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Effect of Pulsed High-Voltage Discharge Process Combined with H_2O_2 and Fe^{2+} on Degradation of Phenol

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Degradation of phenol by pulsed high-voltage discharge is presented in this study. The effect of pulsed peak voltage, pH, temperature, conductivity, discharge gap, treatment time and phenol concentration on phenol degradation were investigated. In addition, the effect of ferrous(II) and hydrogen peroxide on pulsed high-voltage discharge process was evaluated. Experimental data show that the removal efficiency of phenol increased as the pulsed peak voltage, pH, temperature and treatment time increased and discharge gap and conductivity of solution decreased. The removal efficiency of phenol was 48, 46, 42 and 34 %, respectively at 10, 40, 90 and 160 ppm phenol solutions. The experiments were performed under discharge gap of 20 mm, an applied voltage of 24 kV, a solution pH of 10, a solution temperature of 30 ºC and a solution conductivity of 120 µS/cm. The degradation rate of phenol increased dramatically when Fe^{2+} and H_2O_2 were added into the solution. The removal efficiency of phenol reached 78, 72 and 71 % when 0.28-0.56 mM Fe^{2+} were added into phenol solutions of 40, 90 and 160 ppm, respectively. 100 % phenol removal efficiency was achieved when 20-40 mM H_2O_2 was added into phenol solutions of 10, 40, 90 and 160 ppm.

Keywords: Degradation, Ferrous ion, Hydrogen peroxide, Phenol, Pulsed high-voltage.

INTRODUCTION

The pulsed high-voltage discharge (PHVD) process has been a novel alternative method to advanced oxidation processes (AOPs)[1,2]. The PHVD process involves the formation of a non-thermal plasma in an aqueous solution, which can promote both physical and chemical processes. Physical processes include ultraviolet light emission, shock waves, electro-hydraulic cavitation, pyrolysis within plasma channels and supercritical water conditions. Chemical processes simultaneously occur in water, *i.e.* free radical reactions including the formation of short-live reactive radicals, such as hydroxyl radicals, hydrogen radicals, superoxide radicals, perhydroxyl radicals, and the simultaneous production of long-lived molecular species, such as hydrogen peroxide and ozone in aqueous phase[1-3]. These effects are responsible for oxidizing the organic matter in the wastewater.

As one of the advanced oxidation processes, pulsed high-voltage discharge technology has been used in wastewater treatment for the effective elimination of organic compounds, especially with high toxicity and low biodegradability such as degradation of phenol[3-5], chlorophenols[6-9] and organic dye[10-14].

A few researchers combined pulsed high-voltage discharge technology with other techniques to achieve better treatment efficiency, such as ferrous ion[5,10,13,15,16], hydrogen peroxide[4,15], activated alumina[5], titanium dioxide[17-19] and gas bubbling[9,10,15,16,20]. Sugiarto *et al.*[10] reported that the addition of a small amount of hydrogen peroxide and oxygen gas bubbling greatly increased the degradation rate of phenol. Shen *et al.*[15] showed that the effect of various gases (oxygen, argon, nitrogen and ozone) and chemical catalysts (ferrous ion and hydrogen peroxide) by pulsed electrical discharge improves the efficiency of phenol degradation. The effect of various gases on phenol degradation is ranked in following order: ozone > oxygen > argon > nitrogen[15]. Also, addition of ferrous ion and hydrogen peroxide increases the degradation of phenol[15]. Zhu *et al.*[5] shown that removal of phenol improved by activated alumina bed placed in pulsed high voltage electrical field. The removal rate of phenol was 72.1 % as air was added, and 88.2 % as 0.05 mM/L ferrous ion was added into the solution[5]. Wang *et al.*[19] developed a synergistic system of pulsed corona discharge combined with TiO_2 photocatalysis to investigate the degradation rate of phenol solution. The higher phenol removal (66.1 %) was achieved by this synergistic system as compared to pulsed discharge system (55.2 %).

In the pulsed high-voltage discharge system, the structure of the discharge reactor, which was decided by the configuration of the discharge electrode and ground electrode, could influence the formation of active species and organic degradation[21]. Therefore, the design of the discharge reactor is crucial

for expanded use of the technology[22]. The reactors with different geometrical configurations and various volume were developed such as a point-to-plate electrode configuration[9,15,20,23-25], ring-to-cylinder electrode configuration[26], wire to cylinder electrode configuration[27] and needle-point electrode configuration[28]. In this study, a novel reactor, the needle-point electrode reactor with the two electrodes all submerged into water is used.

The pulsed discharge producing from the discharge reactor has several modes such as streamer, spark and spark-streamer mixed corona discharge[10]. The different discharge modes are obtained by adjusting the distances between the needle and plate electrodes[10]. Sugiarto *et al.*[10] reported that the distance between the needle and plate electrodes was 30 mm for the streamer, 15 mm for the spark-streamer mixed, and 7 mm for the spark discharge mode. The spark-streamer mixed mode was found to be the most effective for the decoloration of dye in aqueous solutions in the study reported by previous workers[10,23]. The reported the effect of discharge characteristics, gas sources, peak voltage and conductivity on the density of free radicals. It showed that hydroxyl radical was mainly formed within the discharge channel and the yields of hydroxyl radicals and hydrogen peroxide were higher in case of spark discharge than the streamer or corona discharge with the equal input energy. It was reported that the pulsed discharge mode can affect the degradation of phenol in aqueous solution[4]. Regarding the application of radicals, the degradation of phenol in aqueous solution was studied by Sun *et al.*[2] and Sharma *et al.*[29] using a pulsed streamer corona discharge. Sun *et al.*[3] found that the removal efficiency of phenol in the aqueous solution was higher when it came to the spark discharge than to the streamer corona discharge at same reaction time.

In this study, the toxic and biorefractory organic pollutant phenol was chosen as the removal target for the technique of pulsed high-voltage discharge in water. A new type of reactor was used for phenol degradation in this study. The reactor and processing parameters that affect the degradation of phenol; such as pH, temperature, conductivity, applied voltage, electrode gap, reaction time were evaluated and optimum levels were determined. Furthermore, the effect of hydrogen peroxide and ferrous ion addition into phenol solution with various phenol concentrations on the degradation of phenol were also examined. The optimum dosage of hydrogen peroxide and ferrous ion was determined for various phenol concentrations.

