Degradation of phenol and Bisphenol-A using discharged water generating system

Muhammad Tahir Amin, Seungmin Ryu and Heekyung Park

ABSTRACT

There is a growing interest in the use of AOPs to develop efficient water treatment systems. Chlorination forms different DBPs. Ozonation has been considered to be a less attractive alternative in some applications due to expensive costs and short life-time. To cope with the disadvantages of chlorination and ozonation, a novel oxidants-generating system, named Discharged Water Generating (DWG) System has been invented. The DWG system is an innovative technique to oxidize pollutants. It is based on the principle of lightning discharge in air. This technique uses plasma discharge in 2-phase (Air-Water). Plasma produces NO, NO_2, $O_{3(g)}$. Produced oxidants dissolve in water directly by high pressure of plasma and change to $O_{3(aq)}$, HNO_2 and HNO_3. Moreover plasma discharge can produce many other radicals. These are helpful in degradation of contaminants. The oxidation of phenol and Bisphenol-A (BPA) in aqueous solution has been studied in detail. Phenol degradation was about 50% while BPA was degraded about 80–90% after one hour of oxidation in the DWG system. Higher phenol degradation (more than 80%) was achieved at basic pH confirming the contribution of ozone, OH radical and other oxidants present in the DWG system towards the phenol degradation. Best results for BPA degradation were achieved at pH = 3. Higher initial phenol concentration has an effect on lowering the degradation efficiency of the DWG system. The phenol oxidation product mixture has a complex composition. 2-Nitrophenol has been identified mainly among the oxidation products of phenol which confirms NO_2^- attack on the phenoxide ring and there is no involvement, whatsoever, of any reactive free radicals, such as, NO_2, NO, OH or O^{-2} or any NO_2^+ ion as an active intermediate in the reaction.

Key words | 2-Nitrophenol, BPA, degradation, DWG system, phenol

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INTRODUCTION

As the World comes to the beginning of the 21st century, the water industry is required to produce drinking water of high quality. The conventional water treatment processes are not able to address adequately the removal of a wide spectrum of toxic chemicals and pathogenic microorganisms in raw water. Chlorination forms different Disinfection by-products (DBPs) in portable drinking water. Ozonation has been considered to be a less attractive alternative due to expensive costs and short life-time. As a result, there is growing interest in the use of Advanced Oxidation Processes (AOPs) to develop efficient water treatment systems (Camel & Bermond 1998). This research is focused on the Discharged Water Generating (DWG) process for treating organic materials in water.

To cope with the disadvantages of ozone, a novel ozone-generating system, named DWG system has been invented. The idea to develop the DWG system is taken from the fact that ozone and other various radicals are generated in the Earth's stratosphere due to its ionization by cosmic rays in a chain of chemical reactions. The same concept was applied in

the DWG system. This system can produce ozone, OH radial, nitrate, nitrite, other negative ions and radicals in contact water directly using plasma discharge.

A very particular advantage of the DWG system is the fact, that a highly reactive streamer discharge medium is created. Electric discharges in water produce hydroxyl radicals and hydrogen atoms from the dissociation and ionization of water molecules. In a humid gas phase, electric discharges additionally create radicals, ions and metastables from the dissociation and ionization of the gas phase molecules or atoms. In humid air, the following main oxidizer species are produced: hydroxyl radicals, ozone, atomic oxygen, and hydroperoxyl radicals. Also nitrogen oxides like NOx and N_2O are formed during these reactions (Seungmin *et al.* 2004).

Phenol is an aromatic compound consisting of a benzene ring with hydroxyl group (OH^-) attached. It is toxic at low concentrations, highly stable and difficult to degrade (Autenrieth *et al.* 1991). For the chemical breakdown of this product high energy inputs are required and for the biological breakdown the reaction may be slow as the cells require high amounts of energy to utilise the substrate. However, there are biological systems available to degrade phenol. Over the last two decades, there has been a great deal of research on the degradation of phenol at concentrations between 500–4,000 mg/L (Yang & Humphrey 1975; Bettman & Rehm 1985; Lakhwala *et al.* 1992). Low degradation rates have been observed at low levels of phenol. In batch systems complete degradation occurs, but as the phenol concentration lowers in the reactor so does the biomass population, and so degradation rates decrease significantly (Bettman & Rehm 1984). To overcome this, continuous reactors were used. This allows a viable population of cells to be present for a longer duration (Yang & Humphrey 1975; Erhardt & Rehm 1989; Khoury *et al.* 1992). Chemical processes available for the removal of phenol include chlorination, ozonation and benzol extraction, all giving more than 97% removal efficiency (Bond & Straub 1974). However, toxic by-products can be produced from these processes resulting in secondary effluent problems (Autenrieth *et al.* 1991).

