

## Phenol Removal from Water by Pulsed Power Discharge: A Review

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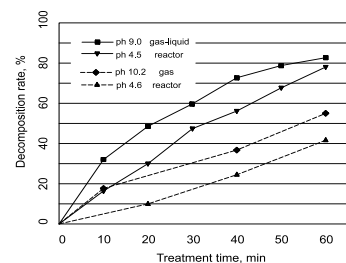
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### Graphical abstract



### Abstract

In the last three decades, pulsed high voltage discharge technology has offered promising techniques for the treatment of wastewaters released to the environment by industry. A significant effort has been directed towards understanding the processes that occur during the discharge of solutions for a variety of reactor configurations. This review presents the disadvantages and advantages of different reactors based on discharge phase. Detailed information is also provided on the principals used in each technique and the advantages and disadvantages associated with each method. Finally, a discussion on the different discharge areas is presented.

**Keywords:** Phenol removal; pulsed streamer discharge; advanced oxidation process

### Abstrak

Tiga dekad yang lalu, nyahcas dedenyut voltan tinggi telah menawarkan suatu teknik yang boleh menjanjikan hasil yang baik untuk rawatan air sisa buangan yang dilepaskan ke persekitaran oleh industri. Satu usaha penting telah ditujukan ke arah memahami proses yang berlaku semasa menunaikan penyelesaian bagi pelbagai konfigurasi reaktor. Ulasan ini membentangkan kelemahan dan kelebihan reaktor yang berbeza berdasarkan fasa pelepasan. Maklumat terperinci juga disediakan kepada prinsip-prinsip yang digunakan dalam setiap teknik serta kebaikan dan keburukan yang berkaitan dengan setiap kaedah. Akhirnya, perbincangan mengenai kawasan pelepasan yang berbeza dibentangkan.

**Kata kunci:** Penyingkiran fenol; nyahcas dedenyut aliran; pengoksidasian dedenyut termaju

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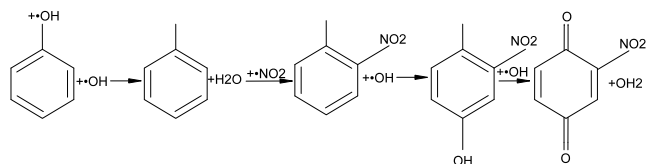
## 1.0 INTRODUCTION

Water polluted with phenol has concerned many scientists due to its harmful impact on human life. The phenols can easily penetrate through natural membranes, causing a broad spectrum of genotoxic, mutagenic and hepatotoxic effects [1]. Conventional methods of wastewater treatment, which are based on chemical, physical and biological processes, possess some defects, such as the dissipation of cost and time, the difficulty in decomposing some pollutants and the need for large facilities, which makes the need for more advanced technologies unavoidable. Research began in the 1980s [2-3], which revealed that the unique characteristics of pulse discharge plasma made it one of the more advanced oxidation processes (AOP) compared with conventional methods. The advantages of this technology include: the removal of several pollutants simultaneously, operation at ambient pressure and temperature, highly efficient destruction and no selection for contamination, which have made it potentially highly suitable as a new method to meet the requirement for a more efficient and complete water purification system. The non-thermal plasma produced in water and aqueous solutions by pulsed high

voltage discharge efficiently causes a variety of effects, such as ultraviolet radiation, shock waves, high electric fields and the generation of chemically active species. Decomposition of phenol in aqueous solutions was studied by Sharma *et al.* [4] using pulsed streamer discharge. Highly active species, formed in the solution to be treated, completely oxidise the organic and oxidisable inorganic materials to water and carbon [5]. Degradation of phenol in water using electrical discharge has been studied in many works [6-9] demonstrating different abilities of purification for a variety of reactors. However, a review on the effectiveness and efficiency of different types of discharging area for contaminant removal has never been done. Generally, the discharging area can be divided into three categories based on the different configurations of reactors and electrodes, which are: the gas-phase electrical discharge [10-11], the liquid-phase electrical discharge [12] and the gas-liquid electrical discharge [13-14]. Each of these phases is able to work in a different status: the glow discharge, the corona discharge, the arc discharge and the dielectric barrier discharge [15]. In the present paper, we reviewed different methods for phenol removal from water based on different discharge areas.