EXPERIMENTAL

The pulsed high-voltage discharge system is shown in Fig. 1. The pulse high-voltage power supply with two rotating spark-gap switches was used to generate high-voltage pulse. A series of diodes are used to full-wave rectify the alternating current and it consisted of a DC high voltage producer. The peak voltage and pulse frequency are 0-24 kV and 0-70 Hz, respectively. Pulsed electrical discharge treatment of the phenol solution is provided by needle to point electrode. Four stainless-steel needles are inserted into the reactor from the top. The needles (steel, ϕ 1 mm) were used as the discharge electrode and they were attached to the pulsed high voltage supply. The stainless-steel electrodes were attached to reactor opposite to

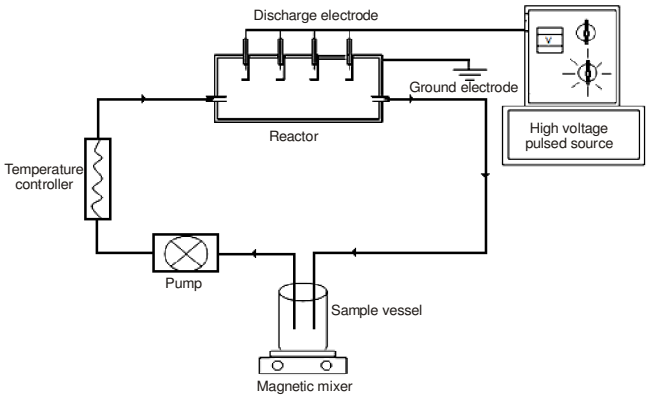

Fig. 1. Schematic diagram of pulsed voltage discharge system

the high voltage discharge electrode, and used as the ground electrode, which was attached to ground. The distance between discharge electrode and ground electrode can be changed. The discharge reactor was made of stainless steel rectangular with effective volume of 180 cm^3. The length, width and height of rectangular are 15, 3 and 4 cm, respectively. A magnetic stirring bar at the bottom of reactor was used to keep the solution mixed well. During treatment of phenol, the solution was circulated through the reactor and temperature controller by peristaltic pump.

Wastewater used in the experiment was prepared by distilled water and phenol. The initial phenol concentration was 20 ppm. The initial pH of phenol solution was adjusted by adding a little amount of H_2SO_4 (0.1 mol/L) and NaOH (0.1 mol/L). The KCl solution was used to adjust the initial conductivity in phenol solution. The volume of phenol solution was 250 mL and circulated with a flow rate of 20 mL/min. The concentration of phenol was measured with photometric method[30] using YSI 9500 spectrophotometer. pH and conductivity of solution were measured using WTW inolab model pH meter and Hach model conductivity meter, respectively. TOC concentration was monitored by VCPH Shimadzu model TOC analyzer. H_2O_2 was measured with YSI 9500 spectrophotometer using potassium iodide methods[30]. All analyses were repeated three times and the values represent the mean of the measurements. Samples were analyzed immediately after being removed from the reactor.

RESULTS AND DISCUSSION

Effect of initial pH and temperature on phenol degradation and optimization: The oxidation process is very sensitive to the pH and temperature of the aqueous solution. It is well known that an increase in the temperature of medium leads to an acceleration in the rate of the reaction. In this study, the effect of pH and temperature on the oxidation degradation of phenol was assessed using Box-Wilson statistical experimental design method. Box-Wilson statistical experimental design is a response surface methodology, which is an empirical modeling technique, devoted to the evaluation of the relationship of a set of controlled experimental factors and observed results[31]. This method was used to investigate the effects of the two independent variables (pH and temperature) on the response functions (phenol removal efficiency) and to

determine the optimal conditions maximizing the percent phenol removal in the pulsed high-voltage discharge process. Box-Wilson statistical experiment design was described in detail by Kusçu and Sponza[32]. The design principle includes three types of combinations, the axial (A), factorial (F), and center (C) points. The axial points include each variable at its extreme levels coded as -k and +k with the others at their center point level. The factorial points, with two levels of each of the factors coded as -1 and +1, include all combinations of intermediate levels. The center points coded as 0, is a single test at the average level of each variable. The coded values for the operating levels of the variables are used for convenience. pH (X_1) and temperature (X_2) were independent variables while the phenol efficiency (Y_1) was the objective function. The low, center and high levels of each variable (X_1, X_2) are designated as -1, 0, and +1, respectively. The pH (X_1) and temperature (X_2) was changed between 10 and 35 °C, pH (X_2) varied between 2 and 12.

The experimental conditions determined by the Box-Wilson statistical design method are presented in Table-1. The experimental conditions are 20 ppm initial phenol concentration, 120 µS/cm solution conductivity and 18 kV pulsed peak voltage. The response functions with determined coefficients were used to estimate phenol removal with the independent variables under different conditions (X_1, X_2). A static 5 computer program was used for determination of the coefficients of response function. Response function and coefficients are present in eqn.1. The predicted phenol removal in determine to eqn.1 and experimental phenol removal are depicted in Table-1. The correlation coefficient between the experimented and predicted values was R = 0.97, indicating good agreement between the measurement and predicted values of phenol removal efficiency.

$$Y = (-0.326) + (1.448) \times X_1 + (-0.162) \times X_2 + (4.46 \times 10^{-13}) \times X_1 \times X_2 + (-0.028) \times X_1 \times X_1 + (0.007) \times X_2 \times X_2 \quad (1)$$

From eqn. 1, we can conclude that pH (X_1) has a more profound effect on percent phenol removal while has a less effect with tempeture (X_2). Phenol removal efficiency obtained by solving the eqn. 1 for different values of pH and temperature is shown in Fig. 2. Phenol degradation was more effective at high pH than low pH value. Phenol removal efficiency increased from 3 to 13 % when pH was increased from 2 to 12 at 20 °C. The phenol degradation in alkaline solution (pH = 12) is approximately four times faster than in acidic solution-(pH = 2). Lukes et al.[28] reported that the efficiency of phenol removal (G37 % = 7.9×10^{-10} mol J^{-1}) in alkaline solution (pH = 10.6) was twice higher than in acidic conditions (G37 % = 4×10^{-10} mol J^{-1}) by use of hydrochloric acid (pH = 3.2). The higher solution pH is favorable for producing H_2O_2 and organic acid, and H_2O_2 could create $OH^{\bullet}$ radicals to degrade phenol in the further reaction[28]. The optimum pH for phenol degradation with pulse discharge process was depicted as 10.8 by *Zhu et al.*[5]. In this study, the phenol removal efficiency is 11, 11.5 and 12 %, respectively at pH = 10, 11 and 12, respectively. The optimum pH value was selected as 10 due to a very small increase (1 %) at phenol removal efficiency for pH values higher than 10. The effect of temperature on the phenol degradation was assessed within a temperature range of 10-35 °C when pH changed between 2 to 12. As seen in Fig. 2, phenol removal efficiency increased with increasing temperature at all pH values. Fig. 3 shows variation of phenol removal efficiency at different temperature and initial pH of 10. When the temperature was raised from 10 to 35 °C, phenol degradation increased from 10 to 14 % at the initial pH of 10. The increase in phenol removal efficiency was approximately 4 % when temperature was increased from 10 to 35 °C. The effect of temperature on phenol removal was very low. The phenol removal efficiency increased from 10 to 11 % when temperature was increased from 10 to 25 °C. The phenol removal efficiency was 11, 13 and 14 %, respectively at 25 , 30 and 35 °C. In this study, the optimum temperature of solution was selected as 30 °C due to both lower increase of removal efficiency and its energy needs. The results inferred that phenol degradation efficiency improved by higher pH and temperature

