μmol/L). *tert*-Butyl alcohol was used as a radical scavenger in this study, the concentration of that was 300 times of 4-CP to ensure radicals scavenged completely.

4-CP and its intermediates were analyzed by Knauer HPLC, equipped with a MS-2 C_{18} column (Ø 4.6 mm × 250 mm) and a UV detector. The UV detector wavelength was set at 278 nm. The mobile phase was prepared by dissolving 1 mL/L H_3PO_4 in deionized water and the ratio between the solution and methanol (V:V) was 50:50. Organic acids were detected by ion chromatograph (792 Basic IC, Metrohm, Switzerland) with DS-plus^{TM} auto-suppressor with mobile phase of sodium carbonate (1.7 mmol/L)/sodium bicarbonate (1.8 mmol/L)/5% acetone at the flow rate of 1.0 ml/min. The separation was performed on

a Metrosep A supp column (Metrohm, Switzerland) with the column temperature of 35 °C. The concentration of ozone in the output gas was determined with the indigo method [19] by running the reactor outlet stream through a gas wash bottle containing indigo carmine. And the dissolved ozone concentration in distilled water was measured at 254 nm using UV–vis spectrophotometer (Techcomp 8500) [12]. The concentration of hydrogen peroxide was determined colorimetrically using the reaction of H_2O_2 with titanyl ions by the analysis of the maximum absorbance of the yellow peroxotitanium (IV) complex at wavelength $\lambda = 410$ nm [20]. A total organic carbon (TOC) analyzer (Tekmar Dohrmann Apollo 9000, USA) was used to analyze the treated water. The conductivity and pH of the treated solution was measured by a conductivity meter (DDS-11 A) and pH meter (pHS-25), respectively.

The pulsed output voltage and current were measured using a digital oscilloscope (Lecroy LT264) with a high-voltage probe (INC P150-GL/5k) and a current transducer (Pearson Electronic M411). In order to mutually compare the discharge energy efficiency of 4-CP removal or ozone and hydrogen peroxide formation, G yield values were calculated, using the number of converted 4-CP molecules or the amount of formed ozone and hydrogen peroxide molecules divided by the energy input required [13,18]:

$$G = \frac{|X_0 - X_t|V}{E_p f t} \tag{1}$$

where X_0 is the initial concentration at $t = 0$ (M), X_t is the concentration at t (min) time, V is the solution volume (L), f is the pulse repetition rate (Hz), and the unit of G is mol/J. E_p is the pulse energy from pulse-forming capacitance (J/pulse), and obtained by the followed equation [21]:

$$E_p = \tfrac{1}{2}CU^2 \tag{2}$$

where C is the capacitance of the pulse-forming (4000 pF), and U is the voltage from the pulse-forming capacitance (19.15 kV). For energy efficiency of 4-CP removal, the value of G_{50} was used when 50% of 4-CP was conversed. And for energy efficiency of ozone and hydrogen peroxide formation, G was calculated when ozone and hydrogen peroxide was formed at 60 min.

The apparent formation rates of hydrogen peroxide and ozone in distilled water were determined from the slope of the plots of their concentrations over time.

3. Results and discussion

3.1. The comparison of removal efficiency of 4-CP, mineralization of TOC and energy efficiency in each electrical discharge reactor

In this study, all experiments were operated under the same conditions of input voltage at 16 kV, pulsed repetition rate at 100 Hz, electrode distance at 20 mm, oxygen flow rate at 0.2 m³/h, initial pH at 5.4 and initial conductivity at 1.5 μS/cm. Fig. 2 shows the comparison of removal of 4-CP in different electrical discharge reactors. After 40 min, 99.7% of 4-CP
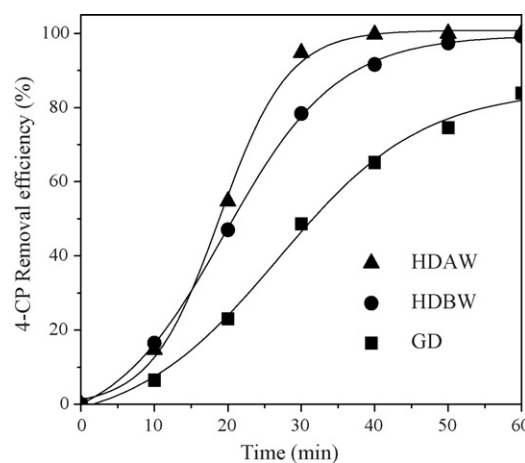