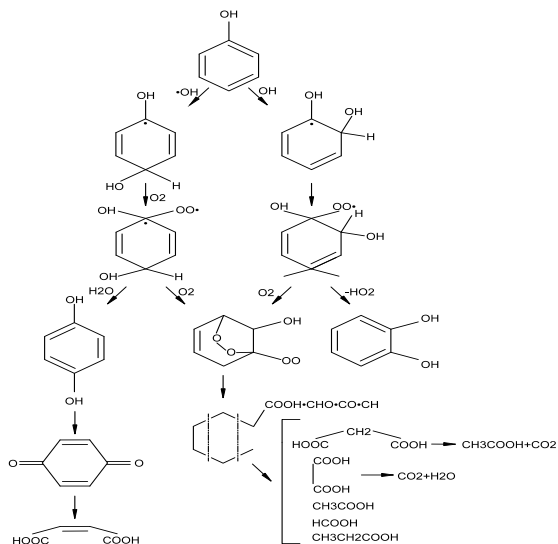
## 2.0 PHENOL REMOVAL

Phenol, a mildly acidic toxic white crystalline solid obtained from coal tar and used in chemical manufacture and in a diluted form (under the name carbolic) as a disinfectant, is believed to be decomposed into dihydroxy benzene as a ring-retaining product. The reaction, illustrated in Figure 1 and Figure 2, shows that phenol initially decomposes to short chain acids and then decomposes to water and carbon dioxide. There is another pathway for the decomposition of phenol by oxidant radicals in the liquid-phase, which is demonstrated in the following reaction [16].



**Figure 1** Decomposition of phenol by oxidant radicals in liquid-phase [16]

Catechol, benzoquinone and 2-nitrophenol with trace amounts of organic acid products are the main by-products of phenol decomposition. Wang *et al.* [17] and Lukes and Locke [18] investigated the mechanism of phenol oxidation in their studies. The attack of the hydroxyl radical on the aromatic ring is the first step of phenol degradation and proceeds by phenol oxidation to 1, 2-dihydroxybenzene or 2-nitrophenol and then to quinines (4-benzoquinone, 2-nitroxy-1 and nitrohydroquinone) [16, 19].

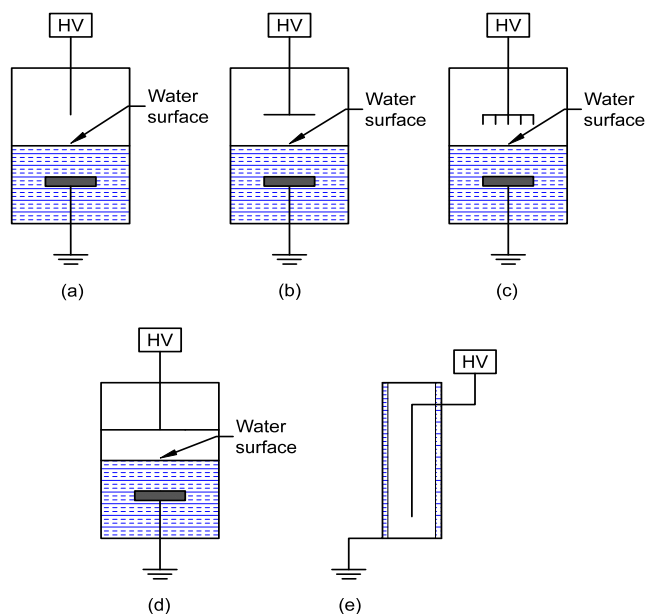


**Figure 2** Degradation pathways of phenol under conditions of oxygen-containing gas [16]

## 3.0 GAS-PHASE ELECTRICAL DISCHARGE

Degradation of phenol in water by gas-phase electrical discharge has been studied in a wide range of studies [13-14, 20] considering the effects of gas injection rate, solution conductivity, solution PH and discharge energy.

Erosion of the discharge electrode in the liquid phase proceeds easily, which results in higher amounts of consumed energy; hence, higher decomposition efficiency and lower erosion of discharge electrodes could be attained by use of an optimised reactor [21].



