Organic pollutants treatment in a water aerosol reactor by pulsed corona discharge at atmospheric pressure

Haixia Wu¹,⁴, Jiawei Fan¹, Yanhua Xu², Feng Liu³ and Zhi Fang³

¹College of Urban Construction, Nanjing Tech University, Nanjing 211816, People’s Republic of China;
²School of Environmental Science and Engineering, Nanjing Tech University, Nanjing 211816, People’s Republic of China;
³School of Automation and Electrical Engineering, Nanjing Tech University, Nanjing 211816, People’s Republic of China
⁴Email:wuhaixia@njtech.edu.cn

Abstract. An atomization reactor with a gas cycler is designed, and the phenol is treated as wastewater by pulse corona discharge, which is sprayed into the reactor through a pneumatic atomization nozzle. To fully utilize the ozone and enhance organic pollutant removal, we maintained continuous gas circulation in the reactor. The resulting phenol solution was subjected to six passes of decomposition treatment. Approximately 87.4% of 100 mg/L phenol concentration was decomposed in the plasma system gas circulation, whereas only 51.9% was decomposed in the same system but without gas circulation after the sixth pass treatment. The decomposition efficiency increased with applied voltage and pH. In addition, homogeneous catalysts such as hydrogen peroxide (H₂O₂) and iron (II) (Fe²⁺) enhanced the removal of phenol. The novel reactor was also used for the deep treatment of phenolic compounds in coking wastewater. Compared with systems using ozonation, the plasma system working under optimal conditions considerably improved the performance of industrial wastewater treatment, which can be regarded as a promising alternative AOP for wastewater remediation.

1. Introduction
The non-thermal plasma (NTP) method effectively produces UV radiation and active chemicals (•OH, H₂O₂, and O₃), which are important to the removal of organic compounds. The NTP technology is an effective and environment-friendly process for pollutant decomposition [1-5]. An increasing number of investigations have focused on improving the efficiencies of electrode configurations and reactors in NTP processes for water treatment. The reaction system can be divided into three main categories according to the discharge characteristics of the gas and liquid phases: discharge reactors for the continuous liquid and dispersed gas phase, those for the continuous gas and dispersed liquid phase, and those for the continuous liquid and gas phases [6]. Typically, the most efficient pulsed-powered reactors for H₂O₂ formation and chemical oxidation in solutions are the discharges formed in the gas phase, and waste solutions are sprayed into the gas [7-10]. The liquid spray expands the contact surface area with plasma in the discharge zone area. With a large surface-to-volume ratio, the reactive substance can diffuse to the sprayed liquid surface over a short distance. Pollutant molecules directly react with O₃ in the plasma zone and with oxidative radicals.
Minamitani et al. [11, 12] studied dye decomposition by spraying water solution into the pulsed-corona discharge reactor of coaxial electrodes. The results showed that spraying water droplets into the gas-phase discharge system can increase the rate and efficiency of water treatment. Ajo [13, 14] designed a reactor with a perforated bottom plate, which can spray wastewater in the discharge system. The treated solutions were showered in jets, droplets and films between the high voltage wires and the grounded plate electrodes through the plasma zone. Chen et al. [15] established a plasma processing system by using DBD arrays in water mist spray. Within 35 min treatment, phenol concentration decreased from 100 mg/L to 9.8 mg/L. Grabowski et al. [16] found that 50% phenol degradation can be reached in 8 min by using a thin layer of water and in less than 30 s by spraying water in a pulsed batch reactor. However, to the best of our knowledge, only a few works have taken full advantage of the exhaust gas discharged from the plasma reactor. Pokryvailo et al. [17] added a compressor to extract air from the reactor exhaust for liquid treatment. The efficiency of circulating the exhaust air into the pulsed corona discharge on organic compounds degradation has not been investigated.