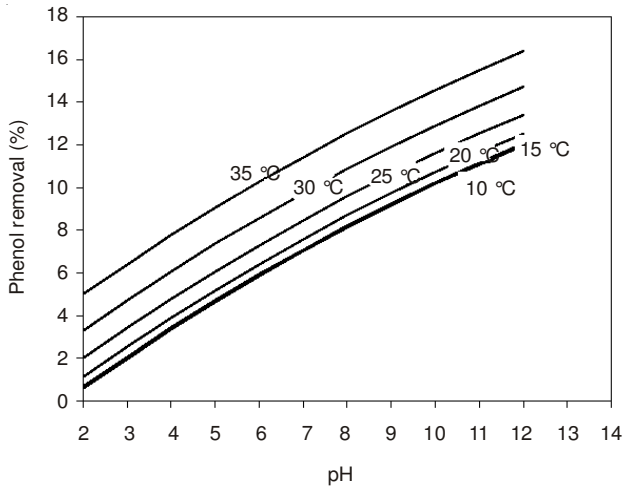

Fig. 2. Variation of phenol removal efficiency with the pH at different temperature values

TABLE-1
EXPERIMENTAL CONDITIONS OF THE BOX–WILSON STATISTICAL DESIGN AND EXPERIMENTAL AND PREDICTED VALUES OF PHENOL EFFICIENCY (Y) DEPEND ON THE INDEPENDENT VARIABLES (X_1, X_2)

Experimental point	pH (X_1)	Temperature (°C) (X_2)	Experimental phenol removal (%)	Predicted phenol removal (%)
A1	7.0 (0)	35 (+k)	12	11
A2	7.0 (0)	10 (-k)	6	7
A3	12 (+k)	22.5 (0)	12	13
A4	2.0 (-k)	22.5 (0)	2	1
F1	11 (+1)	13.66 (-1)	12	10
F2	3.0 (-1)	31.34 (+1)	5	6
F3	11 (+1)	31.34 (+1)	14	14
F4	3.0 (-1)	13.66 (-1)	3	3
C1	7.0 (0)	22.5 (0)	8	8

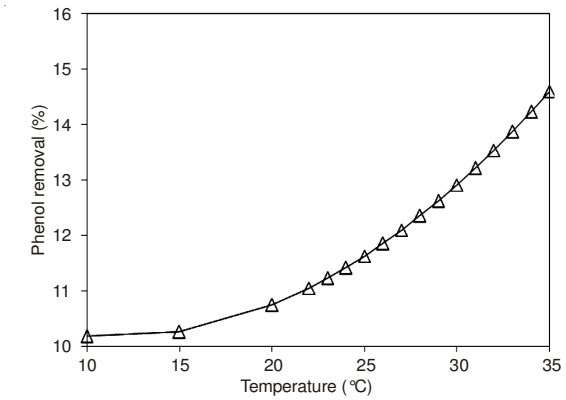

Fig. 3. Variation of phenol removal efficiency at different temperature at pH 10

during treatment with pulsed high-voltage discharge process. However the effect of temperature on phenol removal was lower as compared to pH. In this study, the optimum pH and temperature value that resulted in maximum removal of phenol was found to be 10 and 30 °C, respectively.

Effect of initial conductivity on phenol removal: The electrical conductivity of solution may affect the removal efficiency of the organic pollutant with pulsed high voltage discharge. The degradation of phenol was investigated at different initial solution conductivities. The initial electrical conductivity of 20 ppm phenol solution, at pH of 10 value was about 120 µS/cm. For determined the effect of conductivity on phenol removal, initial conductivity of phenol solution was adjusted to 270, 420 and 620 µS/cm, respectively using 0.01 M KCl. The experimental conditions were pH of 10, 30 °C , 20 ppm phenol concentration, 18 kV voltage and 60 min reaction time. Chen *et al.*[33] reported that phenol degradation decreased by increasing electrical conductivity of the solution. In our experiment, the phenol removal efficiency decreased from 19 to 17.5 % as solution conductivity increased from 120 to 620 µS/cm at 60 min reaction time (Fig. 4). The removal efficiency of phenol was low when the electrical conductivity of the solution was high. However, the experimental result showed that solution conductivity has a very low effect on degradation efficiency of phenol. As a result of experiment, initial electrical conductivity of solution was found to be 120 µS/cm to high phenol degradation.

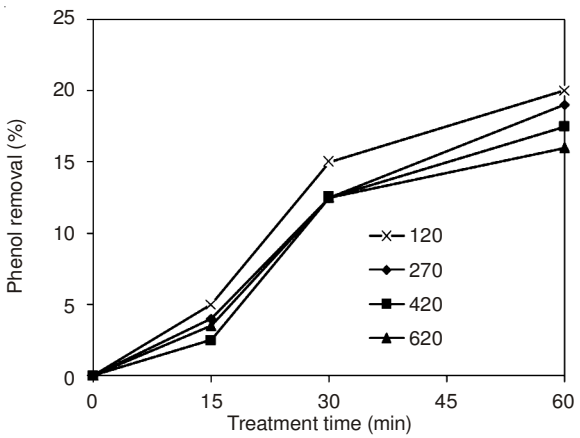

Fig. 4. Effect of electrical conductivity of solution on removal of phenol (120, 270, 420 and 620 µS/cm)

Effect of applied voltage and reaction time on phenol removal: The effect of applied voltage on phenol removal efficiency is shown in Fig. 5. The experiments were performed for 50 ppm phenol concentration at pH 10, 30 °C, and a conductivity of 120 µS/cm. It was shown that the degradation efficiency increased by enhancing the peak voltage. When peak voltage was increased from 6 to 24 kV, phenol efficiency increased from 14 to 29 % at 45 min reaction time. The results indicate that degradation efficiency of phenol was higher at high pulsed peak voltage. Zhu *et al.*[5] reported that when the gap between the discharge electrodes was unchanged, electric field intensity increased with increasing voltage. Li *et al.*[20] reported that discharge intensity increased with higher pulsed peak voltage and electric power injected into reactor and could increase the amount of active species (OH, O_3 and H_2O_2).