Fig. 2. Comparison of 4-CP removal in each electrical reactor.

was removed in HDAW reactor, 91.6% in HDBW reactor and 65.2% in GD reactor. The degradation of 4-CP in HDAW reactor was 8.1% larger than that in HDBW reactor, and 34.5% larger than that in GD reactor. Furthermore, the similar results can be obtained in the energy efficiency by calculating the value of G_{50}. As shown in Table 1, the single pulse energy from pulse-forming capacitance was 0.733 J in each reactor. The time for 50% of 4-CP degradation (t_{50}) in HDAW reactor was the shortest (18.8 min) and the value of G_{50} was the largest (1.18×10^{-9} mol/J). While in HDBW reactor the value of G_{50} decreased to 1.06×10^{-9} mol/J and t_{50} was 20.9 min. In GD reactor the value of G_{50} decreased to the lowest of all (0.718×10^{-9} mol/J) and t_{50} increased to 30.8 min. G_{50} was an expression of the energy efficiency for 4-CP removal. As the difference of 4-CP removal in three reactors was not very distinct, the G_{50} value in HDAW reactor was 10% higher than that in HDBW reactor and 60% higher than that in GD reactor. These results indicated that more energy efficiency was utilized in HDAW reactor than that in other reactors.

Total organic carbon (TOC) analyses were performed to investigate the degree of mineralization during the removal process of 4-CP in each reactor. The measurement results for each reactor are given in Table 2. The TOC of the solution treated for 60 min in HDAW reactor decreased by 62.6% from 28.6 to 10.7 ppm. The mineralization of TOC in HDAW reactor was 50% higher than that in HDBW reactor (12.2%) and 53.5% higher than that in GD reactor (9.1%).

Table 1
Energy efficiency of pulsed discharge treatment for 4-CP in each reactor

Reactor	Discharge modes	E_p (J/pulse)	t_{50} (min)	G_{50} ($\times 10^{-9}$ mol/J)
HDAW	Spark discharge in liquid Arc-like discharge in gas	0.733	18.8 ± 0.37	1.18 ± 0.024
HDBW	Spark discharge in liquid		20.9 ± 0.50	1.06 ± 0.026
GD	Arc-like discharge in gas		30.8 ± 1.36	0.718 ± 0.034

Table 2
The variation of pH, liquid conductivity and TOC of 4-CP solution in each reactor

Reactor	pH		Conductivity (μS/cm)		TOC (ppm)		Mineralization of TOC (%)
	Initial	Final	Initial	Final	Initial	Final	
HDAW	5.4	2.9	1.5	198.8	28.6	10.7	62.6
HDBW		3.1		145.5		25.1	12.2
GD		3.2		138.6		26.0	9.1

The degradation of 4-CP and energy efficiency in HDBW reactor was a little less than that in HDAW reactor, while that in GD reactor was much lower than that in HDAW reactor, which indicated that degradation of 4-CP and energy utilization were mainly performed in the liquid phase, and gas discharge was beneficial to the removal of 4-CP more efficiently. In addition, the mineralization of TOC in HDAW reactor was much higher than that in other two reactors. It indicated that the combination of discharge in both liquid phase and gas phase was beneficial to mineralizing TOC in comparison with separate discharge in liquid phase or gas phase. Therefore, the discharge in liquid phase and gas phase in HDAW reactor could degrade 4-CP more completely than in other two reactors.

The effect of discharge modes and active species (ozone, hydrogen peroxide, radicals, etc.) on removal of 4-CP and the formation of intermediates were further investigated to explore the reason of higher 4-CP degradation efficiency in HDAW reactor than in other two reactors.

3.2. Discharge modes in each electrical reactor

Fig. 3 depicts the discharge modes in each electrical reactor. In HDBW reactor, as shown in Fig. 3(a), spark discharge was produced between high voltage discharge electrodes and ground electrode with bright light. And in HDAW reactor, shown in Fig. 3(b), the intense plasma channels, appeared more similar to an arc-like discharge [11], was formed between the liquid surface and the ground electrode in gas phase with spark discharge in liquid phase. It was distinct that the intense plasma channels connected the sharp edge of ground electrode with high voltage discharge electrodes. In GD reactor, as shown in Fig. 3(c), each high voltage discharge electrode could produce plenty of gas phase non-thermal plasma channels above the water surface.