**Figure 3** Different possible reactor configurations to be used for gas-phase discharge: (a) needle-to-plate, (b) mesh-to-plate, (c) multiple needle-to-plate, (d) wire-to-plate, (e) wire-to-cylinder [22]

Li *et al.* [19] and Sato *et al.* [23] used a stainless steel mesh covered by a ceramic tube as their discharge electrode and the ground electrode was submerged in water. The radical, such as  $O_3$ ,  $O^-$  and  $\bullet O$  are formed in a separated area from the liquid phase and then they are transferred through the pores of a tube to be diffused into water. Production of discharge plasma by this method protects the discharge electrode from erosion while the conductivity of the aqueous solution has little effect on the phenol decomposition rate. M. Dors [22] used different plasma injection for water treatment, shown in Figure 3. While, Yan *et al.* [20] used a gas-phase reactor, shown in Figure 4., to remove phenol from water. Their reactor consists of a ceramic-covered tungsten wire as the discharge electrode and a stainless steel mesh outside the tube as the ground electrode. The illustrated schematic diagram (Figure 4) shows that the reactor includes a plexiglass cylinder discharge reactor, oxygen source and pulse power generator. The ceramic tube contains 97% alumina and was made of linearity ceramic. The discharge electrode in the gas phase is a tungsten wire located in the middle of a ceramic tube and the ground electrode is a stainless steel mesh tightly attached to the inner wall of the reactor vessel in the liquid phase. Pulsed power is applied to the discharge electrode in gas in the ceramic tube when it is filled with gas. The pulse power supply has an adjustable output, a tank capacitor, a rotating spark gap switch and an adjustable pulse-forming capacitance.

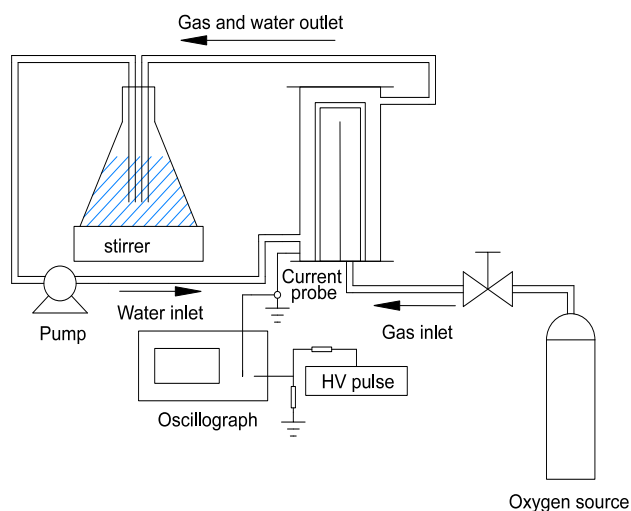


Figure 4 Schematic diagram of the experimental apparatus [20]

#### 4.0 LIQUID-PHASE ELECTRICAL DISCHARGE

According to the location of the electrodes, in liquid-phase reactors the discharge electrode is fully submerged in the aqueous solution, which leads to direct contact with the contaminant. Higher decomposition efficiency of pollutants and also higher electrode erosion are advantages and disadvantages, respectively of this kind of reactor,

Kunitomo and Sun [24] examined three different types of reactors positioned in the liquid phase, which were rod-rod, rod-plate and wire-cylinder electrode constructions, to investigate the best reactor configuration. Figure 5 shows the rod-plate electrode configuration where the electrodes are placed in the centre of a 6l reactor at a distance of 40 mm. The cathode plate can easily be exchanged with the rod electrode. Figure 6 shows a schematic diagram of the wire-cylinder reactor where the cathode and the wire anode are placed along the same axis.

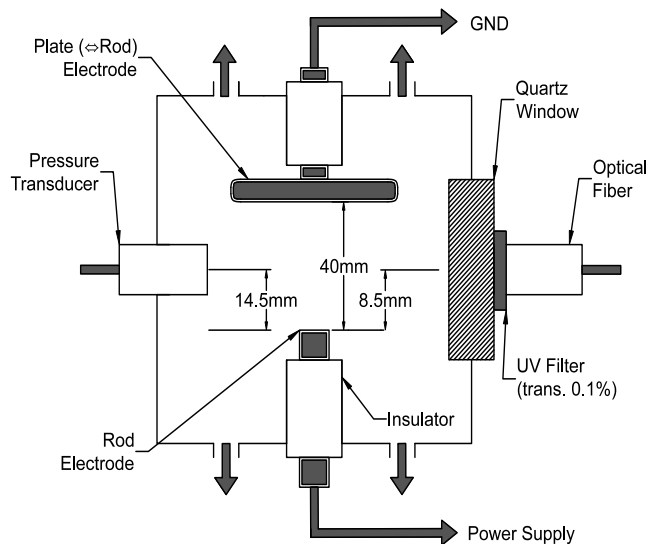


Figure 5 Schematic illustration of the rod-plate (rod) reactor [24]