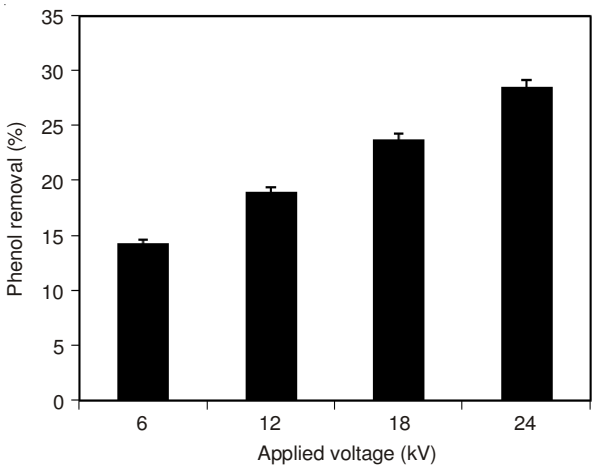

Fig. 5. Effect of applied voltage on removal of phenol

Fig. 6. shows H_2O_2 variations with reaction time and increasing voltage. The study was carried out with distilled water without adding phenol to determine H_2O_2 concentration produced form pulsed discharge. As shown in Fig. 6, the H_2O_2 concentration produced by pulsed discharge increased with reaction time and applied voltage. The H_2O_2 concentration increased from 60 to 260 ppm by increasing voltage from 6 to 12 kV at 60 min reaction time. Hydrogen peroxide concentration was 390 ppm at 24 kV of voltage. Hydrogen peroxide concentration increased also with reaction time. Hydrogen peroxide concentration increased from 160 to 390 ppm with increasing from 15 min to 60 min of reaction time at 24 kV of pulsed peak voltage. This led to an increase in the amount of oxidation of phenol over time. Fig. 7 shows the effect of reaction time on phenol removal efficiency at 24 kV of pulsed peak voltage. It is seen that the phenol degradation efficiency was increased by enhancing the treatment time. By increasing treatment time from 15 to 240 min, phenol degradation efficiency was enhanced from 10 to 68 % at 24 kV of pulsed peak voltage.

Effect of discharge gap on phenol removal: The discharge gap is an important parameter affecting the electrical field between the electrodes. The experiments were performed for 50 ppm phenol concentration at pH 10, 30 °C, 120 µS/cm and a peak voltage of 24 kV. The gaps between point electrode and ground electrode were adjusted between 10 and 40 mm.

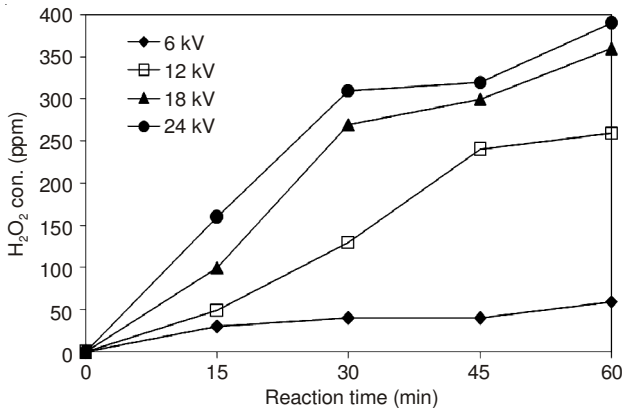

Fig. 6. H_2O_2 variation with applied voltage during reaction time

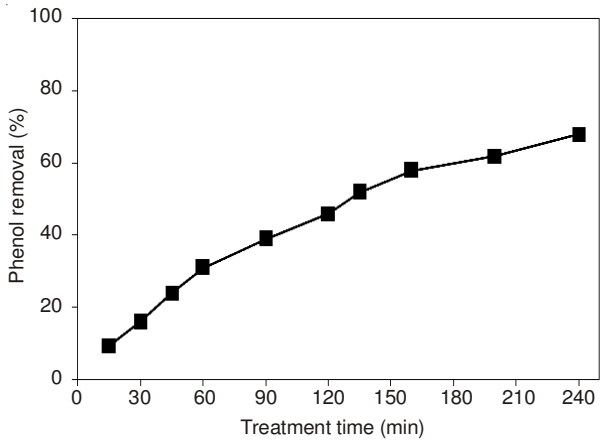

Fig. 7. Effect of reaction time on phenol removal efficiency at a pulsed peak voltage of 24 kV

Fig. 8 shows the effect of the discharge gaps on the phenol removal from aqueous solution. The removal efficiency of phenol was 24 and 21 %, respectively when the discharge gap is 20 and 30 mm at the discharge voltage of 24 kV. It is observed that the best gap between the tip of the point electrode and the ground electrode was about 20 mm. If the gap between electrodes is small, a spark discharge can occur on several needle points, and the corona discharge intensity of other points will descend rapidly on the same time; if the gap is big, the intensity will also be reduced because of the weakened electrical field[34]. Shidong *et al.*[35] reported that when the discharge gap was 4 cm, only weak corona could be seen near the needle electrode. When the discharge gap was shortened, the discharge became intense and the discharge streamers immerged and stretched to the plate electrode. When the discharge gap was shortened to 1 cm, a large discharge streamer formed between the electrodes. In another study, the distance between the needle and plate electrodes was reported as 30 mm for the streamer, 15 mm for the spark-streamer mixed, and 7 mm for the spark discharge mode[10]. In this study, the distance between discharge and ground electrodes with 20 mm was found to be the most effective for the degradation of phenol in aqueous solutions and was reported to form the spark-streamer mixed mode.

