

# An electrohydraulic discharge system of salt-resistance for *p*-chlorophenol degradation

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## Abstract

An electrohydraulic discharge system of salt-resistance has been developed and analyzed for *p*-chlorophenol (4-CP) degradation. The discharge electrodes used in the system consisted of four steel acupuncture needles ( $\varnothing$  0.25 mm) which were covered by capillaries through which gas was supplied to the discharge region, forming gas bubbles. In the comparing system, the aeration capillaries were encapsulated and the bubbling was cancelled. It was confirmed that introducing gas into the discharge zone could reduce the affection of salt content in the pulsed high-voltage electrohydraulic discharge system. In the non-bubbling system, the formation of active species and 4-CP degradation was sharply influenced by increasing salt content. The formation rate of hydroxyl radical and hydrogen peroxide was decreased almost to zero and the 4-CP was hardly removed as the NaCl concentration was higher than  $5.0 \times 10^{-3} \text{ mol L}^{-1}$ . But in the developed system, the formation rates were changed little with increasing the salt concentration. Increasing the NaCl concentration high to  $0.1 \text{ mol L}^{-1}$ , the hydroxyl radical formation rate was  $4.43 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$ , and the removal rate of 4-CP was still high, where more than 90% was removed in 18 min.

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**Keywords:** Electrohydraulic discharge; Salt content; *p*-Chlorophenol degradation; Hydroxyl radical

## 1. Introduction

Electrohydraulic discharge has been proved to be effective for numerous organic compounds degradation, and thus received a considerable attention for wastewater treatment [1–5]. The basic mechanism of it is the formations of plasmas, which can promote both physical and chemical processes leading to strong UV light, local high temperature and intense shock waves and the formations of chemically active species such as  $\bullet\text{OH}$ ,  $\text{H}\bullet$ ,  $\text{O}\bullet$ ,  $\text{O}_2\bullet^-$ ,  $\text{HO}_2\bullet^-$ ,  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ , etc., respectively [6–13]. The pulsed high-voltage discharge in water does not need any aids, and it is a combination of chemical, photochemical, ultrasonic and electrical process.

Industrial wastewater is usually regarded as electrolytes due to the existence of various salts, which have a heavy effect on the organic pollutants degradation in the pulsed high-voltage electrohydraulic discharge system. Several literatures have noticed the

effects of salt content, which was often expressed by the conductivity of the liquid in the discharge system. Sun et al. found that the radical emission intensity reached a maximum at conductivities between 10 and  $80 \mu\text{S/cm}$ , and was stronger in the KOH solution than that in the KCl solution. They concluded that low conductivity of the solution limited the development of corona in the discharge reactor, but it was difficult to build up a strong electric field in the high salt concentration liquid in the discharge zone [10]. Sato observed that the hydroxyl radical density achieved the maximum at conductivity of  $10 \text{ mmol L}^{-1}$  [11]. Our previous work also confirmed that the addition of salt in the solution made the discharge style changing from spark to corona [14]. Therefore, conductivity, i.e., salt content, was an influential factor in an electrohydraulic discharge system. The influence of salt content should be reduced as the electrohydraulic discharge was applied to expanding use.

In present work, sodium chloride was selected as the model salt. The effect of salt content on *p*-chlorophenol (4-CP) degradation and active species formation was explored in two contrastive electrohydraulic discharge systems. The reactor used in novel system (bubbling system) is designed to make

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a different construction of liquid–gas-discharge electrode from other works. The discharge needles and their tips were surrounded by bubbling gas and the gas was surrounded by water. Therefore, strong discharge could be kept still at high salt concentration in the non-equilibrium electrical field. For contrast experiments, the bubbling was cancelled (non-bubbling system). The objectives of this work are to present an electrohydraulic discharge system resistive to salt content, and the related mechanisms are also discussed.

