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## Efficient removal of phenol from aqueous solution by the pulsed high-voltage discharge process in the presence of H<sub>2</sub>O<sub>2</sub>

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### ARTICLE INFO

#### Article type:

Research article

#### Article history:

Received 25 October 2014

Accepted 15 March 2015

Published 01 April 2015

April 2015 Issue

#### Keywords:

Phenol removal

Hydrogen peroxide

Exposure time

Temperature

### ABSTRACT

This study investigates the phenol degradation by pulsed high-voltage discharge (PHVD). The effect of solution pH, temperature, treatment time and initial phenol concentration on phenol degradation were examined. The results showed that the phenol removal efficiency was increased with the rise of pH, temperature and treatment time. The phenol removal efficiency was 48%, 46%, 42% and 34%, respectively at 10, 40, 90 and 160 ppm phenol solutions. The phenol degradation rate was increased markedly when H<sub>2</sub>O<sub>2</sub> was added into the solution. Almost complete phenol degradation (100%) was achieved when 20-40 mM of H<sub>2</sub>O<sub>2</sub> was added into phenol solutions of 40, 90 and 180 ppm.

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**Capsule Summary:** Phenol removal by the pulsed high-voltage discharge process in the presence of H<sub>2</sub>O<sub>2</sub> was studied and it was found that this process is efficient for the removal of phenol from aqueous solution at optimized conditions of pH, temperature, treatment time and initial phenol concentration.

**Cite This Article As:** Murtaza Sayed. Efficient removal of phenol from aqueous solution by the pulsed high-voltage discharge process in the presence of H<sub>2</sub>O<sub>2</sub>. Chemistry International 1(2) (2015) 81-86

### INTRODUCTION

The pulsed high-voltage discharge (PHVD) process is an emerging advance oxidation process (AOP) for the removal of organic pollutants from aquatic environments. The basic mechanism of the technology is the formation of plasmas, which can promote both physical and chemical processes. PHVD technology has been used in wastewater treatment for the efficient removal of organic compounds, particularly with high toxicity and low biodegradability; such as for removal of phenol, chlorophenols, organic dye (Sun et al., 2000; Sugiarto and Sato, 2001). A little work has been carried out on PHVD technology in combination with other techniques to achieve more better results, such as ferrous ion, hydrogen peroxide, activated alumina,

titanium dioxide and gas bubbling along with various other methods are also used for de-pollution (Bian et al., 2008; Bilal et al., 2014; Gong et al., 2008; Iqbal et al., 2013. Iqbal and Bhatti, 2014; Iqbal et al., 2014; Jamal et al., 2015; Li et al., 2007; Manzoor et al., 2013; Sugiarto et al., 2003; Shen et al., Qureshi et al., 2015; 2008; Ullah et al., 2013; Zhu et al., 2007). Sugiarto et al. (2003) reported that the addition of a small amount of hydrogen peroxide and oxygen gas bubbling greatly improved the degradation rate of phenol. Shen et al. (2008) showed that bubbling the solution by various gases (oxygen, argon, nitrogen and ozone) and chemical catalysts (ferrous ion and hydrogen peroxide) by pulsed electrical discharge increases the removal rate of phenol. Also, addition of ferrous ion and hydrogen peroxide increases the degradation of phenol. Zhu et al. (2007) showed improved removal of phenol by activating alumina bed

placed in pulsed high voltage electrical field. The removal rate of phenol was 72.1% when the air was bubbled through the solution, and increased to 88.2% when 0.05 mm/L ferrous ions were added. Wang et al. (2007) developed a synergistic system of pulsed corona discharge combined with TiO<sub>2</sub> photocatalysis to investigate the degradation rate of phenol solution. The higher phenol removal (66.1%) was achieved by a synergistic system as compared to pulsed discharge system (55.2%). In this investigation, a toxic and biorefractory organic pollutant phenol was selected as the target pollutant to study the removal performance of pulsed high-voltage discharge for wastewater treatment processes. The operating parameters that affect the degradation of phenol; such as initial solution pH, temperature, treatment time were optimized. Furthermore, the effect of addition of hydrogen peroxide into phenol solution with varying phenol concentrations for the removal of phenol were also examined. The optimum dosage of hydrogen peroxide was determined for various phenol concentrations.