Removal of phenol with only pulsed discharge: Fig. 9 shows removal efficiency of phenol at different phenol concentrations by pulsed discharge. The experiment was carried out under pH 10, 30 °C, 120 µS/cm, 20 mm discharge gap, 24 kV

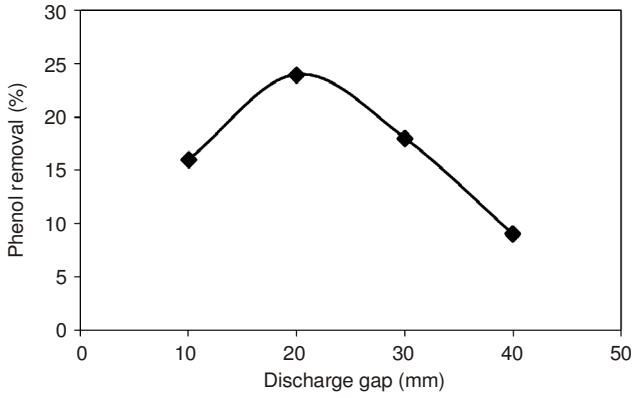

Fig. 8. Effect of discharge gap on phenol degradation

and 120 min reaction time. Phenol degradation was investigated at different phenol concentrations (10, 40, 90 and 160 ppm) by the pulsed discharge. As shown in Fig. 9, the phenol removal efficiency decreased higher phenol concentrations. The phenol removal efficiency was 48, 46, 42 and 34 %, respectively after treatment time of 120 min when the initial concentrations of phenol were present 10, 40, 90 and 160 ppm, respectively.

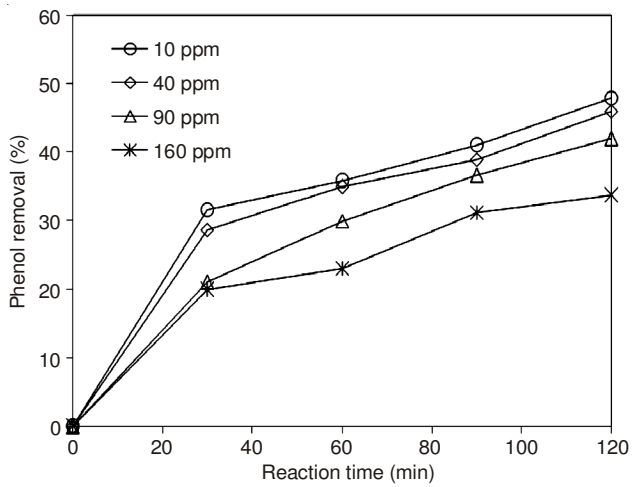

Fig. 9. Removal efficiency of phenol at different phenol concentrations by PHVD treatment

The oxidative degradation of phenol by pulsed high voltage discharge can be explained as follows. It is well know that active species such as the hydrogen peroxide, hydroxyl radicals and aqueous electrons are formed from water and the high energetic electron e^* transforms to low energetic electron e^- when high voltage are applied to generate electrical discharge in water. Hence, reaction 1 and 2 are assumed to be the main reactions during treatment with the pulsed high voltage discharge in water[23,24,29].

$$H_2O + \text{discharge} \rightarrow OH^\bullet + H^\bullet \quad (1)$$

$$2H_2O + \text{discharge} \rightarrow H_2O_2 + H_2 \quad (2)$$

The system is therefore treated as if two separate reactions are occurring at the same time, namely. From these main reactions, the propagation reactions can be gained to produce $H_2O^\bullet$ radical[24]. Furthermore, under ultraviolet radiation produced from the discharge region $OH^\bullet$ can be obtained by reaction[3].

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet} \quad (3)$$

$^{\bullet}OH$ and H_2O_2 formed from water with high voltage pulses react with phenol in water. The main reaction of phenol with the oxidations can be summerized as follows[5]: The OH radical reacts with phenol (C_6H_5OH) and form hydroxycyclohexadienyl radical $^{\bullet}C_6H_5(OH)_2$ as reaction 4[3,15].

$$^{\bullet}C_6H_5(OH) + {}^{\bullet}OH \rightarrow C_6H_5(OH)_2 \quad (4)$$

The hydroxycyclohexadienyl radical $^{\bullet}C_6H_5(OH)_2$ can decay to form the phenoxyl radical $^{\bullet}C_6H_5O$. The phenoxyl radical $^{\bullet}C_6H_5O$ is an intermediate in the radical formation process involving phenol and can also be directly formed under the action of UV ligh produced by discharge[2].

$$^{\bullet}C_6H_5OH + h\nu \rightarrow C_6H_5O + eag- + H. + \quad (5)$$

The phenoxyl radical $^{\bullet}C_6H_5O$ reacts with the $^{\bullet}OH$ radical to form hyroquinone and pyrocatechol, or other products[2]. The phenoxyl radical reacts (C_6H_5O) with $^{\bullet}OH$ radical or oxygen to form pyrocatechol, hydroquinone, and 1,4-benzoquinone or other products[2].

$$^{\bullet}C_6H_5O + {}^{\bullet}OH \rightarrow C_6H_4(OH)_2 \text{ (or product)} \quad (6)$$

Sun *et al.*[3] and Chen *et al.*[33] researched on phenol degradation. The hydroquinone, pyrocatechol, resorcinol, *p*-benzoquinone, and some other unidentified products were reported as the intermediates formed during the phenol degradation process. These primary oxidation products might keep reacting with OH radicals and producing the second class intermediates, mainly organic acids such as formic acid, acetic acid, and oxalic acid, respectively. Through subsequent reactions, the terminal products of CO_2 and H_2O were produced[36].

Variation of total organic carbon during pulsed discharge: In order to investigate the properties of the intermediate products formed during pulsed discharge and determine the level of organic carbon in water, total organic carbon (TOC) analyses were performed. The results of total organic carbon during treatment of 20 ppm phenol concentration by pulsed discharge are shown in Fig. 10. The total organic carbon level of the 20 ppm phenol solution decreased from 18.49 to 13.59 ppm after treatment time of 120 min. Thus, there was 4.9 ppm of TOC evaporated into the reactor. It is known that the degraded organic carbon is converted into carbon dioxide, which escapes from the liquid. This indicates that 26.6 % of intermediate products were degraded. As shown in Fig. 10, the TOC and phenol removal efficiency increased by longer treatment time by pulsed discharge. The removal efficiency of phenol in 20 ppm phenol solution was 46 % after 120 min of discharge treatment, but TOC removal efficiency was 26.6 %. Total organic carbon removal was much lower than phenol removal under same reaction time. The difference between phenol decomposition and TOC removal was because organic degradation products were formed from phenol.