## 2. Experimental

### 2.1. Setup

The schematic diagram of the pulsed high-voltage discharge system is shown in Fig. 1. The power supply was realized by making use of rotating spark gap to produce pulsed high-voltage. It consisted of a current limiting resistor (100 k $\Omega$ ), a transformer, a pulsed capacitance (2 nF) and a filter capacitor (1  $\mu$ F).

The discharge reactor was made of glass. The two sets of electrodes were placed in water. The lower system was connected with the output of the pulsed high-voltage and consisted of four acupuncture needles (steel  $\varnothing$  0.25 mm) which were covered by capillaries through which gas was supplied to the discharge region, forming gas bubbles. The inner diameter of the four capillaries was 2.0 mm and the height was 10.0 mm. In the bubbling experiments, pure oxygen was bubbled from a steel cylinder through the four capillaries and into the liquid chamber. The flow rate was kept on 60 L h<sup>-1</sup>. The needle tips were 0.5 mm higher than the upper end of the capillaries. The upper end of the reactor was plugged by a rubber plug with two holes. A 30 cm long screw stem, connecting with an iron plate in one end and a ground wire in the other, was through the center of the rubber. In the case of non-bubbling, the four aeration capillaries were encapsulated by 504 glues otherwise the condition was the same. The temperature (25 °C) within the reactor was controlled by the contact of cooling water. In all experiments the applied voltage was 20 kV at 150 Hz frequency. The electrode distance was 20 mm. After the gas flux was stabilized at 60 L h<sup>-1</sup>, 100 mL of distilled water, 100 mg L<sup>-1</sup> 4-CP solution or 3.0 g L<sup>-1</sup> 4-hydroxybenzoate (HDB) solution was poured into the reactor through upper end of the reactor. When the voltage was adjusted to a suitable value, the experiments began. 0.5 mL

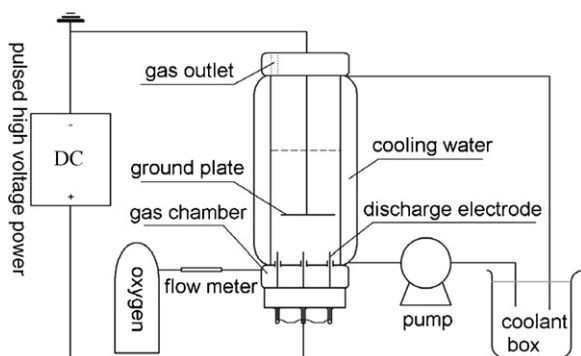


Fig. 1. The schematic of pulsed high-voltage discharge system.

of the samples was taken out of the reactor at an interval of 3 min. All experiments were conducted three times and gave reproducibility within 6%.

### 2.2. Analysis methods

An indirect method was used for determining  $\bullet$ OH formation rate. HDB was chosen as the probe for the advantage that 3,4-dihydroxybenzoic acid (DHDB) is the only isomer of quantitative reaction between HDB and  $\bullet$ OH [15]. If the concentration of HDB is high enough to trap almost all of the  $\bullet$ OH, the steady state of  $\bullet$ OH can be quickly achieved. The balance of molar species for  $\bullet$ OH can be written as:

$$\frac{d[\bullet\text{OH}]}{dt} \approx k_{\text{OH}} - k_{\text{HDB}}[\text{HDB}][\bullet\text{OH}] \approx 0 \quad (1)$$

where  $k_{\text{OH}}$  is the original formation rate in the pulsed high-voltage system and is the second-order rate constant between the HDB and  $\bullet$ OH.

Eq. (1) can be written as:

$$k_{\text{OH}} \approx k_{\text{HDB}}[\text{HDB}][\bullet\text{OH}] \quad (2)$$

$k_{\text{OH}}$  can be calculated by equation:

$$k_{\text{OH}} \approx k_{\text{HDB}}[\text{HDB}][\bullet\text{OH}] \approx \frac{d[\text{DHDB}]}{dt} \quad (3)$$

Experiments were conducted for the optimum of the original HDB concentration. It was found that DHDB formation rate was no longer increased with increasing HDB concentration higher than 3.0 g L<sup>-1</sup>. At this level, HDB concentration was decreased not more than 5% during discharge for 21 min. Therefore, 3.0 g L<sup>-1</sup> HDB was greater enough to trap almost all of the  $\bullet$ OH.