Bisphenol-A (BPA), a suspected endocrine disruptor (ED), is widely used for the production of epoxy resins and polycarbonate (PC) plastics. BPA has a slight to moderate toxicity and low biological concentration factors (BCFs) in aquatic organisms (Staples *et al.* 1998). In the area of degradation and treatment of BPA, many studies have been focused on biodegradation. Tsutsumi reported the removal of estrogenic activities of BPA by oxidative enzymes from lignin degrading basidiomycetes (Tsutsumi *et al.* 2001). Traditional physical-chemical treatment techniques are also used to remove BPA in water such as coagulation, filtration and adsorption (USEPA 2001). Kuramitz reported the electrochemical oxidation application for the removal of BPA using a carbon fiber electrode (Kuramitz *et al.* 2001). Kadoma and Fujisawa indicated that BPA derivatives could play as a free radical scavenger in the polymerization of methacrylate (Kadoma & Fujisawa 2000). While Atkinson and Roy proposed that BPA could be oxidized by H_2O_2 in the presence of peroxidase, in vitro, to produce BPA semiquinone, which could add to DNA causing gene toxicity (Atkinson & Roy 1995). In the last three years, Sajiki and Yonekubo have reported their series studies on the oxidation of BPA leached from PC tubes by the reactive oxygen species (ROS) from Fenton reaction (Sajiki 2001; Sajiki & Yonekubo 2002; Sajiki & Yonekubo 2003). Photooxidation of BPA is easier in the atmosphere than in water (Staples *et al.* 1998). The photooxidation products of BPA could be phenol, 4-isopropylphenol, and a semiquinone derivative of BPA (Howard 1989). Tanizaki reported their results on photocatalytic degradation of BPA in water on a TiO_2 thin film (Tanizaki *et al.* 2002).

MATERIALS AND METHODS

Vertical flow DWG system

The vertical flow type DWG system is used for phenol treatment. Two litres of a sample containing phenol or simply discharged water is circulated by mechanical pumping. Natural air is induced by circulation of water. Optimum electric conditions to produce plasma were inspected. The conditions of power to produce plasma were "20 kV, 2 mA and 1.7 kHz sine wave". In case of vertical flow type DWG system water cooling system was used. The direction of flow was vertical through the plasma which is one of the basic differences between both systems.

During plasma discharging, oxygen in air produces ozone as in a traditional corona discharge system. Additionally, NO_x are produced in lightning and water decomposes to H and OH. OH radical promotes the oxidation of various matters produced during the discharging process. Plasma discharge produces many other radicals which are helpful in the degradation of various organic materials.

Horizontal flow DWG system

The horizontal flow type DWG system was used for BPA treatment. Again two litres of a sample containing BPA or simply distilled water was circulated by mechanical pumping. The conditions of power to produce plasma were "20 kV, 4 mA and 1.7 kHz sine wave". In case of horizontal flow type DWG system air cooling system was used instead of water cooling system. The other basic difference between the two systems was that of the flow direction which is in the horizontal direction in the case of horizontal flow type DWG system while the vertical flow type DWG system used for phenol water moves vertically through the plasma as is clear from Figure 1(b).

HPLC analysis

Batch experiments were adopted in the present study in order to facilitate identification of the optimum operating conditions of the DWG system. Aqueous solutions of phenol of nearly 5, 10, 50 and 100 ppm were prepared in distilled water. Also aqueous solutions of BPA of nearly 5 and 10 ppm were prepared in distilled water. The initial pH values used for both the phenol and BPA aqueous solutions were 3, 7 and 10. These initial pH values were adjusted using NaOH and H_2SO_4 solutions.

The samples were taken at appropriate time intervals and analyzed by high pressure liquid chromatography (HPLC) using a Waters chromatograph (JESCO UV970, pump: JESCO TU980). The analyses were made in reverse phase with C18 Column eluting the injected sample (20 µl) with a mixture of acetonitril-water (50:50 v/v) with a flow rate of $1\,cm^3.min^{-1}$ for phenol and with a flow rate of $0.5\,cm^3\,min^{-1}$ for BPA. In addition, several samples were

also analyzed to determine the Chemical Oxygen Demand (COD) by potassium dichromate titrimetric method.