Variation of the pH and conductivity during pulsed discharge: Fig. 11 shows the changes in the distilled water and phenol solution pH and conductivity during the PHVD treatment. Experiments were carried out with both distilled water and phenol solution of 40 ppm (pH = 10, T = 25 °C and cond. = 120 µS/cm). As observed in Fig. 11, the pH of distilled water decreased from an initial pH 10 to 3.4 at 60 min of reaction time with pulsed discharge. The conductivity of the solution increased depending on the pH value during the pulsed discharge. The pH changed because hydrogen peroxide production (Fig. 6), a weak acid, and becomes more acidic. In other words, the pH of the solution decreases with increasing H_2O_2 concentration during discharge. During treatment of phenol by the PHVD (Fig. 11), the pH of phenol solution decreased from 10 to 4.2 after 250 min of pulsed discharge treatment. This is due to both the degradation products of phenol and product of hydrogen peroxide during PHVD treatment.

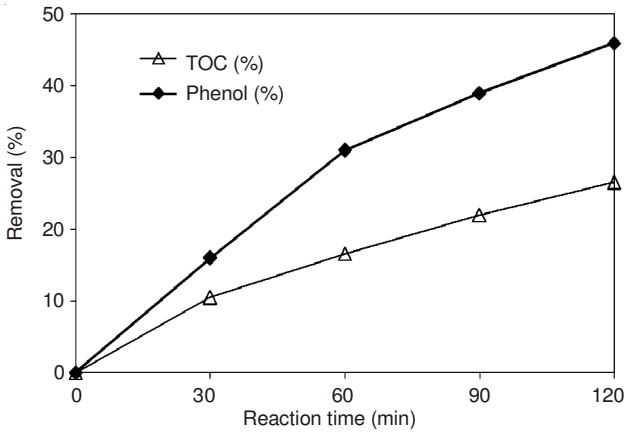

Fig. 10. TOC variations during phenol degradation by PHVD treatment

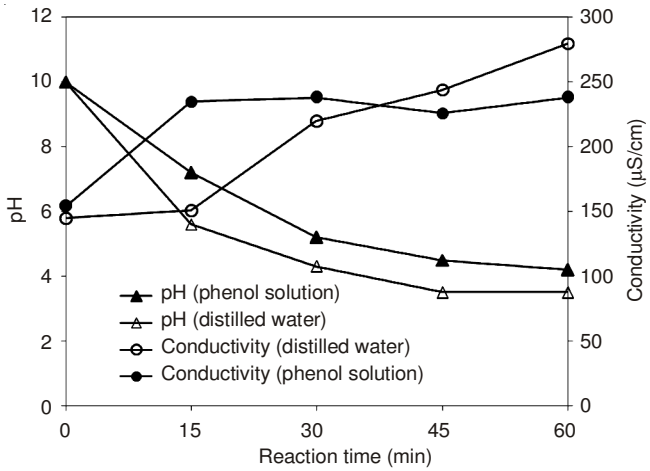

Fig. 11. Initial pH and conductivity variation of distilled water (a) and phenol solution (b) during reaction time by PHVD treatment

Removal of phenol with pulsed discharge in the presence of hydrogen peroxide: The use of hydrogen peroxide for enhancing the removal efficieny is one of the most commonly used methods. The study was performed in four different concentrations of phenol (10, 40, 90 and 160 ppm). The optimum hydrogen peroxide (H_2O_2) dose to be added to the system was determined separately for each concentration of phenol. We performed experiments at three hydrogen peroxide concentrations (5.3, 10.6 and 20 mM) to determine of optimum dose for all phenol concentrations. Fig. 12 shows the degradation of phenol at four different concentrations of phenol by pulsed discharge in the presence of hydrogen peroxide. It can be observed that phenol removal efficiency increased by the addition of hydrogen peroxide to the solution at all phenol concentrations. For 10 ppm of phenol concentration (Fig. 12-a), when the sole pulsed electrical discharge was used for phenol degradation, the phenol removal efficiency was 36 %, whereas phenol removal efficiency enhanced to 100 % after

60 min reaction time with the addition of 5.3 mM hydrogen peroxide in the solution at the beginning of reaction time. When hydrogen peroxide concentration was increased from 5.3 to 10.6 mM, phenol removal efficiency enhanced to 100 % at 30 min reaction time. The reaction time decreased from 60 min to 30 min with increasing H_2O_2 concentration added into the solution. When hydrogen peroxide concentration was increased from 10.6 to 20 mM, the degradation efficiency of phenol did not change (data not shown). The optimum hydrogen peroxide concentration adding to the system was founded as 10.6 mM for 10 ppm of phenol concentration (E = % 100, time = 30 min). As shown in Fig. 12-a, the sole effect of hydrogen peroxide on degradation of phenol was very low due to a very slow reaction of phenol with hydrogen peroxide. The effect of hidrojen peroxide on the phenol degradation was only 8 % with 5.3 mM H_2O_2 dose, and 20 % with 10.6 mM H_2O_2 dose. The removal results are shown in Fig. 12-b for phenol concentration of 40 ppm. The phenol removal efficiency was 100 % after 90 min reaction time by pulsed discharge with addition of 5.3 mM of hydrogen peroxide in phenol solution of 40 ppm, which was 40 % with the sole pulsed electrical discharge. 100 % phenol removal was achieved at 30 min reaction time with addition of 10.6 mM of hydrogen peroxide in solution. When phenol concentration was increased to 90 and 160 ppm, respectively, the % 100 phenol degradation occurred with addition of hydrogen peroxide of 20 mM at 90 and 120 min of reaction times, respectively by pulsed electrical discharge (Figs. 12-c-d). Shen *et al.*[15] reported approximately 70 % phenol removal efficiency (initial phenol conc. = 50 ppm) with 6 mM H_2O_2 at 70 min of reaction time by pulsed electrical discharge. It is reported in our study that 100 % phenol removal efficiency was obtained with 5.3 mM H_2O_2 concentration at 60 min of reaction time for initial phenol conc. of 10 ppm, with 10.6 mM H_2O_2 concentration at 30 min of reaction time for initial phenol conc. of 40 ppm, with 20 mM H_2O_2 concentration at 90 min of reaction time for initial phenol conc. of 90 ppm and with 20 mM H_2O_2 concentration at 120 min of reaction time for initial phenol conc. of 160 ppm. The results of the study confirmed that hydrogen peroxide enhanced significantly the phenol degradation efficiency. The combined pulsed electrical discharge and hyrogen peroxide presented higher phenol degradation than using only pulsed electrical disharge.