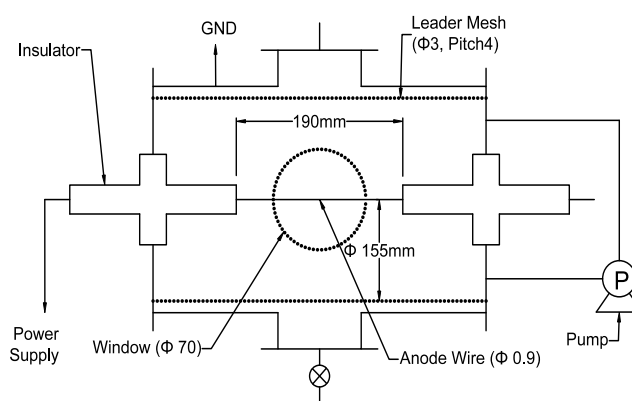


Figure 6 Schematic illustration of the wire-cylinder reactor [24]

#### 5.0 HYBRID GAS-LIQUID ELECTRICAL DISCHARGE

Previously, for the treatment of liquid organic compounds, generally two reactor configurations were used. The first type consists of high voltage needle electrodes and stainless steel planar ground electrodes, which are fully submerged within an aqueous solution [4, 10, 25-27]. In this type of electrical discharge, active species are generated within the liquid phase. Point electrodes above the surface of the water and ground electrodes placed inside the liquid or below the liquid phase is the configuration of electrodes for the second type [28-29]. The second type leads to only gas-phase discharge. In addition, several studies examined oxygen injection through submerged hollow needle electrodes [10]. The amount of produced hydrogen peroxide for this configuration was suppressed compared with the case without bubbling gas for the same electrode arrangement, although oxygen injection through the submerged needle electrodes results in the formation of ozone [30]. High voltage electrical discharge in foam is another novel system for forming ozone in the gas and hydrogen peroxide in the liquid [31-32].

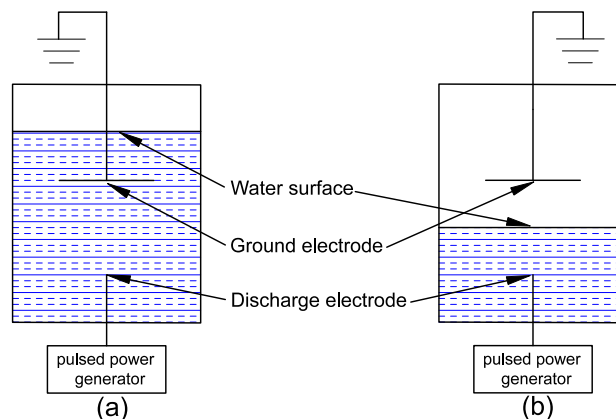


Figure 7 Electrode configurations: (a) discharge and ground electrodes are under the surface of water (liquid phase reactor), (b) Discharge and ground electrodes are under and above the surface of water, respectively (gas-liquid phase reactor) [32]

Gas-phase discharge can be used to form ozone and oxygen radicals in the gas and near the interface and also liquid-phase electrical discharge can be used to form hydroxial radicals and hydrogen peroxide in the liquid. Figure 7 shows another novel

method made an attempt to combine the advantages of gas and liquid phase discharge to propose a more efficient system in such a way that the high voltage electrode is submerged in water and the ground is positioned in the gas phase. Hybrid gas-liquid electrical discharge involves high voltage electrical discharges in water and in the gas phase above the water surface at the same time, producing extra OH radicals in the liquid phase and ozone formation in the gas phase, which finally leads to decomposition into the liquid [32-34]. To enhance Fenton's chemistry and also to speed up absorption and surface-phase reactions, iron salts and activated carbon, respectively can be used because their effects on liquid-phase phenol decomposition in the hybrid gas-liquid reactor have been reported [32].