Based on the device in literature [11], a new type of plasma reactor was proposed. This reactor uses a wire-cylinder configuration with a gas circulation system, thereby increasing O₃ utilization in air exhaust, reducing the pollution of O₃ gas, and enhancing corona discharge efficiency in wastewater treatment. This experiment investigated the effects of parameters such as discharge voltage, initial pH and catalyst addition on the degradation of pollutants. These operating parameters were optimized so that the feasibility of degrading phenol water with the novel reactor can be demonstrated. Furthermore, the novel reactor was also used for the deep treatment of low concentration pollutants in coking wastewater samples. The comparison of the operating costs of the plasma and O₃ oxidation method was studied. This work focuses on the optimization of the corona discharge process, which provides a reference for later practical applications. It is expected to provide a new alternative for coking wastewater and pretreatment method in future commercial applications.

2. Materials and methods

2.1. Experimental device

The reaction system mainly includes an ns-pulsed power supply, a water aerosol reactor and gas lines, as shown in Figure 1. The reactor employed for this study was developed from the one previously described in Ref. [11]. It consists of a stainless steel cylindrical vessel, a stainless steel wire, springs and porcelain insulators. The vessel placed horizontally was 1,525-mm long with an inner diameter of 89 mm, which acts as a grounded electrode. The stainless-steel wire was used as a high voltage electrode with 0.35 mm diameter along the axis of the vessel that was used as grounded electrode. One end of the cylinder was installed with an atomizing nozzle and a vent of 80 mm diameter. The other end was installed with a vent of 50 mm diameter. The two vents were connected to an air fan by the plastic pipes.

![Figure 1. Plasma discharge experimental device diagram.](image-url)

A positive polarity discharge was generated by increasing the voltage between the high voltage electrode and the ground electrode. Gas-liquid mixture was sprayed directly into the reactor by the
nozzle at a rate of 150 mL/min. The air fan continuously circulated the gas obtained from the air exhaust of the reactor in an almost closed loop to fully use the O₃ produced by NTP. A container located below the reactor collected the treated solutions. After treatment, the collected solutions were sprayed into the reactor and treated by plasma again. Solutions were exposed to the plasma six times in a batch plasma treatment experiment. Voltage probe (Tektronix P6015A) was used to adjust the applied voltage of 20-35 kV and digital oscilloscope was used for real-time monitoring (Tektronix TDS3014, 100 MHz, 1.25 GS/s). The discharge was excited using a monopole pulsed power supply with rise time of 150 ns and pulse width of 350 ns.

2.2. Materials and analytical methods
A batch of plasma treatment experiments was conducted using 1 L phenol solution of 100 mg/L initial concentration. The pH and conductivity of the 100 mg/L phenol solution were 6.30 and 15 μs/cm, respectively. The chemical oxygen demand (COD) was approximately 244.6 mg/L. Phenol decomposition was determined by measuring the phenol conversion as a function of passes through the reactor numbers at different experimental parameters. The concentration of phenol in water was monitored by the 4-aminoantipyrine method [18]. The minimum detectable amount of phenol was 0.1 mg/L. The intermediates and final products of phenol were determined by GC/MS (GC-TOF, Micromass). Based on the potassium dichromate oxidation method, the COD value in the solution was determined [18]. The pH value and conductivity of the solution were measured by a pHS-3C pH meter (Shanghai Precision & Scientific Instrument Co. Ltd.) and a DDS-11D conductivity meter (Shanghai Precision & Scientific Instrument Co. Ltd.), respectively. The O₃ content in the solution was determined by the indigo method [19]. The concentration of dissolved H₂O₂ was monitored by the potassium titanium (IV) oxalate method using a UV-vis 2450 spectrophotometer (SHIMADZU Co. Ltd., Japan) [20].

The removal efficiency of phenol is calculated as follows:

\[ \eta\% = \frac{C_0 - C}{C_0} \times 100\% \]  

where \( C_0 \) and \( C \) are the initial and final concentration of phenol in solution, respectively.