The discharge regions in HDAW and HDBW reactor were both between high voltage discharge electrodes and ground electrode, but the discharge region in GD reactor was only in the gas phase from high voltage discharge electrodes to liquid surface, so that the discharge region in GD reactor was less than in HD reactors. The discharge region may affect the degradation of 4-CP and formation of active species.

3.3. Ozone formation in gas phase and liquid phase

Ozone was one of the most important active species produced in gas phase with oxygen existing and then diffused into the liquid phase [22]:
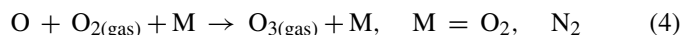
$$O_{2(gas)} + e \rightarrow O + O + e \tag{3}$$

$$O + O_{2(gas)} + M \rightarrow O_{3(gas)} + M, \quad M = O_2, \quad N_2 \tag{4}$$

$$O_{3(gas)} \rightarrow O_{3(aq)} \tag{5}$$

Fig. 4(a) shows gas phase ozone formation in each electrical discharge reactor. The ozone produced largely in GD reactor for about 7.4 mmol/m^3, which was 2.3 times of that in HDBW reactor (3.1 mmol/m^3) and 4.7 times of that in HDAW reactor (1.6 mmol/m^3). The difference of ozone formation in each reactor could be explained by the utilization of high-energy electron. Because a part of high-energy electrons would attack the water molecules to form hydrogen peroxide and hydroxyl radical except for ozone. The main reactions were assumed to be as follows [5,6,18]:

$$H_2O \xrightarrow{e} H^\bullet + {}^\bullet OH \tag{6}$$
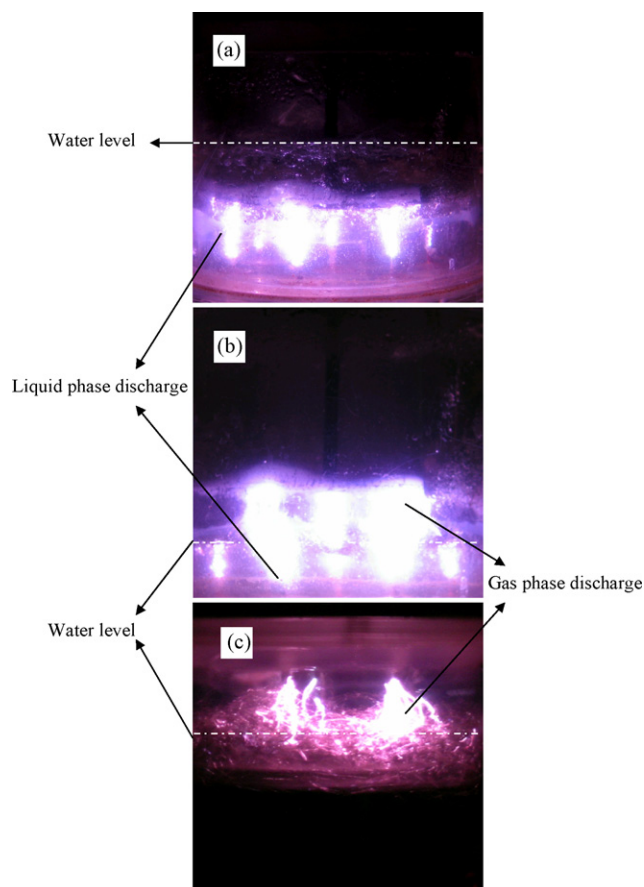
$$2H_2O \xrightarrow{e} H_2O_2 + H_2 \tag{7}$$