IC analysis

Ion Chromatography (IC) (DIONEX 120) is used to measure the nitrite and nitrate concentration in different samples at appropriate time intervals with a flow rate of 1 ml/min.

Some samples are also analyzed for intermediates by HPGC (HP 5890 SERIES2).

Total organic carbon

The carbon content of phenol solutions has been determined versus the oxidation time using a TOC analyzer (DOHRMANN DC-180 ROSEMOUNT). The total organic carbon (TOC) content is determined from the difference of total carbon content (TC) and total inorganic carbon content (TIC). The TC content is calculated from the amount of carbon dioxide that is released from catalytic combustion of the sample. The carbon dioxide concentration is measured by infrared spectroscopy. The TIC content is determined from the carbon dioxide release that occurs after acidification of the sample with phosphoric acid.
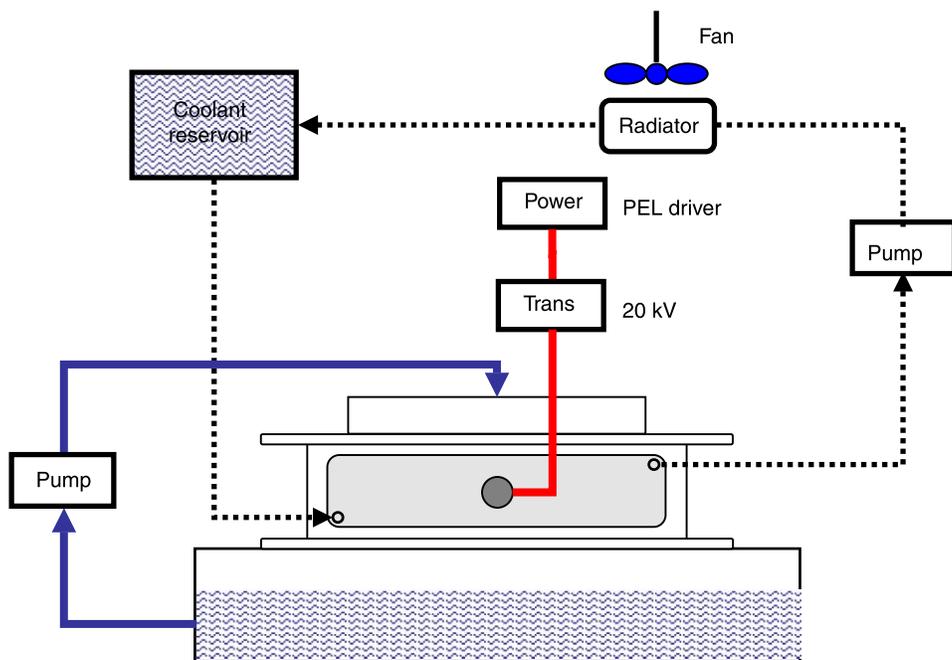
RESULTS AND DISCUSSION

Possible reaction product from both DWG systems

Possible reactions in both horizontal and vertical flow types DWG systems in gas phase where the natural air is discharged using plasma are as follows:

$$N_2\,(gas) \rightarrow 2N° \tag{1}$$

$$O_2\,(gas) \rightarrow 2O° \tag{2}$$

$$N° + O° \rightarrow NO \tag{3}$$

$$2NO + O_2 \rightarrow 2NO_2 \tag{4}$$

$$O° + O_2 \rightarrow O_3 \tag{5}$$

Figure 3 supports the above equations.
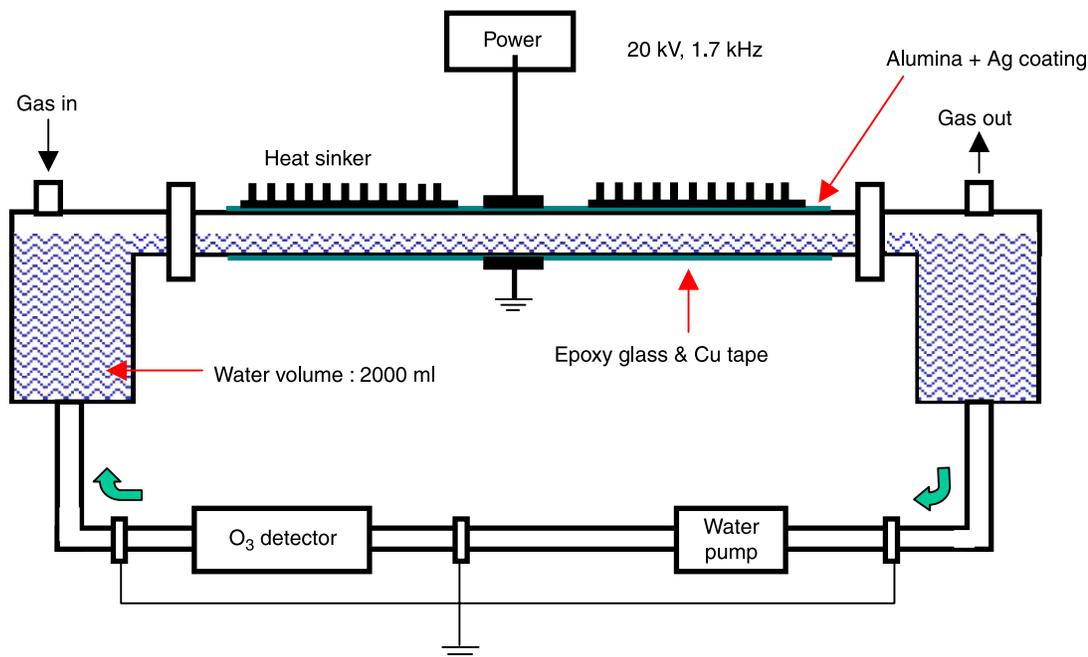
(a) Vertical system

(b) Horizontal system

Figure 1 | (a) Schematic diagram of vertical flow DWG system, (b) Schematic diagram of horizontal flow DWG system.

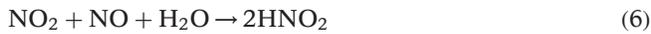In liquid phase possible reactions are as follows:

$$NO_2 + NO + H_2O \rightarrow 2HNO_2 \tag{6}$$

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \tag{7}$$

$$O_3(gas) \rightarrow O_3(aq) \tag{8}$$

$$O_2(aq) + O^{\circ} \rightarrow O_3(aq) \tag{9}$$

$$H_2O \rightarrow H^{\circ} + OH^{\circ} \tag{10}$$

$$OH + HNO_3 \rightarrow NO_3 + H_2O \tag{11}$$

Figure 4 supports some of the above equations.

These systems generate the nitrate radical NO_3. Dinitrogen pentaoxide may also produce and then can form the nitronium ion NO_2^+ and nitrate NO_3^- but the presence of dinitrogen pentaoxide is not confirmed although there are some other reaction species produced during the discharging process.

pH and temperature variation during the process of discharging in both systems

In a DWG system pH of the process water decreases rapidly. Neutral as well as basic solutions become acidic soon after injected in a DWG system. Figure 2 shows the change in pH value for both basic as well as acidic solutions. This trend is the same for both flow type systems. This figure shows the pH variation for phenol solutions with initial pH values of 10 and 3 injected in the DWG machine.

The pH decreased rapidly to about 3 after 5 minutes of discharging and reaches about 1.5 after one and half hours. The pH of DWG water remains constant (2 ~ 3) for
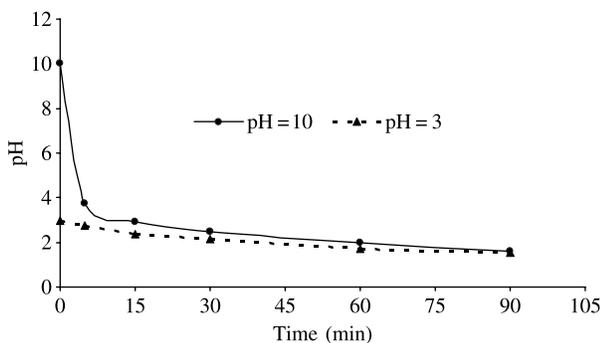

Figure 2 | Changes of pH with discharging time in vertical flow DWG system.

observed time range of about 5 hours after discharging for both systems. This change might be due to ionization of HNO_2 in water.

The final effluent temperature ranges 40–50°C in the case of the vertical flow type DWG system while this range is 50–60°C for the horizontal flow type DWG system. The temperature rises from room temperature to the values mentioned above within 5–10 minutes of the discharging and then remains almost constant at the maximum value for further discharging time untill one hour.