Electric energy per mass (\( E_{EM} \)) is the electric energy in kilowatt-hours [kWh] required to bring about the degradation of a unit mass of a contaminant \( C \) in solution. The \( E_{EM} \) value [kWh/kg] was calculated by using the following formula [21, 22]:

\[ E_{EM} = \frac{P \cdot t \cdot 10^6}{C_0 \cdot R \cdot V} \]  

where \( C_0 \) is the initial concentration of the organic compound (mg/L), \( V \) is the solution volume (L), \( R \) is the decomposition efficiency (%), \( P \) is the rated power (kW) and \( t \) is the treatment time (h).

3. Results and discussion

3.1. Phenol decomposition in the novel reactor

Figure 2 shows the decomposition rate of the 100 mg/L phenol solution in three modes at an applied voltage of 30 kV with a discharge frequency of 600 Hz. Due to the hydrodynamic cavitation volatility of phenol, approximately 5.0%-10.4% phenol was removed through the nozzle from the 1st-6th passage. In the plasma treatment process of the gas circulation system, the phenol concentration decreased rapidly and gradually with cyclic treatment number in this case. After the 6th plasma treatment with gas circulation, 87.4% phenol was decomposed and 65.2% COD was removed, which is higher compared without gas circulation with 51.9% phenol decomposition and 35.6% COD removal.

Discharge at the gas-liquid interface at atmospheric pressure will cause many chemical reactions, which can increase the production of active free radicals [23]. It is a great source of active free radicals which can degrade most organic pollutants. The rate constants for the reactions of \( \text{O}_3 \), \( \text{•OH} \), and \( \text{•H} \) with phenol are \( 1.3 \times 10^3 \text{ L/(mol·s)} \), \( 6.6 \times 10^9 \text{ L/(mol·s)} \), and \( 1.7 \times 10^9 \text{ L/(mol·s)} \), respectively [24, 25].
The high-energy electrons, hydroxyl radicals, O$_3$ and other reactive species formed during discharge can degrade phenol in water. The O$_3$ from the gas exhaust of the vessel also plays an important role on phenol decomposition. Wen [26] found that the use of pulsed corona discharge combined with O$_3$ led to the high degradation rate of 4-CP (96% within 30 min) and COD removal. Therefore, the obvious synergistic effect is attributed to the enhanced O$_3$ decomposition by electron collisions and photolysis in the plasma region.

Figure 2(a). Phenol decomposition in three modes.  
Figure 2(b). COD removal in three modes.

3.2. Dissolved O$_3$ and H$_2$O$_2$ concentration  
O$_3$ ($E^0 = 2.07$ V/SHE) and H$_2$O$_2$ ($E^0 = 1.77$ V/SHE) generated during electrical discharge are powerful oxidants and are relatively stable in aqueous solution. To study the importance of oxidizing substances on phenol degradation, the aqueous concentrations of O$_3$ and H$_2$O$_2$ in pure water and phenol solution were analyzed. Figure 3 shows that the O$_3$ concentrations in the two solutions increase with cyclic numbers following a trend that is almost similar to that of H$_2$O$_2$ concentrations. Due to the consumption of O$_3$ and H$_2$O$_2$ by reacting with phenol, the concentrations of those reactive species are lower in phenol solution than in pure water. During the high-voltage pulsed discharge of air, the second positive system of nitrogen in the wavelength range of 290-420 nm emits and high-energy electrons generate [27]. They can decompose O$_3$ to generate oxygen atoms and O$_2$ [28]. Then excited oxygen reacts with H$_2$O to produce •OH radicals [29]. In addition, O$_3$ generated in the gas phase is hydrolyzed in the aqueous solution, and other reactive oxygen species (such as •O$_2^-$, •OH) are also generated [30-31].

The direct reactions of H$_2$O$_2$ with organic pollutants are generally slow. O$_3$ is an essential oxide which plays an important role in the oxidation of phenol. Therefore, with increasing treatment time increasing, O$_3$ production decreases much more than H$_2$O$_2$ production in the phenol solution.