## MATERIALS AND METHODS

Simulated wastewater was prepared by addition of phenol to triply distilled water. A phenol concentration of 20 ppm was applied as initial concentration. H<sub>2</sub>SO<sub>4</sub> (0.1 mol/L) and NaOH (0.1 mol/L) was used to adjust the initial solution pH. The concentration of phenol was measured using UV-Visible spectrophotometer-Lambda 650. The pH of the solution was measured using NeoMet IStEk model pH meter. All samples were analyzed in triplicate.

## RESULTS AND DISCUSSION

### *Effect of initial pH and temperature on phenol degradation*

In this part of the study, the effect of solution pH and temperature on the oxidative degradation of phenol was examined using Box–Wilson statistical experimental design method. This method was applied to study the effects of the two independent variables (pH and temperature) on the response functions (phenol removal efficiency) and to find out the optimal conditions for maximum phenol removal by the PHVD process. The details about Box–Wilson statistical experiment design is reported elsewhere in detail (Kuşçu and Sponza, 2011). The pH (X<sub>1</sub>) and temperature (X<sub>2</sub>) were the independent variables while the phenol efficiency (Y<sub>1</sub>) was the objective function. The low, centre and high levels of each variable (X<sub>1</sub>, X<sub>2</sub>) are designated as -1, 0, and +1, respectively. The pH (X<sub>1</sub>) and temperature (X<sub>2</sub>) was varied between 10 °C and 35 °C, pH (X<sub>2</sub>) was changed between 2 and 12.

Table 1 represents the experimental conditions determined by the Box–Wilson statistical design method. The applied 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<sub>1</sub>, X<sub>2</sub>). A statica 5.0 computer program was used for determination of the coefficients of response function and are presented in Eq. 1. The predicted phenol removal according to Eq. 1 and experimental phenol removal are presented in Table 1.

The results show good agreement between the experimental measurement and theoretical values of phenol removal efficiency.

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

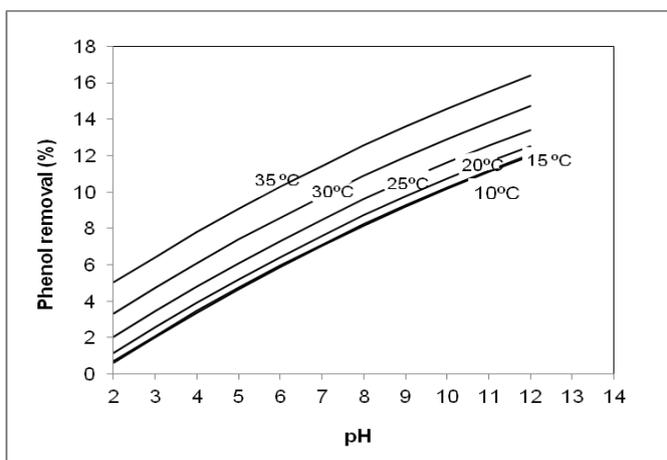
From Eq. 1, it can be concluded that phenol removal is more affected by the pH (X<sub>1</sub>) and is less affected by temperature (X<sub>2</sub>). Fig. 2 represents the degradation of phenol by solving Eq.1 for different values of pH and temperature. It can be seen that phenol degradation was more effective at high pH than at low pH values. Phenol removal efficiency, increased from 3 % to 13% with the increase in the solution pH from 2 to 12 at 20 °C. Lukes et al. (2005) reported the similar results for the removal of phenol. The possible reason of this higher phenol degradation at higher solution pH may be due to production of H<sub>2</sub>O<sub>2</sub> and organic acid and H<sub>2</sub>O<sub>2</sub> could then create ·OH radicals to degrade phenol.