Kusic *et al.* [35] constructed hybrid reactors, shown in Figure 9, for phenol treatment. Standard-reference, hybrid-series and hybrid parallel are three different reactors. In the series configuration, a high voltage electrode and ground electrode are placed in the liquid and gas phases, respectively. In series configuration, streamer discharge is formed in the liquid phase and proceeds to the gas phase by an intense plasma channel above the surface of the water. Parallel configuration has two high voltage electrodes with parallel connections placed in the gas and liquid phases. A gas-phase high voltage electrode is made of reticulated vitreous carbon (RVC) as is the ground electrode. A more detailed description is presented by Lukes *et al.* [33]. Due to the possibility of simultaneous formation of both gas and liquid phase reactive species, both types of reactors have been studied frequently. These kinds of reactor configuration have been established for the treatment of nitrobenzene [36-37] and organic dyes in water [38].

## 6.0 DISCUSSION

Electrical discharge in liquid or gas-liquid phases has higher efficiency due to the direct contact with the solution to be treated

but the amount of generated plasma is affected by the conductivity and uniformity level of the gas-liquid phase [21, 39]. Conductivity of industrial wastewaters is very high, leading to a reduction in discharge current and energy efficiency and an increment in conduct current. Hence, liquid-phase reactors could not decompose contaminant effectively [40]. Unlike Wang and Quan [21] and Chen *et al.* [39], solution conductivity variation has little effect on the decomposition rate in gas and gas-liquid phase electrical discharges.

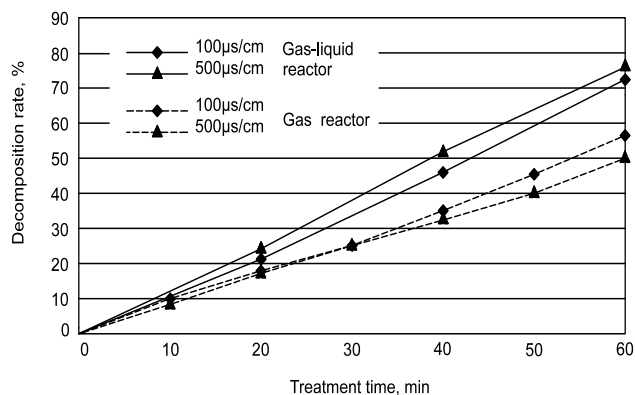


Figure 8 Effect of solution conductivity on decomposition rate of gas and gas-liquid reactors [19-20]

Figure 8 shows a comparison between decomposition rates of gas and gas-liquid phase reactors. It can be seen that variation in solution conductivity has a little effect on decomposition rate of both gas and gas-liquid phase reactors but it can be found that the decomposition rate of the gas-liquid phase reactor is much higher than that of the gas-phase reactor.