Figure 3(a). Concentrations of O$_3$ in the pure water and phenol solution during discharge.  
Figure 3(b). Concentrations of H$_2$O$_2$ in the pure water and phenol solution during discharge.

3.3. Byproducts and changes in pH, and conductivity of the treated solution  
Phenol solution shifted from colorless to faint yellow and then diminished during treatment with gas circulation, indicating the formation of other intermediate products. The pollutants in the original
phenol solution (Figure 4a) and the solution after the second treatments (Figure 4b) were analyzed by GC/MS. The main intermediates during treatment process were benzoquinone, toluene, p-xylene, 3-hydroxyl 1-butyl propionate and other unidentified trace products. The main reaction of phenol decomposition involved •OH radical attacking its aromatic ring. Subsequently, benzoquinone, hydroquinone and catechol were formed. During further oxidation by active species (such as •OH), and ring cleavage occurred. Finally, carbonic acids were formed. Deep oxidation leads to the mineralization of these substances to CO₂ and H₂O.

Figure 5 shows the pH value and conductivity of the solution monitored during phenol decomposition. The solution pH decreased from 6.27 to 3.15 after the 1st treatment and to 2.32 after the 6th treatment. The variation in pH value indicated that the amount of carbonic and carboxylic acids in the solution increased with increasing treatment time. Conductivity growth is caused by the electrolyzable byproducts of phenol degradation formed from phenol degradation. During discharge, the excitation, dissociation and ionization of N₂ and O₂ in air promote the formation of HNO₃ [32, 33]. It also caused variation in conductivity and pH.

3.4. Effect of applied voltage
The effects of applied voltage variation on phenol decomposition efficiency were investigated. Figure 6 shows that the decomposition rate of phenol increased with the increase of applied voltage at the same discharge frequency. The maximum phenol degradation rate reached at 35 kV from 34.0% to 91.5% from the 1st to 6th treatment. The COD removal reached 67.9% at a charging voltage of 35 kV after six times of plasma treatment. In fact, the increase of the applied voltage caused the increase of the discharge power, which made the physicochemical reactions in the reaction process more severe and indirectly enhanced the production of active free radicals in the water. The applied voltage played an important role on the oxidation of phenol.

3.5. Effect of initial pH
The initial pH of the solution is an important factor that influences the decontamination of organic compounds. H₂SO₄ (1.0 mmol/L) or NaOH (1.0 mmol/L) was used to adjust the initial pH of the phenol solution to the desired levels. Figure 7 shows that with increasing pH, the removal rates of phenol increase at 30 kV and 600 Hz. The phenol removal efficiencies in alkaline conditions were
higher than that in acidic solutions. At pH 9 and 11.0, more than 90.0% phenol was decomposed after the 2nd treatment, and the overall decontaminations were almost equal. Similar to the results of phenol removal, the COD removal are higher in alkaline conditions than in acidic conditions. COD removals were 69.0% at pH 9 and 82.3% at pH 11, respectively.

The results were similar to the conclusions reported in other literature [34]. As the pH of the solution gradually increased, O\textsubscript{3} would decompose faster, and the yield of •OH would increase [35]. The existence of OH\textsuperscript{-} species enhanced the decomposition of O\textsubscript{3} into the hydroxyl radical. Although •OH can participate in a side reaction, which transforms OH\textsuperscript{-} to its less reactive species (e.g. HO\textsubscript{2}, O\textsubscript{2}\textsuperscript{-}) [36]. But the influence of this transformation was eliminated by O\textsubscript{3} decomposition during the treatment stage for high alkaline solution. In addition, many H\textsuperscript{+} in the acidic solution may reduce the effective role of high-energy electrons. Few activated species such as HO\textsubscript{2} and O\textsubscript{2} are formed, and the formation of •OH, •H, and O\textsubscript{3} was reduced. Therefore, the decomposition of phenol in alkaline solutions was higher than that in acidic ones.