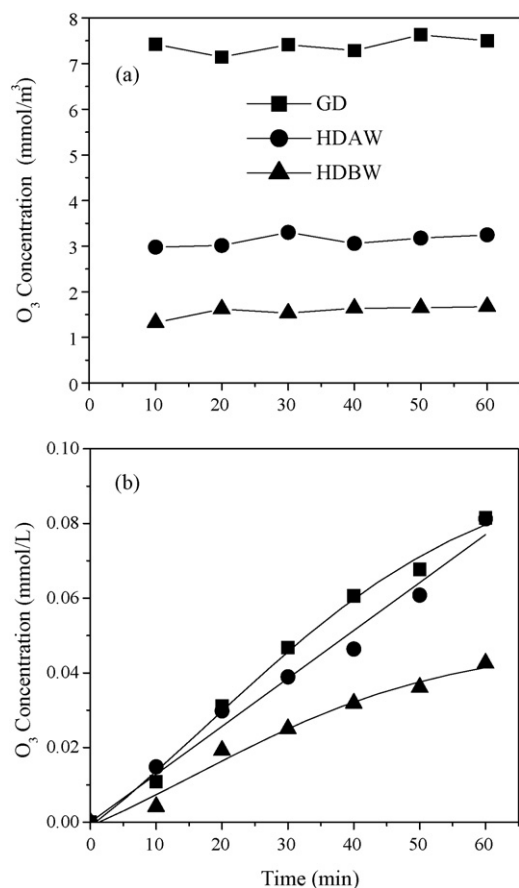Fig. 3. Discharge modes in HDBW reactor (a), HDAW reactor (b) and GD reactor (c).

Fig. 4. Ozone formation in each electrical reactor. (a) Gas phase and (b) Liquid phase.

In HDBW reactor, oxygen was dispersed into the liquid phase so that the discharge region for ozone formation was limited and water molecules could obtain plenty of electronic energy. However, in HDAW reactor, ozone could be formed not only in liquid phase with gas bubbling but also in gas phase where the discharge area was expended. In addition, the formation of ozone in GD reactor was mainly in gas phase and the consumption of high-energy electrons with water molecules was a little. Therefore, oxygen accepted more high-energy electrons to form plenty of ozone in GD reactor, followed by HDAW reactor and HDBW reactor. It also indicated that the discharge modes could affect the formation of gas phase ozone. Furthermore, the different polarity of gas phase electrodes may also affect the magnitudes of ozone concentrations in HDBW and GD reactor [11], more ozone produced by a discharge of positive polarity occurred in gas phase of GD reactor compared to a negative polarity discharge in HDAW reactor.

Although the formation of gas phase ozone in HDAW reactor was much less than in GD reactor, the formation of liquid phase ozone in HDAW reactor was close to that in GD reactor. As depicted in Fig. 4(b), the concentration of ozone in HDAW reactor was a little less than that in GD reactor during the discharge process. The formation rate of liquid phase ozone was about 2.13×10^{-8} mol/(L s) in HDAW reactor, which was similar with that in GD reactor (2.35×10^{-8} mol/(L s) and about

twice of that in HDBW reactor (1.25×10^{-8} mol/(L s)). It can be concluded that more ozone was diffused into liquid phase in HDAW reactor than in HDBW reactor.

After 60 min of spark discharge in HDAW reactor, the formation of ozone per energy input calculated by the value of G using the Eqs. (1) and (2) was 9.1×10^{-9} mol/J, which was 8.3 times higher than the result with corona discharge (1.1×10^{-9} mol/J) with oxygen flowed above the liquid solution reported by Grymonpré et al. [10]. The experimental condition in reference was that treated volume of 0.78 L, input energy of 1.3 J/pulse and frequency of 60 Hz. The larger concentration of ozone diffused into liquid phase in HDAW reactor was probably due to the higher ozone mass transfer by gas bubbling into the liquid phase in comparison to oxygen flowed above the liquid solution in reference [10].mol/(L·s)

3.4. Hydrogen peroxide formation in liquid phase

The formation of hydrogen peroxide in distilled water in different electrical discharge reactor is performed in Fig. 5. It was obtained that the formation rate of hydrogen peroxide in HDAW reactor (1.27×10^{-6} mol/(L s) was 1.5 times of that in HDBW reactor (0.85×10^{-6} mol/(L s)) and 2.2 times of that in GD reactor (0.59×10^{-6} mol/(L s)). Hydrogen peroxide was mainly formed by water ionization with high-energy electron (as seen in Eq. (7)) and active radical ($H^\bullet$, $^\bullet OH$, $HO_2^\bullet$) synthesis (as seen in Eqs. (8)–(11)) [5,6].