The phenol removal efficiency was 11%, 11.5% and 12%, respectively, for pH=10, pH=11 and pH=12. The optimum pH value was selected as 10 due to negligible increase (1%) of phenol removal for pH values higher than 10. The effect of temperature on the phenol degradation was investigated within a temperature range of 10 –35 °C when pH changed between 2 to 12. As can be seen in Fig. 1, phenol removal efficiency was enhanced with increasing temperature at all pH values. Fig. 2 depicts the variation of phenol removal at different temperatures at initial pH of 10. It was observed that keeping the initial solution pH 10, raising the temperature from 10 °C to 35 °C, phenol degradation increased from 10 to 14 %. The increase in phenol removal efficiency was approximately 4 % when the temperature was increased from 10 °C to 35 °C. The results indicate that phenol degradation can be improved by higher pH and temperature during treatment with PHVD process. However, the effect of temperature on phenol removal was lower as compared to pH.

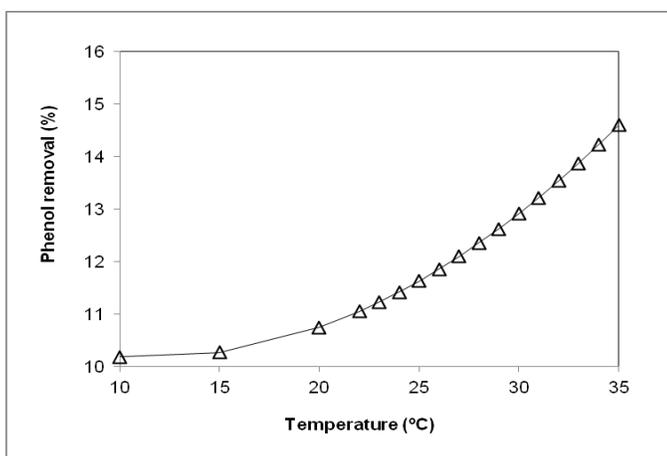
### *Effect of treatment time on phenol removal*

The effect of reaction time on phenol degradation is represented in Fig. 3. It is seen that the phenol degradation efficiency was enhanced by increasing the treatment time. The phenol degradation efficiency was increased from 10% to 68% by increasing the treatment time from 15 min to 240 min. at 24 kV of pulsed peak voltage.

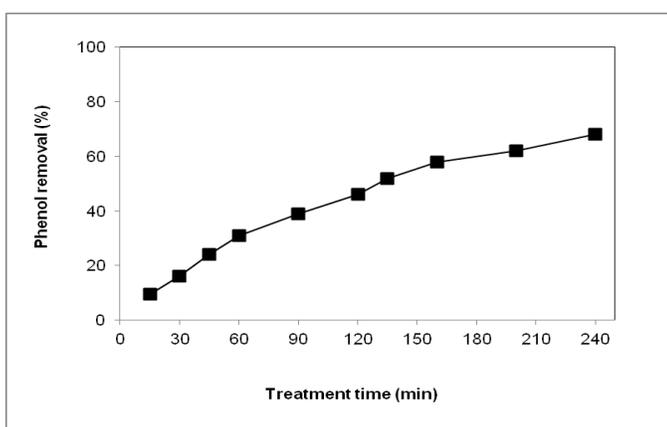
### *Removal of phenol with sole pulsed discharge*