The increase of phenol degradation with hyrogen peroxide addition was due to reactions of phenol with hyroxyl radicals produced by photolysis of hyrogen peroxide. The photolysis could be due to the UV radiation emitted by electrical disharge plasma. The temperature in plasma channel formed during an electrohydraulic discharge can reach values of 14.000-15.000 K and this is a blackbody radiation source[37]. The vacuum UV light emitted from the hot plasma is in the region of the spectrum λ = 75-185 nm and is absorbed immediately in the water layer surrounding the plasma channel, but the UV ragion of the spectrum $\lambda > 185$ nm expands into the bulk of solution, and then it reacts with organic contaminants in aquous solution[10,37-39]. This process was described as follows[3,15].

$$H_2O_2 + h\nu \rightarrow {}^{\bullet}OH + {}^{\bullet}OH \quad (7)$$

Hydrogen peroxide is formed by the pulsed discharge. However sufficient concentration of hydroxyl radicals can not be obtained because of the short residence time in the reactor. Adding hydrogen peroxide to the solution, hydrogen peroxide photolyses by ultraviolet radiation is generated during pulsed electrical discharge. Therefore, a large number hydroxyl radicals are formed by the UV discharge photolysis (1 mol H_2O_2 produced 2 mol $^{\bullet}OH$)[15,23], which leads to a rapid increase in the degradation rate of phenol.

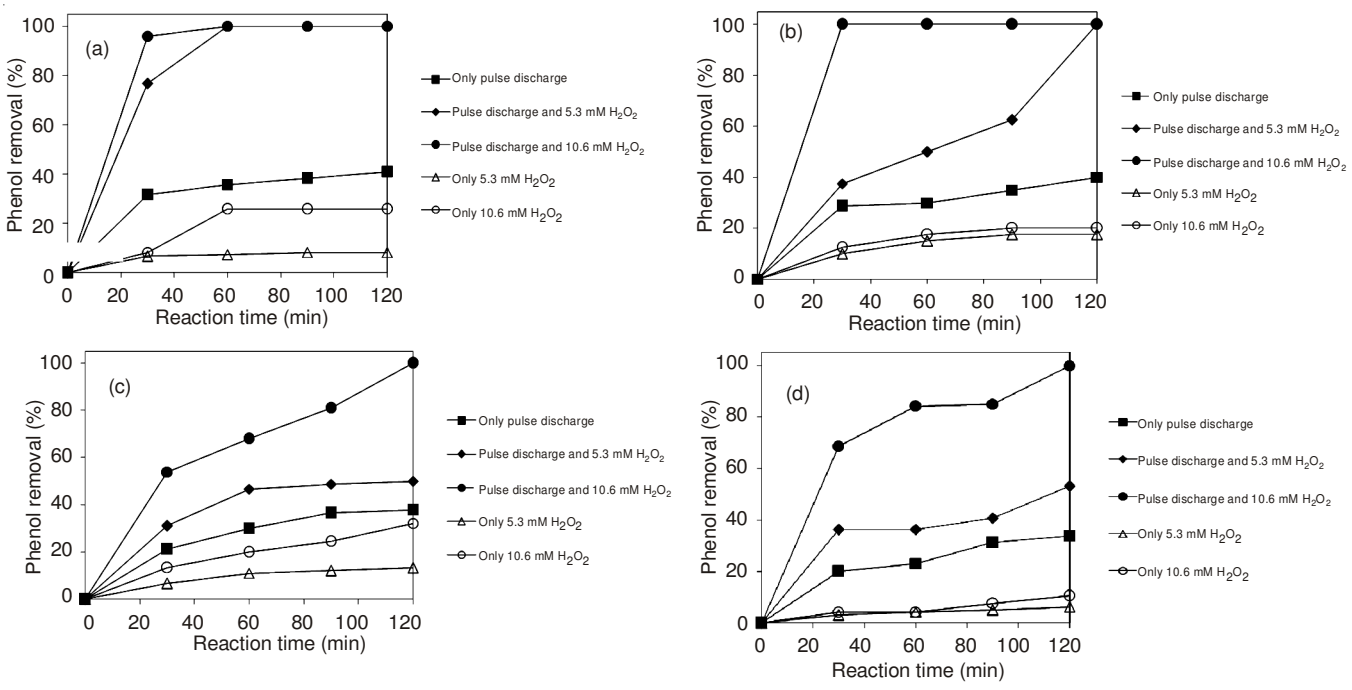

Fig. 12. Phenol removal efficiencies for 10 ppm (a), 40 ppm (b), 90 ppm (c) and 160 ppm (d) initial phenol concentration as a fuction of the reaction time at only H_2O_2 concentration, only pulse electrical discharge and pulse electrical discharge with H_2O_2 (24 kV, 120 µS/cm, pH 10, 30 °C)

Removal of phenol with pulsed discharge in the presence of Fe^{2+}: In this study, the effect of adding Fe^{2+} to the solution on the phenol removal efficiency was investigated. Fig. 13 shows the degradation of phenol with 40, 90 and 160 ppm by pulsed discharge in the presence of Fe^{2+}. It can be seen that the removal of phenol increased in the precence of Fe^{2+}. The increase of phenol degradation in the precence of Fe^{2+} is due to the presence of Fenton's reaction. Degradation of phenol with pulsed discharge in the presence of Fe^{2+} is represented by the following reactions (reactions 8-15)[15].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (8)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^{2+} + H^+ \leftrightarrow Fe^{2+} + {}^{\bullet}HO_2 + H^+ \quad (9)$$

$$Fe^{3+} + OH^- \rightarrow Fe(OH)^{2+} \leftrightarrow Fe^{2+} + {}^{\bullet}OH \quad (10)$$

$$^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (11)$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow {}^{\bullet}OH + H_2O + O_2 \quad (12)$$

$$HO_2^{\bullet} + HO_2^- \rightarrow {}^{\bullet}OH + OH^- + O_2 \quad (13)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad (14)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^+ + O_2 \quad (15)$$