All reagents were used as received. HDB, DHDB and 4-CP was analyzed by HPLC (Knauer K-2005), equipped with a MS-2 C<sub>18</sub> column ( $\varnothing$  4.6 mm  $\times$  250 mm) and a UV detector. The UV detector wavelength was set at 262 nm for DHDB and HDB, and 278 nm for 4-CP. The mobile phase was prepared by dissolving 1 mL L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> and methanol. The ratio (v/v) was 50/50.

H<sub>2</sub>O<sub>2</sub> was determined by UV–vis Spectrophotometry (Tech-comp 8500) at wavelength of 400 nm [16].

### 2.3. The energy efficiency

The total input energy to the reactor in one pulse is calculated by the following:

$$E_{\text{in}} = \int_0^T u(t) \times i(t) dt \quad (4)$$

where  $u(t)$  and  $i(t)$  is the voltage and current at  $t$  time, respectively.  $T$  is the time-consuming of one pulse (about 5000 ns). The input energy efficiency of the reactor from the pulsed capacitor is calculated by the following [17,18]:

$$\theta = \left( \frac{E_{\text{in}}}{1/2CU^2} \right) \times 100\% \quad (5)$$

where  $C$  and  $U$  are the capacitance (3 nF) and the voltage of the pulsed capacitor (19.5 kV).

### 3. Results

#### 3.1. The effect of salt content on input energy efficiency

Table 1 shows the input energies ( $E_{in}$ ) and input energy efficiencies ( $\theta$ ) of one pulse into the reactor in the two systems. It is seen that the input energy and input energy efficiency increases with increasing salt concentration from 0 to  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> and changes little with further increasing the salt concentration. As a whole, the input energy and input energy efficiency in the bubbling system was higher than that in the non-bubbling system at the same salt concentration. The input energy efficiency varied significantly in the non-bubbling system compared with that of the bubbling one. For example, the input energy efficiency was only 3.33% at the salt concentration of 0 mol L<sup>-1</sup>, while it increased rapidly to 31.70% at the salt concentration of  $5.0 \times 10^{-4}$  mol L<sup>-1</sup>. With bubbling, the input energy and input energy efficiency varied less than that in the non-bubbling system: the lowest value of input energy and input energy efficiency were 0.22 J and 38.53% at the salt concentration of 0 mol L<sup>-1</sup> and the highest were 0.486 J and 85.11% at the concentration of  $5.0 \times 10^{-3}$  mol L<sup>-1</sup>. The input energy and input energy efficiency was changed little when varied the salt concentration from  $1 \times 10^{-3}$  to 0.1 mol L<sup>-1</sup>. The  $E_{in}$  was ranged from 0.422 to 0.486 J and the input energy efficiency was ranged from 73.90% to 83.54%, respectively.

#### 3.2. The effect of salt concentration on active species formation

##### 3.2.1. Hydroxyl radical formation

The hydroxyl radical formation rates are shown in Table 2. In the non-bubbling system, it is seen that the formation rate of hydroxyl radical is increased by increasing the salt concentration from 0 to  $1.0 \times 10^{-3}$  mol L<sup>-1</sup>, and achieves the best at the concentration of  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> while the input energy was also increased. But the formation rate of hydroxyl radical is decreased rapidly by further increasing the salt concentration to  $5.0 \times 10^{-3}$  mol L<sup>-1</sup>. Few hydroxyls radical was detected at the salt concentration of  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> or higher than that

Table 2

The formation rate ( $\times 10^{-7}$  mol L<sup>-1</sup> s<sup>-1</sup>) of hydroxyl radical in different salt concentration in the two systems