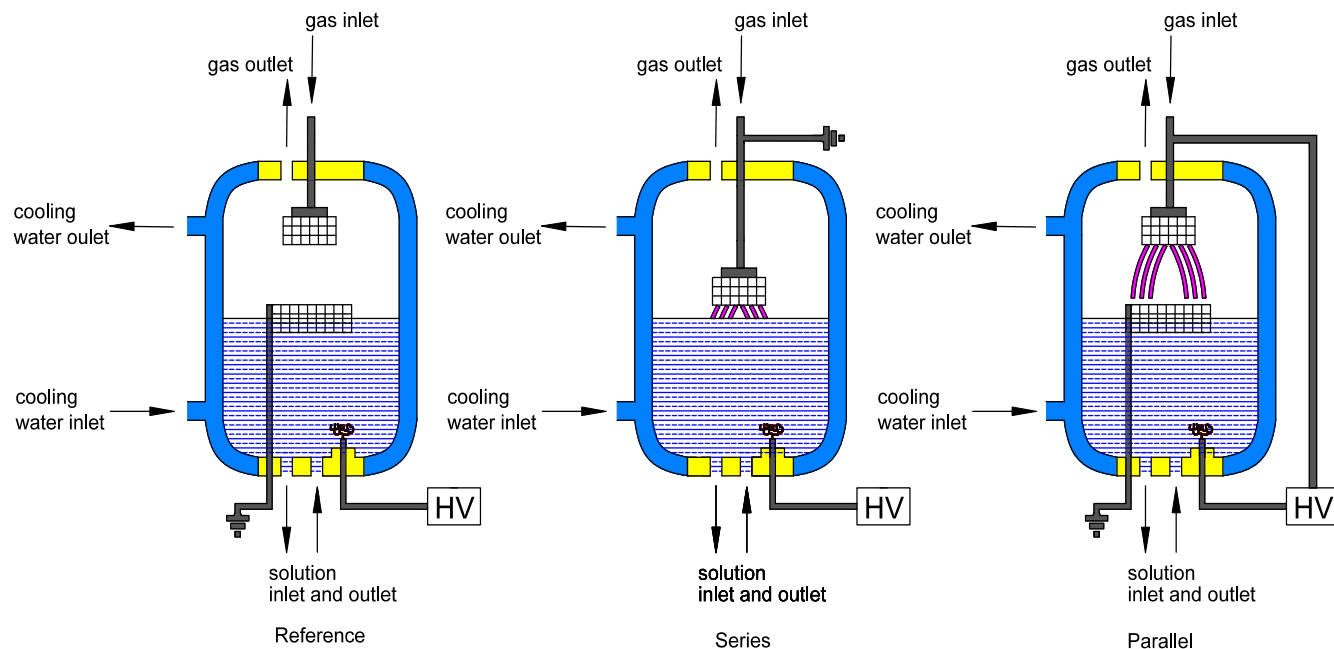
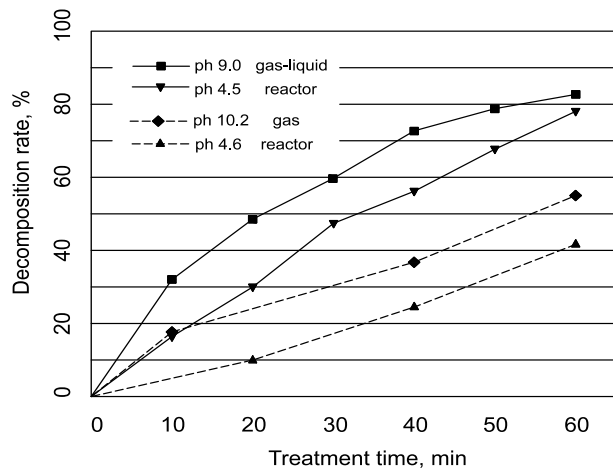


Figure 9 Schematic diagram of three reactor configurations [33]

Figure 10 depicts the change of decomposition rate for both gas and gas-liquid reactors under different pH values. It can be deduced from the plot that the decomposition rate was lower in the acidic condition than in the basic condition with pulse discharge [41-42]. The reason for this result is that in the basic condition the ozone produced in the solution can be easily transformed into  $\cdot\text{OH}$ , which possesses stronger oxidation capability than ozone, leading to higher decomposition efficiency [43].



**Figure 10** Effect of PH variation on decomposition rate of gas and gas-liquid reactors [19-20]

## 7.0 CONCLUSION

Increasing population and consequently the increment in production of wastewater by different human activities have caused clean water to become critically important for the survival of our planet. Drawbacks in current water purification systems demand more cost effective, compact and efficient technologies. The present study reviewed the development of previous and current reactor electrode configurations that can be used to decompose phenol within aqueous solutions.

New technologies effectively replace traditional concepts. Gas-liquid phase electrical discharge produces hydrogen peroxide in water and ozone in the gas phase. Generated ozone in the gas phase results in higher concentrations of reactive species in the liquid phase. Comparison of data shows higher efficiency for hybrid gas-liquid phase discharge than has been seen previously for gas and liquid phase electrical discharge. Various key issues and challenges need to be addressed for a more complete understanding of the mechanisms in such reactors.

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## References

[1] J. W. Yager, et al. 1990. Characterization Of Micronuclei Induced In Human Lymphocytes By Benzene Metabolites. *Cancer Res.* 50: 393–