![Figure 7. Effect of initial pH on the phenol decomposition and COD removal.](image)

![Figure 8. Effect of Fe\textsuperscript{2+} on the phenol decomposition and COD removal.](image)

3.6. Effects of ferrous ions and H\textsubscript{2}O\textsubscript{2} addition
In order to make full use of the physicochemical effects of the plasma discharge process, a combination of pulsed discharge and catalysts was proved effective. The combination was applied in several commercialized products [37]. Ferrous salt was added to facilitate the Fenton reaction in plasma gas-liquid reactors as studied in literature. To determine the influence of ferrous ions on decomposition efficiency, different FeSO\textsubscript{4}\cdot7H\textsubscript{2}O dosages (calculated by Fe\textsuperscript{2+} concentration) were added to phenol solutions before passing through the plasma region. Figure 8 shows that the changes in the removal efficiency with treatment times for Fe\textsuperscript{2+} addition at 30 kV and 600 Hz. The degree of decomposition and degradation were improved in the presence of different Fe\textsuperscript{2+} dosages. Treatment with 0.3 mmol/L Fe\textsuperscript{2+} improved the phenol decomposition rate from 93.0% for pure phenol solution to 98.1%, and the COD removal rate from 65.8% to 84.8% at the 6th treatment. Experiments with Fe\textsuperscript{2+} showed the influence on the phenol removal for the concentration of H\textsubscript{2}O\textsubscript{2} produced during the plasma discharge process, which implied that the Fenton reaction can occur without adding H\textsubscript{2}O\textsubscript{2}.

To determine the influence of H\textsubscript{2}O\textsubscript{2} addition on phenol removal, different volume concentrations of 30% m/m H\textsubscript{2}O\textsubscript{2} (0.1‰, 0.3‰, 0.9‰) were added to the solution. Phenol degradation can be accelerated in the presence of H\textsubscript{2}O\textsubscript{2}, as shown in Figure 9. The removal of phenol increased with the addition of H\textsubscript{2}O\textsubscript{2}. Phenol removal rate was 64.8% with the addition of 0.9‰ H\textsubscript{2}O\textsubscript{2} at the 1st treatment, which was more effective than 31.8% in plasma treatment alone. The results show that H\textsubscript{2}O\textsubscript{2} can initiate a variety of free radical reactions and promote the decomposition of phenol. It is attributed to the more efficient •OH generation in the water by adding the proper concentration of H\textsubscript{2}O\textsubscript{2} [10, 38].

3.7. Treatment of coking wastewater
Phenolic compounds are the main organic pollutants in coking wastewater, accounting for about 80% of COD [39-41]. To investigate the oxidizing capability of the reactor with gas circulation, a kind of refractory and toxic coking wastewater (phenols 35 mg/L, COD 250 mg/L) was examined.
Figure 10 shows that the composition of phenolic compounds was 92.0%, and COD removal reached 38.6% at the 6th treatment. For refractory organic compounds in the coking wastewater, COD degradation rate was low. With 9‰ H₂O₂ addition, 89.8% of phenolic compounds decomposed at the 2nd treatment and 99.9% at 6th treatment, which was almost equal with the addition of 0.3 mmol/L Fe²⁺. COD removal with 0.9‰ H₂O₂ addition reached 61.3%, which is 22.7% higher under the addition of NTP during the 6th pass. In the NTP/Fe²⁺ treatment, COD removal reached 66.1%. The addition of H₂O₂ and Fe²⁺ played an important role in accelerating organic matter degradation and thoroughly oxidizing organic compounds.

**Figure 9.** Effect of H₂O₂ addition on the phenol decomposition and COD removal.

**Figure 10.** Effect of H₂O₂ and Fe²⁺ on the phenolic compounds decomposition and COD removal.

O₃ oxidation is a common treatment method for coking wastewater [41]. Ozonation experiment was performed in a Plexiglas column (Ø50×1,000 mm). About 16 mg/(L•min) of O₃ was added to 1 L of coking wastewater by aeration device, and the concentration of O₃ in the water was 80 mg/L. After 60min of reaction, 85.6% phenol decomposition and 40.11% COD removal were obtained, as shown in Figure 11. In the same reaction time, the degradation efficiency of phenolic compounds and COD removal by plasma technology are better, which is mainly due to various physical and chemical effects produced during the discharge process to improve the oxidation of pollutants.