Salt content (mol L <sup>-1</sup> )	Non-bubbling		Bubbling oxygen	
	$k_{OH}$	$R$	$k_{OH}$	$R$
0	1.48 ± 0.06	0.9905	1.96 ± 0.02	0.9986
$1 \times 10^{-4}$	3.17 ± 0.15	0.9797	2.75 ± 0.04	0.9981
$5 \times 10^{-4}$	3.84 ± 0.32	0.9623	–	–
$1.0 \times 10^{-3}$	5.19 ± 0.45	0.9679	2.47 ± 0.06	0.9946
$5.0 \times 10^{-3}$	6.7 ± 0.08	0.9346	–	–
$1 \times 10^{-2}$	0	0	2.61 ± 0.13	0.9840
0.1	0	0	4.43 ± 0.29	0.9782

value, while the input energy had little change. With bubbling, the formation rate is increased with the increase in the salt concentration from 0 to  $1 \times 10^{-4}$  mol L<sup>-1</sup>, while the input energy was also increased. However, it changes little in the salt concentration ranged from  $1 \times 10^{-4}$  to  $1.0 \times 10^{-2}$  mol L<sup>-1</sup>, while the input energy had a little increase. The hydroxyl radical formation rate is increased when further increasing the salt concentration to 0.1 mol L<sup>-1</sup>, while the input energy had little change.

##### 3.2.2. Hydrogen peroxide formation

Fig. 2 shows the effect of salt content on hydrogen peroxide formation in the non-bubbling system. It is seen that the hydrogen peroxide is almost increased in line as the salt concentration is ranged in 0– $1.0 \times 10^{-3}$  mol L<sup>-1</sup>. But the yields are decreased sharply at the concentration of  $5.0 \times 10^{-3}$  mol L<sup>-1</sup>. There is almost no hydrogen peroxide detected at the concentration of  $1.0 \times 10^{-2}$  mol L<sup>-1</sup>. Keeping the salt concentration at  $5.0 \times 10^{-2}$  or 0.1 mol L<sup>-1</sup>, similar results were gotten as that at  $1.0 \times 10^{-2}$  mol L<sup>-1</sup>.

Salt content only had very little effect on the hydrogen peroxide formation in the bubbling system. Fig. 3 shows some results. It is seen that the yields of hydrogen peroxide is almost same at the salt concentration of 0,  $1.0 \times 10^{-3}$  and 0.1 mol L<sup>-1</sup>. The yields are slightly higher at  $1 \times 10^{-4}$  mol L<sup>-1</sup>.

Table 1

The total input energies and energy utilization efficiencies in different salt concentration in the two reactors

Salt content (mol L <sup>-1</sup> )	Non-bubbling		Bubbling oxygen	
	$E_{in}$ (J)	$\theta$ (%)	$E_{in}$ (J)	$\theta$ (%)
0	0.032	3.33	0.220	38.53
$1 \times 10^{-4}$	0.124	30.65	0.270	56.04
$5 \times 10^{-4}$	0.267	31.70	0.346	60.59
$1.0 \times 10^{-3}$	0.429	40.28	0.422	73.90
$5.0 \times 10^{-3}$	0.401	40.63	0.486	85.11
$1 \times 10^{-2}$	0.390	59.37	0.456	79.86
0.1	0.438	75.13	0.477	83.54

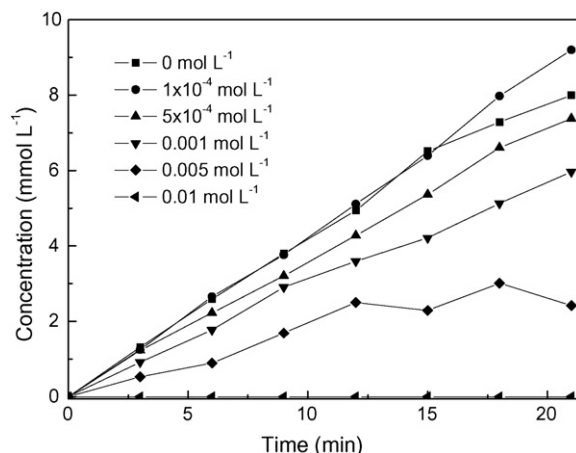


Fig. 2. The effect of salt content on hydrogen peroxide formation in the non-bubbling system.