$$Phenol + {}^{\bullet}OH \rightarrow Intermediates \quad (16)$$

$$Intermediates + {}^{\bullet}OH \rightarrow CO_2 + H_2O \quad (17)$$

In the precence of Fe^{2+}, the hydrogen peroxide formed by pulsed discharge reacts with Fe^{2+} to produce hydroxyl radical (reaction 8). The generation of the radicals involves a complex reaction sequence in aqueous solution (reactions 10-15). These reactions cause the carbon chain in the organic pollutant structure to rupture (reaction 16) and finally yield CO_2 and H_2O (reaction 17). In the presence of larger concentrations of an organic compound, hydroxyl radicals may preferentially react with the organic compounds rather than Fe^{2+} (reaction 14 and 16). Therefore, the optimum dose of Fe^{2+} added into solution is important for oxidation process. Fig. 13 shows phenol removal efficiency and optimum dose of Fe^{2+} for 40 (a), 90 (b) and 160 ppm (c) initial phenol concentration. As shown in Fig. 13, the phenol removal efficiency increased with the addition of Fe^{2+}. The phenol removal efficiency received 78 % after 120 min treatment time when Fe^{2+} is 0.28 mM, while it is 58 % by adding Fe^{2+} of 0.56 mM at initial phenol concentration of 40 ppm (a). The optimum Fe^{2+} concentration added in pulsed discharge system was found as 0.28 mM for 40 ppm of phenol concentration. The phenol removal efficiency increased 44 % by adding Fe^{2+} of 0.28 mM into phenol solution of 40 ppm during treatment with pulsed discharge when compered to treatment only pulsed discharge. When phenol concentration was increased from 40 ppm to 90 ppm, the phenol removal efficiency was 72 % at Fe^{2+} dose of 0.28 mM (b). The efficiency increased 34 % by adding of Fe^{2+} of 0.28 mM than when only pulsed discharge was used. For phenol concentration of 160 ppm, the phenol removal efficiency increased from 33 to 71 % with adding of Fe^{2+} of 0.56 mM (c), which was optimum dose. Shen *et al.*[15] had carried out on phenol degradation by pulsed electrical discharge, where they found that for 5 ppm phenol concentration, maximum phenol removal efficiency was 88.2 % after 90 min treatment time with 0.05 mM Fe^{2+} in solution. In our study, even with higher phenol concentrations, high removal efficiencies (E = 70-78 %) were obtained at 120 min treatment time by pulsed discharge system adding Fe^{2+}.

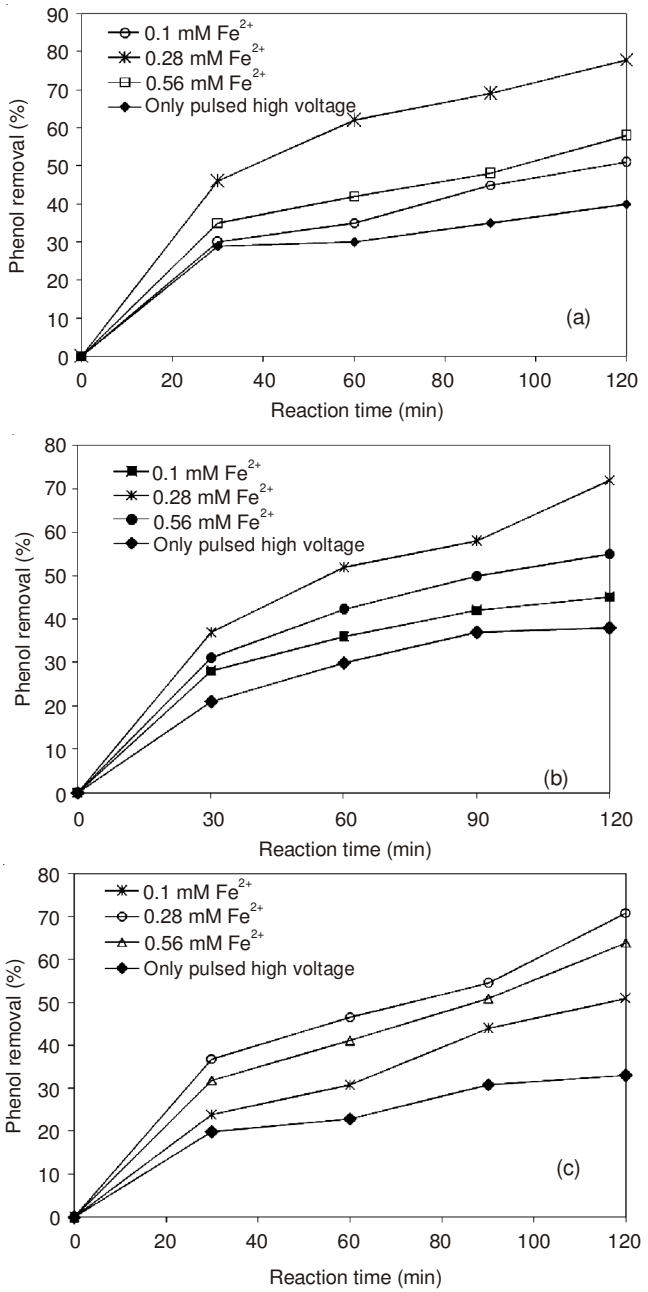

Fig. 13. Phenol removal efficieny for 40 ppm (a), 90 ppm (b) and 160 ppm (c) initial phenol concentration as a fuction of the reaction time in the presence of Fe^{2+} with 0.1, 0.28, 0.56 and 1.12 mM ((24 kV, 120 µS/cm, pH 10, 30 °C)

Conclusions

In this paper, the degraradation of phenol by pulsed discharge was investigated . The results obtained in this study could be summarized as:

• The reactor design used in this paper could achieve the degradation of phenol in aqueous solutions. The phenol degradation efficiency increased with the increase of pulsed peak voltage, pH, temperature and treatment time, decrease of discharge gap and conductivity of the solution. The optimum operation conditions were: discharge voltage of 24 kV, discharge gap of 20 mm, pH 10, temperature of 30 ºC, solution conductivity of 120 µS/cm.

• The pH of the solution increased during discharge. This result was likely due to production of hydrogen peroxide and

organic acid such as formic acid, acetic acid, oxalic acid, malonic acid and maleic acid. The conductivity of the solution increased with decreased pH.

• The phenol in the aqueous solution was degraded by pulse electrical discharge process. Phenol removal efficiency was 40, 38 and 33 %, respectively at 40, 90 and 160 ppm of initial phenol concentration after treatment time of 120 min. During phenol degradation by pulsed discharge, TOC level also decreased. The removal efficiency of total orgnaic carbon was lower than phenol removal efficiency due to organic degradation products formed from phenol.

• When hyrogen peroxide was added to the solution at a concentration of 5.3, 10.6 and 20 mM, the removal efficiency of phenol increased dramatically. The removal efficiency of phenol was 100 % at initial phenol concentration of 10, 40, 90 and 160 ppm. This is due to hydrogen peroxide photolyses by ultraviolet radiation generated during pulsed electrical discharge.

• The addition of Fe^{2+} enhances the phenol removal efficiency, but not as much as hydrogen peroxide. The additive of Fe^{2+} in the aqueous solution could promote the phenol removal efficiency due to reaction with the hyrogen peroxide to form hydroxyl radicals by Fenton's reaction. The phenol removal efficiency by adding 0.28 mM and 0.56 mM Fe^{2+} to phenol concentrations of 40 , 90 and 160 ppm was 78, 72 and 71 %, respectively.

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