$$2^\bullet OH \rightarrow H_2O_2 \tag{8}$$

$$H^\bullet + O_2 \rightarrow HO_2^\bullet \tag{9}$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \tag{10}$$

$$H^\bullet + HO_2^\bullet \rightarrow H_2O_2 \tag{11}$$

In addition, ozone has the potential to convert free electrons and $H^\bullet$ into a strong oxidizing $^\bullet OH$ [18,23]:

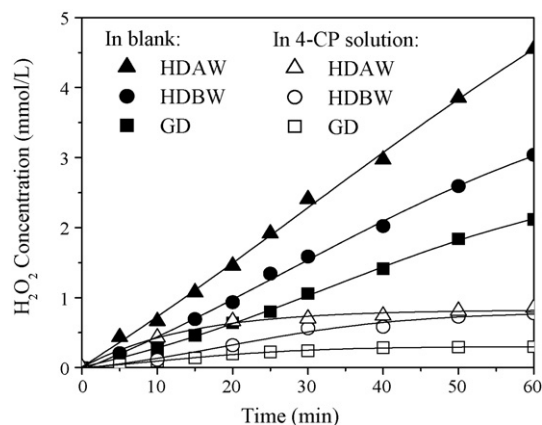$$e^- + O_3 \rightarrow O_3^{\bullet-} \tag{12}$$

$$H^\bullet + O_3 \rightarrow HO_3^\bullet \tag{13}$$

$$O_3^{\bullet-} + H^+ \rightarrow HO_3^\bullet \tag{14}$$

Fig. 5. Hydrogen peroxide formation in each electrical reactor.

$$HO_3^{\bullet} \rightarrow {}^{\bullet}OH + O_2 \qquad (15)$$

And then ${}^{\bullet}OH$ could synthesize hydrogen peroxide by Eq. (8). If discharge occurred in HDAW reactor without bubbling, the formation of hydrogen peroxide was only about 1.87 mmol/L after 60 min discharge, which was about 2.4 times less than that with oxygen bubbling (4.55 mmol/L). This result showed that the oxygen bubbling led to high hydrogen peroxide. In addition, when the gas flow rate increased from 0.05 to 0.3 m^3/h, the concentration of hydrogen peroxide increased from 0.34 to 5.97 mmol/L. It was also observed that the high gas bubbling flow rate was beneficial to formation of hydrogen peroxide. During bubbling, more initial bubbles accelerated electrons to obtain higher energy electrons so that excitation and ionization of water molecules occurred in the bubbles and solution to produce more radicals [14,16].

In HDBW reactor, the hydrogen peroxide was formed distinctly by discharge in liquid phase and the effect of ozone was little because the concentration of ozone was the least of all. While in GD reactor, the discharge was mainly produced in gas phase, so that the effects of high-energy electron attacking water molecule and active radical synthesis in liquid phase were small. In HDAW reactor, hydrogen peroxide was formed not only by discharge in liquid but also by ozone enhancement. Therefore, the concentration of hydrogen peroxide in HDAW was larger than that in other reactors, and the discharge modes influenced the formation of hydrogen peroxide as well.

After 60 min of spark discharge in HDAW reactor, the higher amount of hydrogen peroxide produced per energy input was 5.2×10^{-7} mol/J in comparison to the result with corona discharge (3.8×10^{-7} mol/J) reported by Grymonpré et al. [10]. In our study, the electrode distance was 2.0 cm for spark discharge, while 5.0 cm in the cited paper for corona discharge. In the spark discharge, the current density was higher, and the excitation and ionization were more intense, so that more ${}^{\bullet}OH$ radicals were formed [6,7]. In addition, the intensity of ultraviolet and shockwave was much higher with spark discharge than that with corona discharge, and ultraviolet photolysis and oxidation by active radical such as ${}^{\bullet}OH$ radicals were enhanced [17,18]. Therefore, the liquid phase spark discharge in HDAW reactor was obviously efficient for hydrogen peroxide formation compared to corona discharge.