Phenol degradation with vertical flow type DWG system

Major species produced during the reaction

Despite all the possible reactions that occur in the DWG system, the trend of two major species, nitrate and nitrite, which are produced in the DWG system is shown in Figure 3. The observed time range here is 4 hours with only one hour discharging in the system and then four hours at room temperature with continuous mixing. Changes during one hour of discharge are not shown. "During Discharge" represents the discharging of phenolic solutions injected in the DWG system for one hour and "After Discharge" represents the one hour discharging of distilled water in the DWG system and then mixed with phenol after discharging to observe the changes for a further four hours. During discharging, high concentrations of ozone, OH and some other species are produced that react with any target compound as compared to the case when the discharged distilled water is mixed with target compounds where it contains low concentrations of ozone and other species.

This comparison of nitrite and nitrate changes is carried out with a phenol concentration of 5 ppm. Initial values of nitrite and nitrate at one hour represent the respective concentrations after one hour running of the DWG system. In the case of "During discharge", these initial values on y-axis represent nitrate and nitrite concentrations in phenolic solutions and then changes are observed for a further four hours at room temperature with continuous mixing. In the case of "After discharge", these initial values on y-axis represent nitrate and nitrite
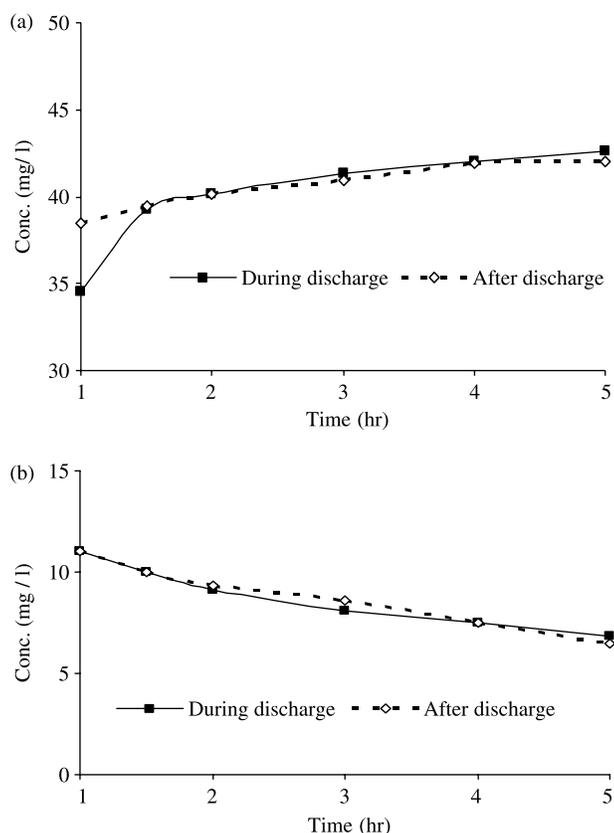
(a)

(b)

Figure 3 | (a) $NO_3^- $–N and (b) NO_2^-–N concentration changes in "After discharge" and "During discharge" cases during phenol degradation after one hour of discharging time.

concentrations in discharged distilled water without phenol and changes for a further four hours by adding phenol in one-hour discharged distilled water are observed again at room temperature with continuous mixing. It can be observed from these figures that initial nitrate values for both cases differ only by 3 mg/l while these initial values are the same in the case of nitrite. So it is concluded from this result that nitrate reacted with phenol when phenolic solutions were discharged to form several byproducts. In both "After discharge" and "During discharge" cases, with passage of time nitrite changes to nitrate, as shown in Figure 3, and the reactions that are involved during this change are;

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2 \tag{12}$$

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ \tag{13}$$

Phenol degradation in DWG system during discharge

In case of "During discharge" process different initial concentrations of phenolic solutions in distilled water i.e. 5, 10, 50 and 100 ppm each at different initial pH values i.e. 3, 7 and 10 were injected in the DWG machine and then these phenolic solutions were discharged for one hour. The results are presented in Figure 4.

Different initial pH values were selected to check the maximum efficiency of the DWG system for phenol degradation. Basic pH was adjusted by adding dilute sodium hydroxide and acidic pH was achieved by adding dilute sulfuric acid. These pH values represent only initial values at the time when phenolic solutions of different initial concentrations are injected in the system. The pH values change freely during discharging and these values are in the pH range of $2 \sim 3$ after about one hour of discharging irrespective of the initial pH values (Figure 2).