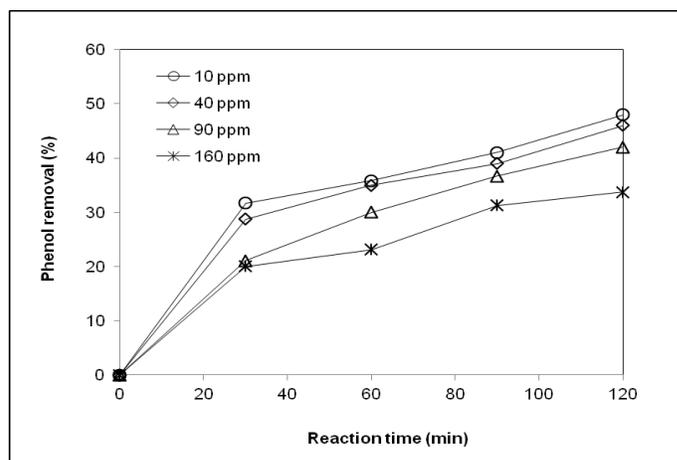
**Fig. 1:** Changes in percent removal of phenol at varying temperatures with the pH



**Fig. 2:** Dependence of phenol removal with temperature at pH = 10.



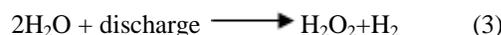
**Fig. 3:** The dependence of phenol removal on treatment time



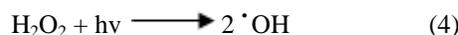
**Fig. 4:** The effect of initial phenol concentration on phenol removal by pulsed discharge.

of 10, 40, 90 and 180 ppm by pulsed discharge alone process. It can be seen that the phenol removal efficiency was decreased as the phenol initial concentration was increased. The phenol removal efficiency was 48%, 46%, 42% and 34%, respectively at treatment time of 120 min., when the initial concentration of phenol is 10, 40, 90 and 180 ppm.

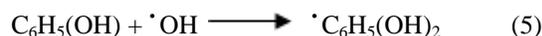
It is well known that by applying high voltage electrical discharges, active species such as the hydrogen peroxide, hydroxyl radicals and aqueous electrons are produced. as shown by reaction 2 and 3 (Joshi et al., 1995; Sharma et al., 1993; Sun et al., 1997).



Furthermore,  $\text{H}_2\text{O}_2$  can then be converted to  $\cdot\text{OH}$  as shown by reaction 4 (Sun et al., 2000).