**Figure 11.** The removal rate of phenolic compounds and COD by ozone oxidization.

### 3.8. Comparison of processes and cost evaluation

Based on the amount of catalyst and the power consumption of the reaction, the operation cost of different processes was evaluated. For the two processes, the O₃ generator power was 10.2 kW and the NTP system was 2.68 kW (power supply 1.5 kW, air fan 1.1 kW, air compressor 0.08 kW). For COD reduction, the $E_{EM}$ values of NTP and ozonation were 18.5 kWh/g (30 kV, 6th pass) and 101.7 kWh/g, respectively. NTP/H₂O₂ and NTP/Fe²⁺ were 11.7 and 10.8 kWh/g, respectively. Considering the oxygen consumption, the cost of ozonation treatment was approximately $16.65 per gCOD. The cost of plasma treatment was approximately $1.90 per gCOD. Therefore, for coking wastewater treatment, the plasma system was more economical than the O₃ oxidation. Compared with other wastewater treatment processes such as biological method and adsorption method, plasma discharge system can reduce treatment time, land occupancy rate and cost.
4. Conclusions
The decomposition of organic pollutants was studied experimentally by applying plasma generated by the pulsed discharge in a novel gas-liquid reactor with an exhaust gas circulation system. Two different systems for phenol degradation were examined: 87.4% phenol decomposition and 65.2% COD removal were observed in the 6th treatment by the plasma with gas circulation, which was higher without gas circulation with 51.9% phenol decomposition and 35.6% COD removal. The apparent improvement of treatment efficiency is attributed to the full utilization of O$_3$ in the exhaust gas of the plasma reactor. The removal efficiency of phenol increased with the increase of applied voltage and pH value. The addition of 0.9‰ H$_2$O$_2$ and 0.3 mmol/L Fe$^{2+}$ apparently enhanced the phenol removal. The reactor was also used to treat phenolic compounds in coking wastewater. Compared with other processes, the plasma system has higher treatment efficiency and is suitable for the treatment of industrial wastewater.

Acknowledgments
This work was funded by the Natural Science Foundation of China (No. 51707093 and No.51777091).