Fig. 5 also shows the formation of hydrogen peroxide in 4-CP solution in each electrical discharge reactor. The concentration of hydrogen peroxide was obviously lower in 4-CP solution than in distilled water. Compared with the change of hydrogen peroxide concentration in distilled water and 4-CP solution, there were 3.7 mmol/L, 2.26 mmol/L and 1.82 mmol/L of hydrogen peroxide were utilized for 4-CP removal in HDAW, HDBW and GD reactor, respectively. As the utilization of hydrogen peroxide in HDAW reactor was the largest, it was helpful to degrade 4-CP and mineralize TOC completely.

As well known, little 4-CP was degraded by direct oxidation of hydrogen peroxide, so the direct reaction of hydrogen peroxide with 4-CP was neglectable. On the one hand, the hydrogen peroxide could be formed by hydroxyl radical synthesis, as seen in Eqs. (8)–(11). When hydroxyl radical reacted with 4-CP, the formation of hydrogen peroxide was interfered. On the other hand, hydroxyl radical's consumption accelerated the hydrogen peroxide decompose, as seen in Eqs. (16)–(18) [5,18]:

$$H_2O_2 \xrightarrow{hv} 2{}^{\bullet}OH \qquad (16)$$

$$H^{\bullet} + H_2O_2 \rightarrow H_2O + {}^{\bullet}OH \qquad (17)$$

$$e^- + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- \qquad (18)$$

In order to investigate the effect of hydrogen peroxide on 4-CP removal, the radical scavenger was added into the solution to capture the active radicals. It was found that the concentration of hydrogen peroxide was only 0.46 mmol/L in HDAW reactor with radical scavenger adding, which validated that generation of hydrogen peroxide was interfered by hydroxyl radical reaction with organic compounds.

3.5. Effect of active radicals on 4-CP removal

Active radicals in liquid, such as $O^{\bullet}$ and ${}^{\bullet}OH$, were important oxidants to react with 4-CP and intermediate products in pulsed high voltage discharge system. Fig. 6 shows the degradation of 4-CP with adding *tert*-butyl alcohol as a radical scavenger in different reactors. The degradation efficiency of 4-CP in HD reactors was similar with each other about less than 50% after 60 min treatment. While the conversion of 4-CP in GD reactor was less than that in HD reactors, which was only about 25% after 30 min, and degradation trend changed slowly from 30 to 60 min. Compared with 4-CP removal in Fig. 3, the effects of active radicals on removal of 4-CP was about 53–69% in HDAW reactor and 58–64% in HDBW reactor after 20 min. While in GD reactor, the effect of radicals on removal of 4-CP was only about 16% after 20 min and then increased to 59% after 40 min. It was because that the concentration of hydrogen peroxide in GD reactor was small in the first 20 min and ${}^{\bullet}OH$ formed by hydrogen peroxide was small as well. After 20 min, the effect of active radicals was significant. It was obviously to find that the effect of active radicals oxidation on 4-CP removal played an important role in these three reactors.
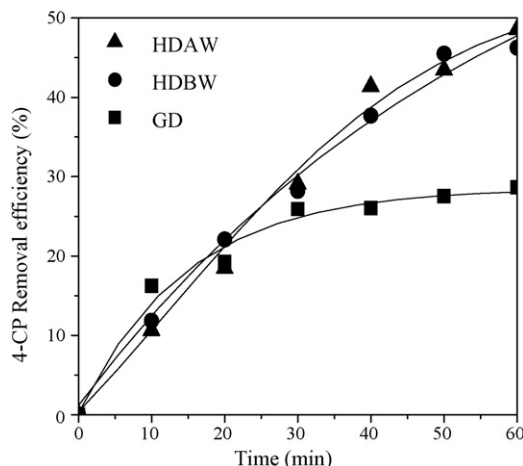

Fig. 6. Degradation of 4-CP with scavenger added in each electrical reactor.

Ozone could react directly with dissolved substances, and the direct oxidation reaction rate of ozone with 4-CP was about 2437 L/(mol s) [24], which was less than the reaction rate of •OH radical with 4-CP (7.6×10^9 L/(mol s)) [25]. However, the concentration of ozone was about 0.04–0.08 mmol/L at 60 min, so the direct oxidation of ozone also affected on 4-CP removal. The removal efficiency between 30 and 50% with radical scavenger adding respected to the effects of ozone direct oxidation and several physical processes such as ultraviolet radiation, intense shock waves and pyrolysis.