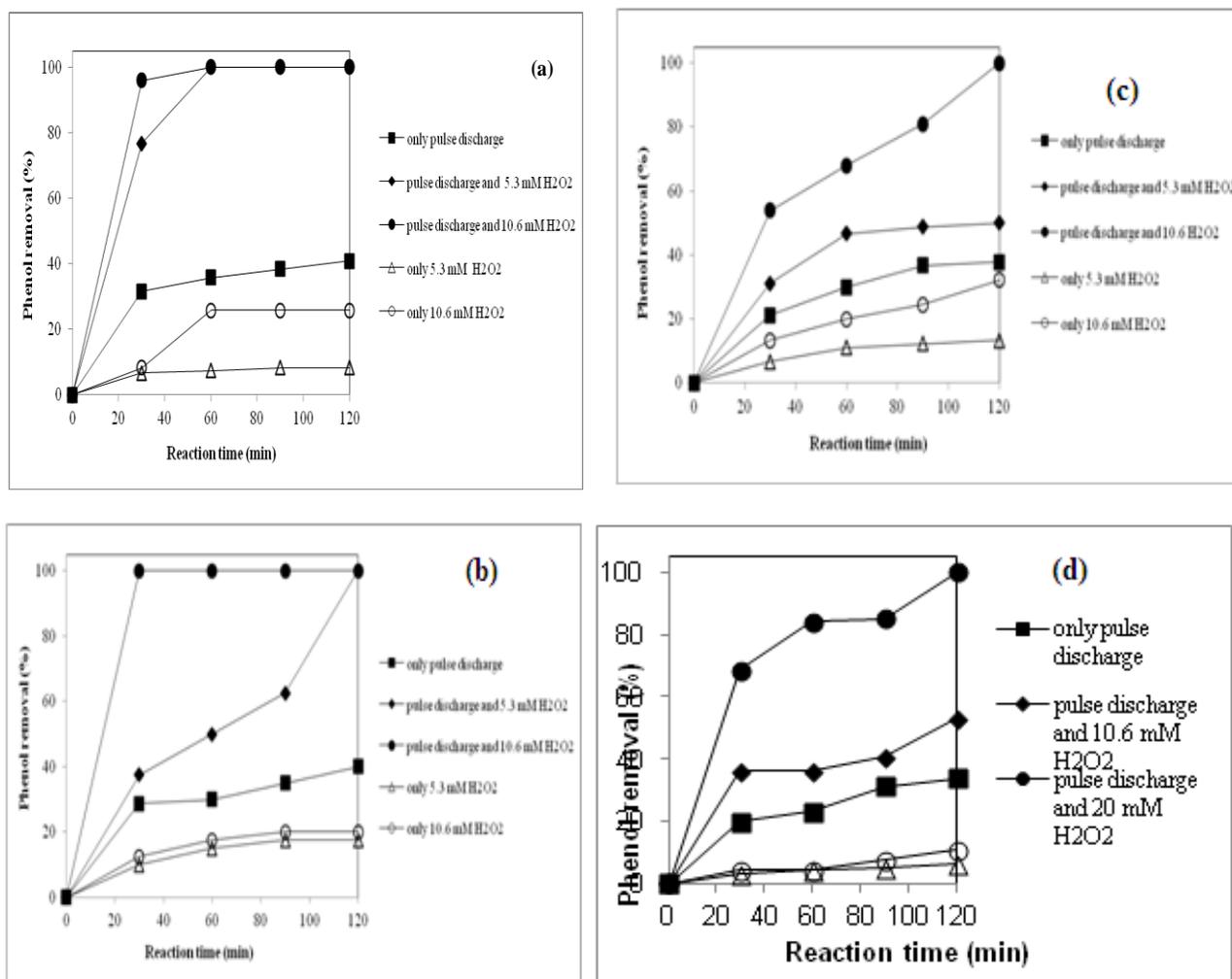
$\cdot\text{OH}$  and  $\text{H}_2\text{O}_2$  thus formed, then reacts with phenol in water causing its degradation (Zhu et al., 2007). The  $\cdot\text{OH}$  radical reacts with phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) and form hydroxycyclohexadienyl radical  $\cdot\text{C}_6\text{H}_5(\text{OH})_2$  as given by reaction 5 (Sun et al., 2000; Shen et al., 2008).



The hydroxycyclohexadienyl radical  $\cdot\text{C}_6\text{H}_5(\text{OH})_2$  then converts to an intermediate specie phenoxyl radical  $\cdot\text{C}_6\text{H}_5\text{O}$  as shown in Eq. 6a.



Fig. 4 represents the removal of phenol at phenol concentrations



**Fig. 5:** Phenol degradation efficiency for 10 ppm (a), 40 ppm (b), 90 ppm (c) and 160 ppm (d) initial phenol concentration as a function of the reaction time at  $V=24$  kV, liquid conductivity= $120 \mu\text{S}/\text{cm}$ ,  $\text{pH}=10$ , temperature= $30^\circ\text{C}$ , only  $\text{H}_2\text{O}_2$  concentration, only pulse electrical discharge and pulse electrical discharge with  $\text{H}_2\text{O}_2$

- Only pulse discharge    ◆ Pulse discharge and 5.3 mM  $\text{H}_2\text{O}_2$
- Pulse discharge and 10.6 mM  $\text{H}_2\text{O}_2$     ▲ only 5.3 mM  $\text{H}_2\text{O}_2$
- only 10.6 mM  $\text{H}_2\text{O}_2$

The phenoxyl radical  $\text{C}_6\text{H}_5\text{O}$  on further reaction with the  $\cdot\text{OH}$  radical converts to hydroquinone, pyrocatechol and other products as given by reaction 6b (Sun et al., 1999).