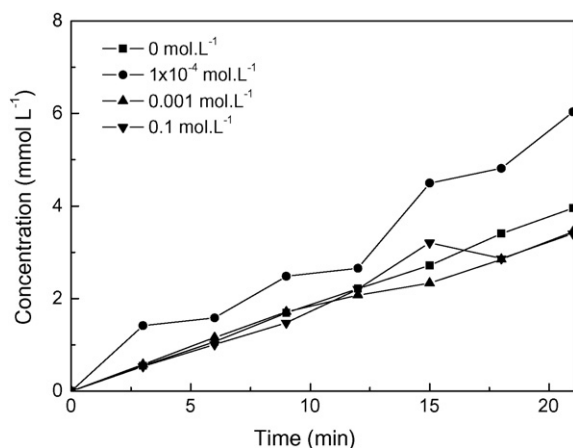


Fig. 3. The effect of salt content on hydrogen peroxide formation in the bubbling system.

Table 3  
The formation rate ( $\times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$ ) of hydrogen peroxide in different salt concentration in the two systems

Salt content ( $\text{mol L}^{-1}$ )	Non-bubbling		Bubbling oxygen	
	$k_{\text{H}_2\text{O}_2}$	$R$	$k_{\text{H}_2\text{O}_2}$	$R$
0	$6.53 \pm 0.13$	0.9963	$3.11 \pm 0.02$	0.9995
$1 \times 10^{-4}$	$7.23 \pm 0.05$	0.9995	$4.61 \pm 0.18$	0.9830
$5 \times 10^{-4}$	$5.77 \pm 0.05$	0.9993	$2.87 \pm 0.05$	0.9972
$1.0 \times 10^{-3}$	$4.67 \pm 0.07$	0.9981	$2.74 \pm 0.06$	0.9951
$5.0 \times 10^{-3}$	$2.81 \pm 0.2$	0.9290	$2.35 \pm 0.10$	0.9817
$1 \times 10^{-2}$	0	0	$2.45 \pm 0.10$	0.9790
0.1	0	0	$2.89 \pm 0.13$	0.9774

The formation rates calculated by Figs. 2 and 3 are shown in Table 3. It is seen that the variation trend of hydrogen peroxide formation rates has a little difference with that of hydroxyl radical formation rate in the same range of the salt concentration. In the non-bubbling system, with the salt concentration increased from  $0 \text{ mol L}^{-1}$  to  $1 \times 10^{-4}$ ,  $5 \times 10^{-4}$  or  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ , the hydroxyl radical formation rate was increased while the hydrogen peroxide formation rate is only increased in the salt concentration of  $1 \times 10^{-4} \text{ mol L}^{-1}$  and decreased obviously in the salt concentration of  $5 \times 10^{-4}$  or  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  (Table 2). With bubbling, the hydrogen peroxide formation rate is increased about 1.4 times with increasing the salt concentration from 0 to  $1 \times 10^{-4} \text{ mol L}^{-1}$ , and decreased a little with increasing the salt concentration to  $5 \times 10^{-4} \text{ mol L}^{-1}$ . When the salt concentration is more than  $5 \times 10^{-4} \text{ mol L}^{-1}$ , increasing salt concentration has little effect on the formation rate of hydrogen peroxide. Similar as the hydroxyl radical formation, few hydrogen peroxide is produced in the salt concentration of  $1.0 \times 10^{-2}$  or  $0.1 \text{ mol L}^{-1}$  in the non-bubbling system.