In conclusion, combination of spark discharge in liquid phase and arc-like discharge in gas phase in HDAW reactor was beneficial to producing plenty of hydrogen peroxide and ozone. Hydrogen peroxide and ozone converted to active oxidants such as hydroxyl radicals, as seen in Eqs. (12)–(18). The major mechanism for the degradation was due to hydroxyl reactions and accompanied with ozone direct reaction. Therefore, plenty of hydrogen peroxide and ozone formed in HDAW reactor enhanced 4-CP removal and TOC mineralization.

3.6. Comparison of intermediates formation in each reactor

The changes of pH and liquid conductivity was depicted in Table 2 to reveal intermediates characteristics of 4-CP in detail. During removal of 4-CP in each reactor, the pH all decreased and liquid conductivity increased. In the case of 4-CP solution, in addition to hydrogen peroxide, other substances such as organic acids may be produced and ionized plenty of ions, which resulted in the solution becoming more acidic and higher liquid conductivity with increasing residence time. And the organic acids such as formic acid, acetic acid and oxalic acid, were determined by IC in our study, which was in agreement with above-mentioned discussion of pH and liquid conductivity change. In HDAW reactor, the pH decreased from 5.4 to 2.9, which were lower than that in other reactors (3.1 in HDBW reactor and 3.2 in GD reactor). And the liquid conductivity of 4-CP solution increased from 1.5 to 198.8 μS/cm in HDAW reactor, which was higher than that in HDBW reactor (145.5 μS/cm) and GD reactor (138.6 μS/cm). The results indicated that small molecules such as organic acids produced in HDAW reactor was more than in other two reactors. Therefore 4-CP was degraded more completely in HDAW reactor than in other reactors.

Samples of solution treated in three reactors were all analyzed by HPLC. The kinds of intermediates in each reactor were similar with each other because the gas additive into each reactor was the same. Fig. 7 shows the typical HPLC chromatogram during the degradation of 4-CP. As could been seen, aromatic substances including 1,4-benzoquinone, catechol, hydroquinone, and 4-chlorocatechol were determined, which were coincident with that reported in the literature [26]. The main suggested pathway for 4-CP degradation was that •OH radical attacked on the ortho position of OH– to form 4-chlorocatechol or the Cl-position to form hydroquinone. Electrophilic attack of an ozone molecule on 4-CP yielded the same intermediates as in the case of •OH radical attack. Then these primary intermediates (4-chlorocatechol and hydroquinone) were converted to secondary intermediates, such as 1,4-benzoquinone, catechol, formic acid,
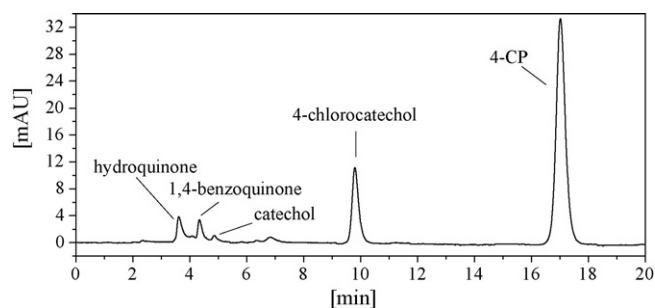
Fig. 7. The typical HPLC chromatogram during the degradation of 4-CP.

acetic acid, oxalic acid and so on. Ozone also reacted through a 1, 3-dipolar cycloaddition mechanism, which caused direct ring cleavage of the aromatic ring. Finally the intermediates were mineralized to H_2O, CO_2, including inorganic ions Cl^-. The detailed degradation pathway was discussed in our other study [27]. Therefore, we selected 4-chlorocatechol and hydroquinone as typical primary oxidation intermediates during degradation of 4-CP.