Figure 4 shows that phenol degradation is higher at basic pH value i.e. 10 and with low initial phenol concentration of 5 ppm. It is quite obvious from the results in Figure 4 that higher initial phenol concentration is difficult to degrade as compared to lower initial phenol concentration. Hence higher initial phenol concentration has an effect on lowering the degradation efficiency of the DWG system. This fact is due to the reason that more phenol is available for the resonance effect of Hydroxyl group and NO_2^- attack on the phenoxide ring.

The reactivity of phenol is caused by the strong resonance activating effect of the OH group. The phenol oxidation product mixture has a complex composition. 2-Nitrophenol (Ortho-Nitrophenol) has been identified mainly among the oxidation products of phenol which confirms NO_2^- attack on the phenoxide ring and there is no involvement, whatsoever, of any reactive free radicals, such as, NO_2, NO, OH or O^{-2} or any NO_2^+ ion as an active intermediate in the reaction.

There were some other intermediates. Although not confirmed, these possible intermediates might be para-nitrophenol small amounts of para-benzoquinone, 2,4-dinitrophenol and 2,6-dinitrophenol. Hydroquinone and Catechol were not observed which are the major reaction intermediates during the degradation of phenol by ozone. Reaction involved in the formation of ortho-nitrophenol from phenol is;
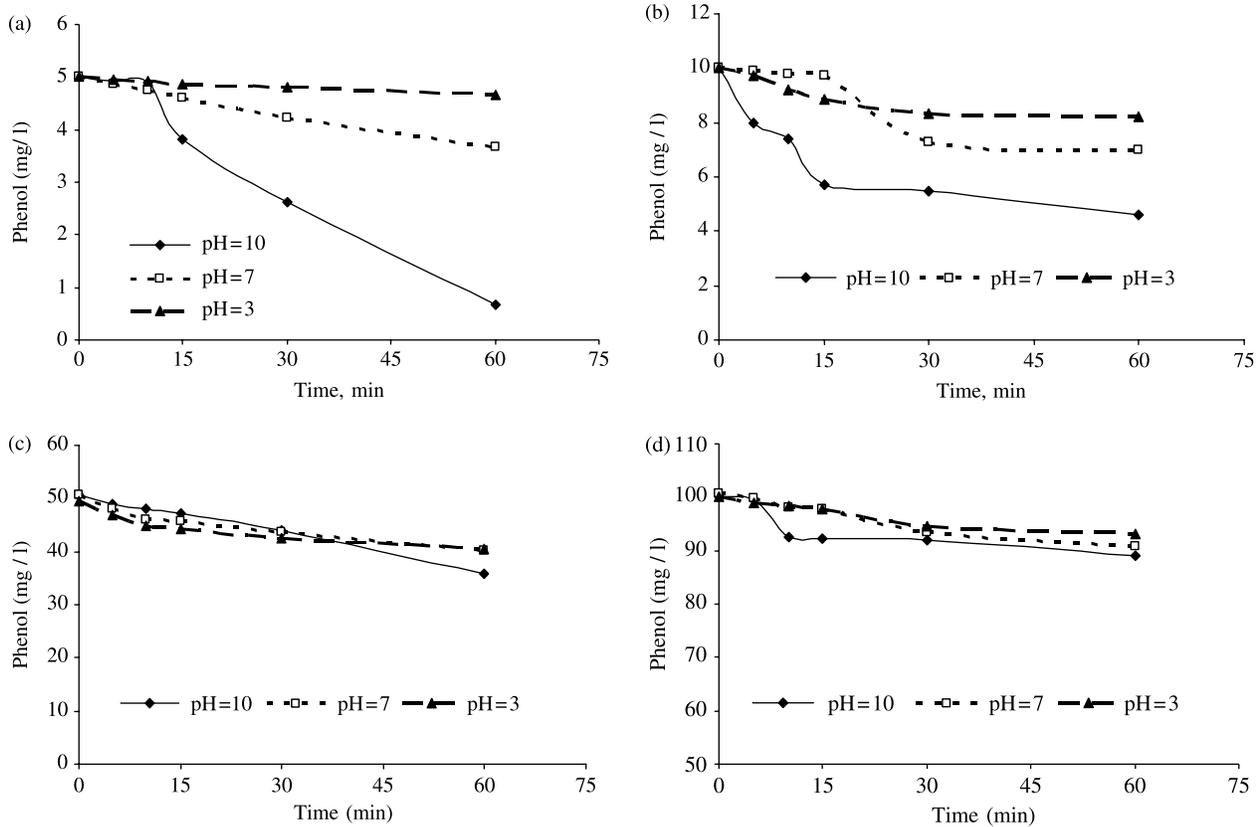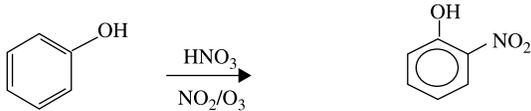
Figure 4 | Phenol degradation using DWG system during discharging at different pH and various initial phenol concentrations. (a) 5 mg/l, (b) 10 mg/l (c) 50 mg/l, (d) 100 mg/l.