Table 4  
 $G_{18}$  values (%) at different salt concentration in the two systems

Salt content ( $\text{mol L}^{-1}$ )	0	$1 \times 10^{-4}$	$1.0 \times 10^{-3}$	$5.0 \times 10^{-3}$	0.01	0.1
Bubbling	59.41	–	71.71	–	48.72	89.86
Non-bubbling	23.54	71.71	97.07	4.33	0.22	–

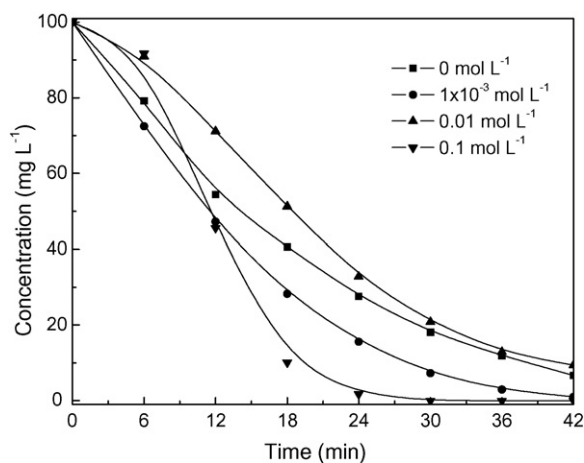


Fig. 4. The effect of salt content on 4-CP degradations in the bubbling system.

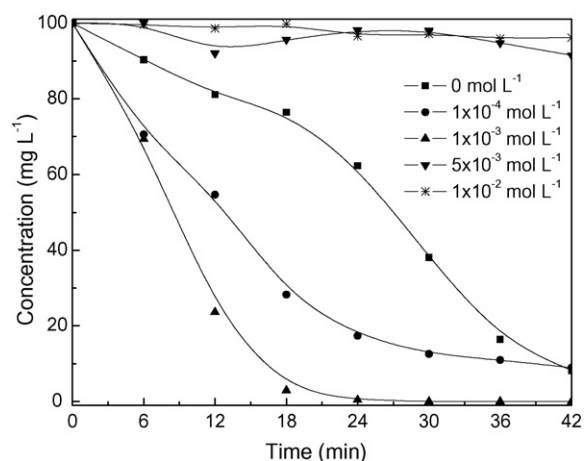


Fig. 5. The effect of salt content on 4-CP degradations in the non-bubbling system.

### 3.3. The effect of salt content on 4-CP degradation

Fig. 4 shows salt concentration on 4-CP degradation in the bubbling system. It is seen that the removal rate of 4-CP varies lightly with the salt concentration ranging from 0 to  $0.1 \text{ mol L}^{-1}$ . The lowest removal percent in 42 min is more than 93% and the best removal percent is near 100%. In the non-bubbling system, the removal of 4-CP varies sharply by changing salt concentration (Fig. 5). The removal rate speeds up by increasing the concentration from 0 to  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  and drops quickly when further increasing the concentration to  $5.0 \times 10^{-3}$  or  $1.0 \times 10^{-2} \text{ mol L}^{-1}$ . The removal percent of 4-CP in 42 min is nearly 100% at the concentration of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ , and almost zero at the concentration of  $1.0 \times 10^{-2} \text{ mol L}^{-1}$ . Therefore, the 4-CP removal percent varies much less with salt content in the bubbling system than that in the non-bubbling system.

If  $G_{18}$  is defined as the removal percentage of 4-CP in 18 min, higher  $G_{18}$  value means faster removal rate. Table 4 shows the values of  $G_{18}$  in the two systems at different salt concentration. With bubbling,  $G_{18}$  is increased by about 12% when the salt concentration increases from 0 to  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ . It decreased by about 22% with further increase in the concentration up to  $1.0 \times 10^{-2} \text{ mol L}^{-1}$ , but the best value of 89.96% is achieved at the salt concentration of  $0.1 \text{ mol L}^{-1}$ . In the non-bubbling system,  $G_{18}$  increases firstly with increasing salt concentration from 0 to  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  and then decreases with increasing salt concentration, giving the best value of 97.07% at  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ . However, further increase in salt concentration led to the declination of 4-CP removal. Only 4% of the 4-CP was degraded after discharge for 18 min at the concentration of  $5.0 \times 10^{-3} \text{ mol L}^{-1}$ , and it was not more than 0.22% removed at the concentration of  $1.0 \times 10^{-2} \text{ mol L}^{-1}$ . The value of  $G_{18}$  varied from 48.72% to 89.86% in the bubbling system, while it changed from 0.22% to 97% in the non-bubbling system. Therefore, 4-CP degradation was not so sensitively depended on the variation of the salt content in the bubbling system than that in the non-bubbling system.