Even though the kinds of intermediates produced in each reactor were similar with each other, the amounts of intermediates formed in each reactor were very different. The concentration of 4-chlorocatechol and hydroquinone during the degradation of 4-CP are shown in Fig. 8. The maximum concentration of 4-chlorocatechol formed in HDAW reactor (0.053 mmol/L) was a little higher than that in HDBW reactor (0.032 mmol/L) and GD reactor (0.043 mmol/L). But 4-
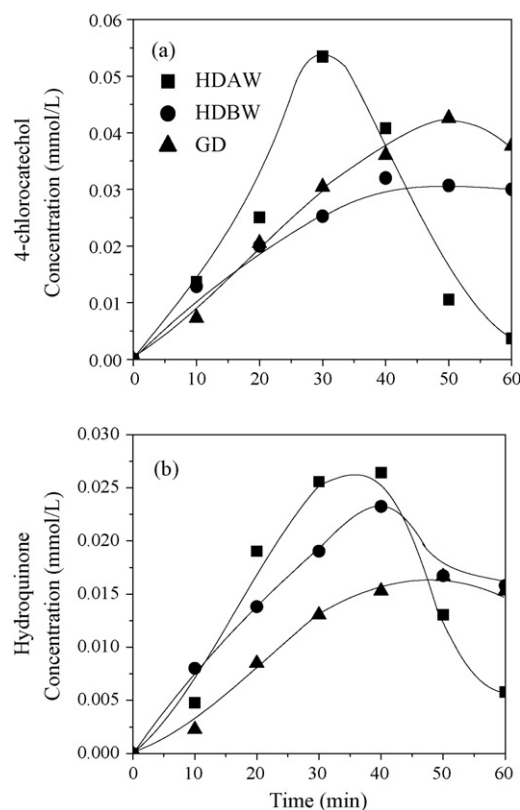
Fig. 8. Formation of byproducts in each electrical reactor. (a) 4-Chlorocatechol and (b) hydroquinone.

chlorocatechol was degraded to a much lower concentration of 0.004 mmol/L after 60 min in HDAW reactor, which was 13% of that in HDBW reactor (0.030 mmol/L) and 11% of that in GD reactor (0.038 mmol/L). The same results were obtained for comparison of hydroquinone formation and degradation in these three reactors. Therefore, the conversion of intermediates in HDAW reactor was faster than that in other two reactors, which implied that combination of high ozone and high hydrogen peroxide in HDAW reactor was beneficial to extend the degradation range of intermediates.

After 60 min discharge, there were 0.389 mmol/L of 4-CP was degraded in HDAW reactor, 0.386 mmol/L in HDBW reactor and 0.326 mmol/L in GD reactor. And the concentration of primary oxidation intermediates was only 0.0098 mmol/L in HDAW reactor, which was about 20% of that in HDBW reactor (0.046 mmol/L) and GD reactor (0.053 mmol/L). Hence, the amount of primary oxidation intermediates accounted typically for only about 2.52% of total conversion of 4-CP at 60 min in HDAW reactor, 11.90% in HDBW reactor and 16.24% in GD reactor. It was apparent that 4-CP in HDAW reactor was degraded completely and converted into the secondary intermediates or mineralized to H_2O, CO_2 quickest of all. The conclusion supported the result that the mineralization of TOC in HDAW reactor was much higher than that in other two reactors.

4. Conclusions

Three types of electrical discharge reactors were compared for removal of 4-CP. In HDAW reactor, 99.7% of 4-CP was removed after 40 min, and 62.6% of TOC was mineralized after 60 min, and 1.18×10^{-9} mol/J of energy efficiency was utilized, all of those values were higher than that in HDBW and GD reactor. In the case of HDAW reactor, liquid phase spark discharge and gas phase arc-like discharge was formed simultaneously. The discharge modes could affect the formation of ozone and hydrogen peroxide. The discharge in gas phase could produce higher concentration of ozone than discharge in liquid phase. Hydrogen peroxide was mainly formed in liquid phase and ozone could enhance the formation of hydrogen peroxide. The combination of ozone in gas phase and hydrogen peroxide in liquid phase enhanced the degradation of 4-CP. The mechanism of degradation was mainly to the oxidation by radicals in all of three reactors and the effect of radical oxidation on removal of 4-CP in HDAW reactor was the largest. Furthermore the typical primary oxidation intermediates of 4-CP (4-chlorocatechol and hydroquinone) were degraded more rapidly in HDAW reactor than in other two reactors.

In conclusion, the combination of discharge in both liquid phase and gas phase could enhance the degradation of 4-CP. It appears that novel HDAW reactor is promising for 4-CP removal.

Acknowledgments

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