399.  
 [2] K. Yan, et al. 1998. Corona Induced Non-Thermal Plasmas: Fundamental Study and Industrial Applications. *Journal Of Electrostatics.* 44: 17–39.  
 [3] L. R. Grabowski, et al. 2007. Breakdown Of Methylene Blue And Methyl Orange By Pulsed Corona Discharge. *Plasma Sources Sci. Technol.* 16: 226–232.  
 [3] A. K. Sharma, et al. 1993. A Preliminary Study Of Pulsed Streamer Corona Discharge For The Degradation Of Phenol In Aqueous Solutions. *Hazard. Waste Hazard. Mater.* 10: 209.  
 [4] H.-J. Wang and X.-Y. Chen. 2011. Kinetic Analysis And Energy Efficiency Of Phenol Degradation In A Plasma-Photocatalysis System. *Journal Of Hazardous Materials.* 186: 1888–1892.  
 [5] R. Xie, et al. 2010. Phenol Degradation By A Hybrid Gas-Liquid Discharge Reactor With Digital-Analog Mixed Control. In *Proceedings Of The 29th Chinese Control Conference*, Beijing, China. 5013–5016.  
 [6] M. Sato, et al. 2008. Aqueous Phenol Decomposition By Pulsed Discharges On The Water Surface. *Ieee Transactions On Industry Applications.* 44: 1397–1402.  
 [7] L. Xiaoyong, et al. 2012. Enhanced Degradation Of Phenol By Carbonate Ions With Dielectric Barrier Discharge. *Ieee Transactions On Plasma Science.* 40: 112–117.  
 [8] S. Mayank And R. L. Bruce. 2006. Degradation Of Chemical Warfare Agent Simulants Using Gas-Liquid Pulsed Streamer Discharges. *Journal Of Hazardous Materials.* B137: 1025–1034.  
 [9] J. S. Clements, et al. 1987. Preliminary Investigation Of Prebreakdown Phenomena And Chemical Reactions Using A Pulsed High-Voltage Discharge In Water. *Industry Applications, Ieee Transactions On.* Ia-23: 224–235.  
 [10] B. Sun, et al. 1997. Optical Study Of Active Species Produced By A Pulsed Streamer Corona Discharge In Water. *J. Electrostatics.* 39: 189–202.  
 [11] M. Muhammad Arif, et al.. 2002. Synergistic Effect Of Pulsed Corona Discharges And Ozonation On Decolorization Of Methylene Blue In Water. *Plasma Sources Science And Technology.* 11: 236.  
 [12] L. R. Grabowski, et al. 2006. Corona Above Water Reactor For Systematic Study Of Aqueous Phenol Degradation. *Plasma Chemistry And Plasma Processing.* 26: 3.  
 [13] W. F. L. M. Hoeben, et al. 1999. Gas Phase Corona Discharges For Oxidation Of Phenol In An Aqueous Solution. *J. Phys. D: Appl. Phys.* 32: L133–L137.  
 [14] B. R. Locke, et al. 2005. Electrohydraulic Discharge And Nonthermal Plasma For Water Treatment. *Industrial & Engineering Chemistry Research.* 45: 882–905. 2006/02/01.  
 [15] M. Elsaywah, Et Al. 2012. Corona Discharge With Electro spraying System For Phenol Removal From Water. *Ieee Transactions On Plasma Science.* 40: 29–34.  
 [15] H. Wang, et al.. 2007. Formation Of Hydrogen Peroxide And Degradation Of Phenol In Synergistic System Of Pulsed Corona Discharge Combined With TiO<sub>2</sub> Photocatalysis. *J. Hazard. Materials.* 141: 336–343.  
 [16] P. Lukes and B. R. Locke, 2005. Degradation Of Substituted Phenols In A Hybrid Gas-Liquid Electrical Discharge Reactor. *Ind. Eng. Chem. Res.* 44: 2921–2930.  
 [17] J. Li, et al. 2007. Degradation Of Phenol In Water Using A Gas-Liquid Phase Pulsed Discharge Plasma Reactor. *Thin Solid Films.* 515: 4283–4288.  
 [18] W. Yan, et al. 2009. Decomposition Of Phenol In Water By Gas Phase Pulse Discharge Plasma. In *Industry Applications Society Annual Meeting, 2009. Ias 2009. Ieee.* 1–4.  
 [19] H. Wang, et al. 2006. Decoloration Of Azo Dye By A Multi-Needle-To-Plate High-Voltage Pulsed Corona Discharge System In Water. *Journal Of Electrostatics.* 64: 416–421.  
 [20] M. Dors. 2010. Plasma For Water Treatment. Ed. Poland.  
 [21] M. Sato, et al. 2005. Decoloration Of Organic Dye In Water By Pulsed Discharge Plasma Generated Simultaneously In Gas And Liquid. *J. Adv. Oxid. Technol.* 8: 198–204.  
 [22] S. Kunitomo and S. Bing. 2001. Removal Of Phenol In Water By Pulsed High Voltage Discharge. In *Pulsed Power Plasma Science, 2001. Ppps-2001. Digest Of Technical Papers.* 2: 1138–1141.  
 [23] A. A. Joshi, et al. 1995. Formation Of Hydroxyl Radicals, Hydrogen Peroxide and Aqueous Electrons by Pulsed Streamer Corona Discharge In Aqueous Solution. *Journal Of Hazardous Materials.* 41: 3–30.  
 [24] B. Sun, et al. 1999. Oxidative Processes Occurring When Pulsed High Voltage Discharges Degrade Phenol In Aqueous Solution. *Environmental Science & Technology.* 34: 509–513. 2000/02/01.  
 [25] P. Sunka. 2001. Pulse Electrical Discharges In Water And Their Applications. *Phys. Plasmas.* 8: 2587.  
 [26] W. F. L. M. Hoeben, et al. 1999. Gas-Phase Corona Discharges For