Two possibilities are there when NO_3 radicals react with phenol in the absence of ozone and a different situation happens when phenol reacts with NO_3 radicals in the presence of ozone. Phenols are known to react with NO_3 in aqueous acidic conditions via a Single Electron Transfer (SET) giving a cation radical which is in prototropic equilibrium with the phenoxy radical a nitrate anion. Reaction of phenoxy radical with NO_2 should give both 2-nitrophenol and 4-nitrophenol. This behaviour is also observed in the reaction of NO_3 with electron-rich aromatics. The phenoxy radical may also derive from the direct hydrogen abstraction from the phenolic hydroxyl (H-ABS).

Phenol degradation comparison between "During discharge" and "After discharge" processes

"During discharge" and "After discharge" processes are compared for phenol degradation. In the case of "After discharge" distilled water is discharged in the DWG machine for one hour and then phenol is added to this discharged distilled water. Hence the graph shown in Figure 5 represents five hours observations after one hour discharged distilled water is mixed with phenol. Different initial pH is meaningless in the case of discharge distilled water because 2 ∼ 3. Phenolic solutions are always discharged for one hour in the DWG system (During discharge case) for comparison purposes. So the line representing "During discharge" shows the first one hour degradation in the DWG system itself and for the remaining four hours degradation is observed by keeping the solutions at room temperature with continuous mixing. The 5 ppm initial phenol concentration was used with free evaluation
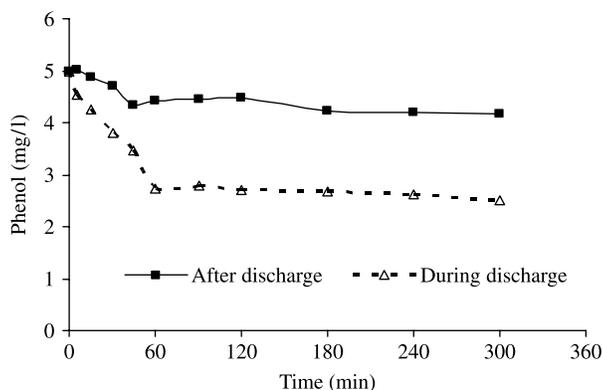
Figure 5 | Comparison for Phenol degradation during and after discharging.

Figure 6 | Phenol degradation using nitrite and nitrate mixture water, A = NO_2^- – N = 1 mM, NO_3^- –N = 2 mM & B = NO_2^- –N = 1 mM, NO_3^- –N = 4 mM.

of pH and temperature for comparison purposes. All solutions were prepared at room temperature. "During discharge" is found more effective in terms of phenol degradation (Figure 5). Higher efficiency of "During discharge" than "After discharge" towards phenol degradation might be due to the contribution of high electrical energy, ozone, OH radical and other oxidants present in the DWG system during discharging.

Phenol degradation using mixture water

Phenol degradation is also checked by using mixture water to find out the contribution of nitrite and nitrate which are the major reaction species produced during the discharging process and hence to compare the results of phenol degradation with the DWG system during and after discharging to confirm the contribution of other oxidants produced in the system except nitrite and nitrate for phenol degradation (Figure 6).

In Figure 7 A represents the mixed concentrations of nitrite and nitrate as $NO_2^- - N = 1$ mM and $NO_3^- - N = 2$ mM and B represents $NO_2^- - N = 1$ mM and $NO_3^- - N = 4$ mM. A represents the nitrite and nitrate concentrations equivalent to the nitrate and nitrite concentrations in discharged water after half an hour of discharging. B represents the nitrite and nitrate concentrations equivalent to the nitrate and nitrite concentrations present in approximately one hour discharged water.