From the experimental results presented above, it is seen that the 4-CP degradation rate is in accordance with the magnitude of hydroxyl radical formation rate. For example, when the hydroxyl radical formation rate achieved the highest, the 4-CP degradation rate reached the best. In the condition of non-bubbling, the biggest value for the above items was occurred at the salt concentration of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ . These results indicated that the degradation of 4-CP was mainly dependent on hydroxyl radical formation rate.

Additional, the electrodes had no noticeable changes in more than 1000 h discharge.

#### 4. Discussion

For non-bubbling system, Sun et al. concluded that the hydroxyl radical density was high in conductivity of  $10\text{--}80 \mu\text{S cm}^{-1}$  (salt concentration ranging from about  $1 \times 10^{-4}$  to  $2 \times 10^{-3} \text{ mol L}^{-1}$ ). He thought that this was caused by relatively weak discharge and small discharge current and streamer length at low salt concentration and difficult to build up a strong electric field in the high salt concentration liquid [10]. In the present work, similar results for hydroxyl radical formation were achieved in the non-bubbling system, but the different interpretation of the results is presented in this paper.

In the non-bubbling system, all the species around the needle tip is water molecules, and the hydroxyl radical and hydrogen peroxide is mainly produced by following [10,11,13]:



Increase in salt concentration maybe lead three alterations taking place in the discharge reactor. Firstly, it is the increase of the input energy for the resistance of the reactor decreased by increase in conductivity. More energy input into the reactor makes  $\text{H}_2\text{O}$  got more energy to form the active species.

The second is the increase in amount of ions in the solution, which delivers electrons to be accelerated to form high energy electrons in the field. High energy electrons may impact the water mole to form hydroxyl radical and hydrogen peroxide through Eqs. (6) and (7). It was known from above that the formation rate of hydroxyl radical increased with the salt concentration changed from 0 to  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  and reached the best at the salt concentration of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  in the non-bubbling system. Proper quantities of ions (ionic strength is not more than  $1.0 \times 10^{-3}$ ) made the input energy increased. When more energy could be used in the reactor, more hydroxyl radical were formed. Compared the hydrogen peroxide formation rate with the hydroxyl radical formation rate, it is seen that high energy electrons maybe speed up the decomposition of the hydrogen peroxide when the salt concentration is more than  $1 \times 10^{-4} \text{ mol L}^{-1}$ . The third is the increase in the ionic density in the liquid. The ions could compete with  $\text{H}_2\text{O}$  for the input energy in higher ion density (ionic strength was more than  $1.0 \times 10^{-3}$ ). When most of energy is gained by ions, the water mole could get little energy in the field. Hydroxyl radical and hydrogen peroxide might not be produced when  $\text{H}_2\text{O}$  could not get the energy in-situ, because Eqs. (6) and (7) are the main formation routes in the reactor. It was known from above that the formation of hydroxyl radical and hydrogen peroxide decreased sharply when the salt concentration was higher than  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ . Additional, the impacting probability between the high energy electrons and the ions was increased when the salt concentration was high. The ions could capture the electrons generated from the non-equilibrium field, though the active species formation process was changed and formation rate of hydroxyl radicals and hydrogen peroxide was relatively decreased. Therefore, in the non-bubbling system, the first and second alteration (increase in the input energy and increase in the amount of ions) took main role when the salt concentration was not more than  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ . But the third alteration (increase in ionic density) worked more and more when the salt concentration was more than that.