#### Removal of phenol with pulsed discharge in addition to hydrogen peroxide

The addition of hydrogen peroxide to solution having target pollutant is one of the most commonly used methods for improving the degradation efficiency. The study was performed by using different initial concentrations of phenol i.e. 10, 40, 90 and 160 ppm. The optimum dose of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) for addition to the system was determined separately for each phenol concentration. Initially,  $\text{H}_2\text{O}_2$  was applied at the

concentrations of 5.3 mM, 10.6 mM and 20mM for all phenol concentrations. Fig. 5 shows the removal of phenol at four different initial concentrations of phenol by pulsed discharge in the presence of hydrogen peroxide. It can be seen that phenol removal efficiency was increased by the addition of hydrogen peroxide to the solution at all phenol concentrations. For 10 ppm of phenol concentration (Fig. 5a), when the sole pulsed electrical discharge was applied for phenol removal, the phenol degradation efficiency has been just 36%, which was increased to 100% after 60 mins. Reaction time by addition of 5.3 mM of  $\text{H}_2\text{O}_2$ . When the amount of  $\text{H}_2\text{O}_2$  was increased from 5.3 mM to 10.6 mM, phenol was completely degraded (100%) at 30 min of reaction time. Further addition of  $\text{H}_2\text{O}_2$  from 10.6 mM to 20 mM didn't change the removal efficiency of phenol (not shown here).

The effect of addition of hydrogen peroxide on the phenol removal was only 8% with 5.3 mM  $\text{H}_2\text{O}_2$  dose, and 20% with

**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 ( $^{\circ}$ 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

10.6 mM  $H_2O_2$  dose. When the phenol concentration was increased to 40 ppm the removal efficiency was 100% after 90 min. of reaction time with addition of 5.3 mM of  $H_2O_2$  which was 40% with the sole pulsed electrical discharge. Complete phenol removal (100%) was observed at 30 min of reaction time with the addition of 10.6 mM of hydrogen peroxide in 40 ppm phenol solution. When the phenol concentration was further increased to 90 ppm and 180 ppm, respectively, the 100% phenol removal was observed at 90 and 120 mins. Of reaction time, respectively, by addition of 20 mM of  $H_2O_2$  (Figs. 5c-d).

This increase of phenol degradation with the addition of hydrogen peroxide to the system was mainly due to excess amount of  $\cdot OH$  radical production produced by photolysis of hydrogen peroxide. The photolysis could be due to the UV radiation emitted by electrical discharge plasma. The excessive production of  $\cdot OH$  by photolysis of  $H_2O_2$  can be presented as follows (Sun et al., 2000; Shen et al., 2008).



The hydrogen peroxide is formed by the pulsed discharge; however sufficient concentration of hydroxyl radicals cannot be obtained because of the short residence time in the reactor. If the additional hydrogen peroxide is added in 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 of  $H_2O_2$  produced 2 moles of  $\cdot OH$ ), which leads to a rapid increase in the degradation rate of phenol.

## CONCLUSIONS

The main conclusions of this investigation are; (1) The phenol degradation efficiency, increased with the increase of initial solution pH, temperature and treatment time and increased by increasing initial phenol concentration. (2) Phenol removal efficiency was 40%, 38% and 33% respectively, for 40, 90 and 180 ppm of initial phenol concentration at treatment time of 120 min. (3) When hydrogen peroxide was added to the solution at a concentration of 5.3 mM, 10.6 mM or 20 mM, the phenol removal efficiency increased dramatically. The phenol removal efficiency was 100% at initial phenol concentration of 10, 40, 90 and 160 ppm. This is due to enhanced production of  $\cdot OH$  by hydrogen peroxide photolyses.

## ACKNOWLEDGMENTS

Author is highly thankful to Higher education commission of Pakistan (HEC) for financial support of this study.

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