References
[1] Bruggeman P J, Kushner M J, Locke B R, Gardeniers J G E, Graham W G, Graves D B, Hofman-Caris R C H M, Marie D, Reid J P, Ceriani E, Fernandez Rivas D, Foster J E, Garrick S C, Gorbanev Y, Hamaguchi S, Iza F, Jablonowski H, Klimova E, Kolb J, Krema F, Lukes P, Machala Z, Marinov I, Mariotti D, Mededovic Thagard S, Minakata D, Neyts E C, Pawlat J, Petrovic Z Lj, Pflieger R, Reuter S, Schram D C, Schröter S, Shiraiwa M, Tarabová B, Tsai P A, Verlet J R R, Woedtke T, Wilson K R, Yasui K, Zvereva G 2016 Plasma-liquid interactions: a review and roadmap Plasma Sources Sci. Technol 25 053002
[2] Locke B R, Sato M, Sunka P, Hoffmann M R, Chang J S 2005 Electrohydraulic discharge and nonthermal plasma for water treatment Ind Eng Chem Res 45(3) 882-905
[3] Guo H, Jiang N, Wang H, Shang K, Lu N, Li J, Wu Y 2019 Enhanced catalytic performance of graphene-TiO$_2$ nanocomposites for synergetic degradation of fluoroquinolone antibiotic in pulsed discharge plasma system Appl Catal B: Environ 248 552-566
[4] Wang T, Qu G, Ren J, Yan Q, Sun Q, Liang D, Hu S 2016 Evaluation of the potentials of humic acid removal in water by gas phase surface discharge plasma Water Res 89 28-38
[5] Joanna Pawlat 2013 Electrical discharges in humid environments. Generators, effects, application. Lublin, Poland: Lublin University of Technology
[6] Chen B, Zhu Ch, Fei J, He X, Yin Ch, Wang Y, Gao Y, Jiang Y, Wen W, Chen L 2016 Yield of ozone, nitrite nitrogen and hydrogen peroxide versus discharge parameter using APPJ under water Plasma Sci Technol 18(3)278-286
[7] Hsieh K C, Wang H, Locke B R 2016 Analysis of electrical discharge plasma in a gas-liquid flow reactor using optical emission spectroscopy and the formation of hydrogen peroxide Plasma Process Polym 13(9) 908-917
[8] Burlica R, Shih K Y, Locke B R 2013 Formation of H$_2$ and H$_2$O$_2$ in a water-spray gliding arc nonthermal plasma reactor Ind Eng Chem Res 52 (37) 13516-13516
[9] Magureanu M, Mandache NB, Parvulescu VI 2015 Degradation of pharmaceutical compounds in water by non-thermal plasma treatment Water Res 81 124-136
[10] Malik M A 2010 Water purification by plasmas: which reactors are most energy efficient Plasma Chem Plasma Process 30(1) 21-31
[11] Minamitani Y, Shoji S, Ohba Y, Higashiyama Y 2008 Decomposition of dye in water solution by pulsed power discharge in a water droplet spray IEEE T Plasma Sci 36(5)2586-2591
[12] Handa T, Minamitani Y 2009 The Effect of a water-droplet spray and gas discharge in water treatment by pulsed power IEEE T Plasma Sci 37(1) 179-183
[13] Ajo P, Krzymyk E, Preis S, Kornev I, Kronberg L, Louhi-Kultanen M 2016 Pulsed corona
discharge oxidation of aqueous carbamazepine micropollutant. Environ Technol 37(16)2072-2081.

[14] Ajo P, Kornev I, Preis S 2015 Pulsed corona discharge in water treatment: the effect of hydrodynamic conditions on oxidation energy efficiency Ind Eng Chem Res 54(30) 7452-7458.

[15] Chen B, Zhu C, Fei J, He X, Yin C, Wang Y, Jiang Y, Chen L, Gao Y, Han Q 2016 Water content effect on oxides yield in gas and liquid phase using DBD arrays in mist spray Plasma Sci Technol 18(1) 41-50.

[16] Grabowski L R, van Veldhuizen E M, Rutgers W R 2005 Removal of phenol from water: A comparison of energization methods J Adv Oxid Technol 8(2) 142-149.

[17] Pokryvailo A, Wolf M, Yankelevich Y, Wald S, Grabowski LR, van Veldhuizen EM, Rutgers WR, Reiser M, Glocker B, Eckhardt T, Kempenaers P, Wellemann A 2006 High-power pulsed corona for treatment of pollutants in heterogeneous media IEEE Trans Plasma Sci 34(5) 1731-1743.

[18] APHA AWWA WEF 2012 Standard methods for the examination of water and wastewater, 22nd edition. In APHP, Washington, DC.

[19] Bdaer H, Hoigne J 1981 Determination of ozone in water by the indigo method Water Res 15(4) 449-456.

[20] Selles R M 1980 Spectrophotometric determination of hydrogen peroxide using potassium titanium(IV) oxalate Analyst 105(1255) 950-95.

[21] Bolton J R, Bircher K G, Tumas W, Tolman C A 2001 Figures of merit for the technical development and application of advanced oxidation technologies for both electric and solar driven systems Pure Appl Chem 73(4) 627-637.

[22] Selçuk Kuşçu Ö, Eke E 2015 Treatment of olive oil mill wastewater by a pulsed high - voltage discharge process; process optimization and combination with Fe2+ and H2O2 J Chem Technol Biot 90(6) 1040-1050.