- Oxidation Of Phenol In An Aqueous Solution. *J. Phys. D: Appl. Phys.* 32: L133.
- [27] J. A. Robinson, et al. 1998. A New Type Of Ozone Generator Using Taylor Cones On Water Surfaces. *Ieee Trans. Ind. Appl.* 34: 1218.
- [28] D. R. Grymonpre, et al. 2003. Suspended Activated Carbon Particles And Ozone Formation In Aqueous Phase Pulsed Corona Discharge Reactors. *Ind. Eng. Chem. Res.* 42: 5117–5134.
- [29] J. Pawlat, et al. 2001. Studies On Electrical Discharge In A Foaming Environment. *Jpn. J. Appl. Phys.* 40: 7061.
- [30] D. R. Grymonpre, et al. 2004. Hybrid Gas-Liquid Electrical Discharge Reactors For Organic Compound Degradation. *Ind. Eng. Chem. Res.* 43: 1975.
- [31] P. Lukes, et al. 2004. Hydrogen Peroxide And Ozone Formation In Hybrid Gas-Liquid Electrical Discharge Reactors. *Ieee Trans. Ind. Appl.* 40: 60–67.
- [32] P. Lukes, et al. 2004. Degradation Of Phenol In Hybrid Series Gas-Liquid Electrical Discharge Reactor. In *Proceedings Of The Isnnp4*. Panama City, Fl, Usa. 120–125.
- [33] K. Hrvoje, et al. 2005. Decomposition Of Phenol By Hybrid Gas/Liquid Electrical Discharge Reactors With Zeolite Catalysts. *Journal of Hazardous Materials*. B125: 190–200.
- [34] A. T. Appleton. 2002. A Study Of The Effectiveness Of Different Hybrid Pulsed Corona Reactors In Degrading Aqueous Pollutants. M.S. Thesis, Dept. Chem. Eng., Florida State Uni., Tallahassee.
- [35] A. T. Appleton, et al. 2002. Study Of Effectiveness Of Different Hybrid Pulsed Corona Reactors in Degrading Aqueous Pollutants. In *Contributed Papers HAKONE VIII*, Puhajarve, Estonia. 313–317.
- [36] H. Kusic, et al. 2002. Gas/liquid Hybrid Electrical Discharge Reactors for the Degradation of Organic Dyes and Phenol in Water. Presented at the 8th Int. Conf. Advanced Oxidation Technologies for Water and Air Remediation, Toronto, ON, Canada, Nov. 17–21.
- [37] Y. S. Chen, et al. 2004. Pulsed High-voltage Discharge Plasma for Degeradation of Phenol in Aqueous Solution. *Separation and Purification Technology*. 34: 5–12.
- [38] M. J. Kirkpatrick and B. R. Locke. 2005. Hydrogen, Oxygen, and Hydrogen Peroxide Formation in Aqueous Phase Pulsed Corona Electrical Discharge. *Industrial & Engineering Chemistry Research*. 44: 4243–4248. 2005/06/01.
- [39] K. Faungnawakij, et al. 2006. Modeling of Experimental Treatment of Acetaldehyde-Laden Air and Phenol-Containing Water Using Corona Discharge Technique. *Environmental Science & Technology*. 40: 1622–1628. 2006/03/01.
- [40] P. S. Lang, et al. 1998. Oxidative Degradation of 2,4,6-Trinitrotoluene by Ozone in an Electrohydraulic Discharge Reactor," *Environmental Science & Technology*. 32: 3142–3148. 1998/10/01.
- [41] A. T. Sugiarto, et al. 2003. Oxidative Decoloration of Dyes by Pulsed Discharge Plasma in Water. *Journal of Electrostatics*. 8.