In the bubbling system, the case was something different. When gas was bubbled into reactor through the aeration microtubule (Fig. 1), the gas molecules would surround around the discharge electrode, i.e., tip of acupuncture needles. As pulsed high voltage was input, the molecules around the needle tip would be dissociated to plasma [19]:



The  $\text{O}^\bullet$  would react with  $\text{H}_2\text{O}$ :



Because the aeration microtubule was very slim (about 1 mm at diameter), some water molecules mixed with the gas molecules around the discharge electrodes got energy from the non-equilibrium field. When the salt concentration was higher than  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ , water molecules might not get energy from the field directly any more, but the gas molecules around the needle tip in the bubbling gas still had a chance to gain energy and

form oxygen plasma. The oxygen plasma would take part in the liquid chemical process, and the hydroxyl radical and hydrogen peroxide could also be produced by Eqs. (9) and (10). Therefore, the effect of salt concentration (salt content) on the hydroxyl radical formation in the bubbling system was less obvious than that in the non-bubbling system. From the Section 3.3, it was known that the input energy was increased from 0.22 to 0.486 J by increasing the salt concentration from 0 to  $1.0 \times 10^{-2} \text{ mol L}^{-1}$ , and it was merely varied at this level when further increasing the salt concentration. Compared them with the active species formation rate, it was resulted that the increased energy by higher salt concentration of  $1.0 \times 10^{-4}$  or  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  (from  $0 \text{ mol L}^{-1}$ ) did not induce more hydroxyl radical and hydrogen peroxide formation. It was thought that the increased energy was mainly utilized by the ions in the liquid. Above all, the interactions among the ions were strengthened and the degree of activity of ions was decreased at high salt concentration. It could not be excluded that salt ions would take part in the radical chemical process when their concentration was high [20]. The hydroxyl radical formation rate at the salt concentration of  $0.1 \text{ mol L}^{-1}$  was higher than that at the salt concentration of  $1.0 \times 10^{-3}$  or  $1.0 \times 10^{-2} \text{ mol L}^{-1}$ , while the input energy into the reactor was almost equal. This means the ions at very high salt concentration would promote the liquid chemical process to form hydroxyl radicals. Additional, the salt ions maybe promote the decomposition of hydrogen peroxide in higher salt concentration.

It is resulted that introducing gas into the discharge zone could reduce the affection of salt content in the pulsed high-voltage electrohydraulic discharge system. When the salt concentration was ranged from 0 to  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ , variations on salt concentration caused alterations on the waveform of input voltage and current. The alterations made the input energy changed. The input energy increased when increasing the salt concentration, which made the yields of hydroxyl radical changed in certain range, but the ions in the solution maybe took part in the chemical process to promote hydrogen peroxide decomposed in the liquid. When further increasing the salt concentration higher than  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ , the input energy had only little change. The hydroxyl radical and hydrogen peroxide formation rate had little change with bubbling, but it decreased to nearly zero in the non-bubbling system for most of the input energy was gained by ions. The coactions between the ions at higher salt concentration were strengthened and the degree of activity was decreased, which make the chemical process changed and affected the active species formation. Eventually, the 4-CP degradation rate was varied and was in accordance with the magnitude of the hydroxyl radical formation rate.

## 5. Conclusion

In the non-bubbling system, the input energy into the reactor and hydroxyl radical formation rate were increased with increasing the salt concentration ranged in  $0\text{--}1.0 \times 10^{-3} \text{ mol L}^{-1}$ . Further increasing the conductivity more than  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ , the input energy was not obviously increased any more, but the formation rate of hydroxyl radicals and hydrogen peroxide were

decreased sharply. In the bubbling system, the input energy into the reactor was varied similar as that in the non-bubbling system by increasing salt content, but the species formation rate had no obvious variation with bubbling. The effect of salt content was reduced by introducing gas into the discharge zone.

The degradation rate of 4-CP was in accordance with the magnitude of the hydroxyl radical formation rate. The removal rate and hydroxyl radical formation rate achieved the best value at the concentration of  $0.1 \text{ mol L}^{-1}$  with bubbling, where more than 90% of 4-CP was removed in 18 min. In the non-bubbling system, there were almost no active species formed and only little 4-CP was removed at the same salt concentration.

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