[23] Aziz KHH, Miessner H, Mueller S, Kalass D, Moeller D, Khoshid I, Rashid MAM 2017 Degradation of pharmaceutical diclofenac and ibuprofen in aqueous solution, a direct comparison of ozonation, photocatalysis, and non-thermal plasma Chem Eng J 313 1033-1041.

[24] Ramseier M K, Gunten U V 2009 Mechanisms of phenol ozonation—kinetics of formation of primary and secondary reaction products Ozone Sci Eng 31(3) 201-215.

[25] Buxton G V, Greenstock C L, Helman W P, Ross A B 1988 Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (•OH/•O-) in aqueous solution J Phys Chem Ref Data 17(2) 513-886.

[26] Wen Y, Jiang X, W Liu 2002 Degradation of 4-chlorophenol by high-voltage pulse corona discharges combined with ozone Plasma Chem Plasma Process 22(1) 175-185.

[27] Wang W, Zhang J, Liu F, Liu Y, Wang Y 2004 Study on density distribution of high-energy electrons in pulsed corona discharge Vacuum 73 (3-4) 73333-339.

[28] Kitayama J, Kuzumoto M 1997 Theoretical and experimental study on ozone generation characteristics of an oxygen-fed ozone generator in silent discharge J Phys D: Appl Phys 30 (17) 2453-2461.

[29] Tarr M A 2003 Chemical degradation methods for wastes and pollutants: environmental and industrial applications. Marcel Dekker, Inc, New York.

[30] Joshi A A, Locke B R, Arce P, Finney W.C 1995 Formation of hydroxyl radicals, hydrogen peroxide and aqueous electrons by pulsed streamer corona discharge in aqueous solution J Hazard Mater 41(1) 3-30.

[31] Burlica R, Locke B R 2008 Pulsed plasma gliding-arc discharges with water spray IEEE T Ind Appl 44(2) 482-489.

[32] An G, Sun Y, Zhu T, Yan X 2011 Degradation of phenol in mists by a non-thermal plasma reactor Chemosphere 84 (9) 1296-1300.
[33] Singh R K, Babu V, Philip L, Ramanujam S 2016 Applicability of pulsed power technique for the degradation of methylene blue J Water Process Eng 11 118-129

[34] Roth J A, Sullivan D E 1981 Solubility of ozone in water Ind Eng Chem Fundamen 20(2) 137-140

[35] Haghighat G, Sohrabi A, Shaibani P M, Neste C W V,Naicker S, Thundat T 2017 The role of chloride ions in plasma-activated water treatment processes Environ Sci: Water Res Technol 3(1) 156-168

[36] Kawai Y, Ikegami H, Sato N, Matsuda A, Uchino K, Kuzuya M, Mizuno A 2010 Industrial plasma technology-applications from environmental to energy technologies Wiley-VCH

[37] Kirkpatrick M J, Locke B R 2005 Hydrogen, oxygen, and hydrogen peroxide formation in aqueous phase pulsed corona electrical discharge Ind Eng Chem Res 44 (12) 4243-4248

[38] Zhang F, Wei C, Hu Y, Wu H 2015 Zinc ferrite catalysts for ozonation of aqueous organic contaminants: phenol and bio-treated coking wastewater Sep Sci Technol 156(2) 625-635

[39] Chen T, Huang X, Pana M, Jin S, Peng S, Faligren P H 2009 Treatment of coking wastewater by using manganese and magnesium ores J Hazard Mater 168(2-3) 843-847

[40] Yang Y, Liu Y, Yang T, Lv Y 2017 Characterization of a microbial consortium capable of heterotrophic nitrifying under wide C/N range and its potential application in phenolic and coking wastewater Biochem Eng J 120 33-40

[41] Wei Q, Qiao S, Sun B, Zou H, Chen J, Shao L 2015 Study on the treatment of simulated coking wastewater by O₃ and O₂/Fenton processes in a rotating packed bed RSC Adv 5(113) 93386-93393