Again, as it is clear from Figure 6 that phenol degradation is only 3–7% by using this kind of mixed water, it confirms the contribution of other oxidants for
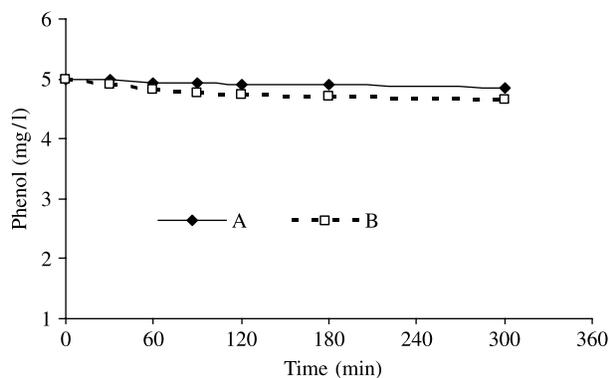
phenol degradation, when phenolic solutions are injected in the DWG system or even when discharged distilled water from the DWG system is mixed with phenol, other than nitrite or nitrate and these might be quite high electrical energy, ozone, OH radical and other oxidants, radical and species.

Table 1 represents the phenol degradation after 1 and 2 days in nitrite and nitrate mixture water.

It is obvious that by using the mixture water of nitrite and nitrate, phenol degradation is much less even after two days and it is not comparable either with the DWG system degradation or the DWG degradation after discharging. Hence the contribution of other radicals is confirmed for phenol degradation in the DWG system during and after discharging.

Mineralization (TOC analysis) during phenol degradation

During the oxidation of phenol solutions, TOC has been measured every 15 minutes during one hour. The DWG parameters were V = 20 kV and I = 20 mA, sine wave.

Phenolic solutions of different initial phenol concentration were discharged at different initial pH values. TOC level remains almost constant during oxidation while the degradation of phenol increases as it is clear from phenol degradation data. This means, that oxidation products are likely to remain in the liquid phase for the observed range of one hour and this fact is also confirmed by HPLC results which show the presence of intermediate products with the degradation of phenol. Additionally the DWG system
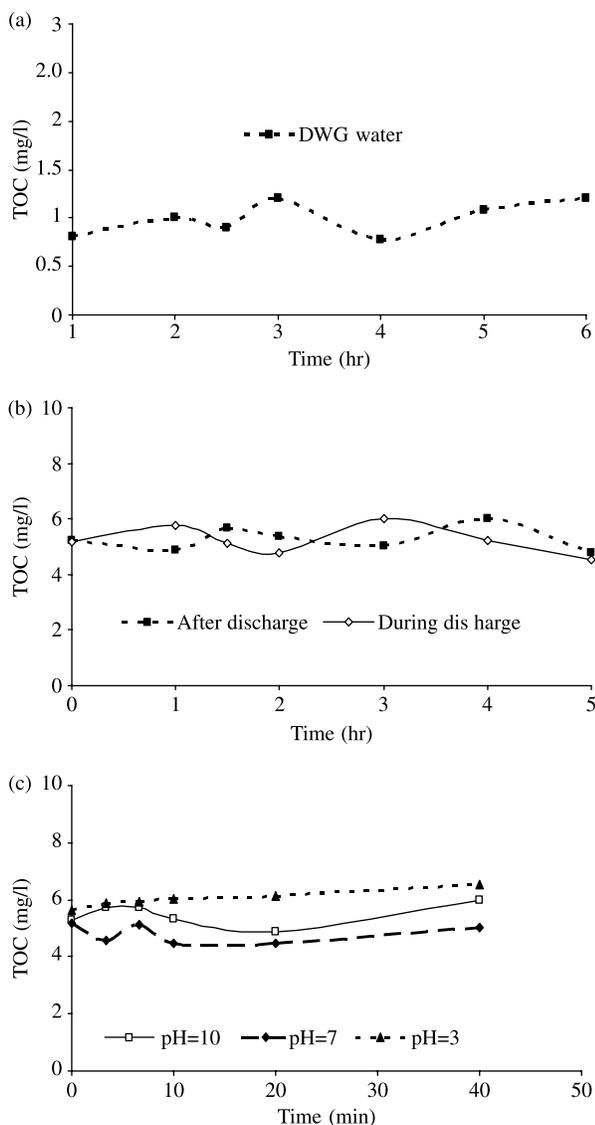
Figure 7 | TOC analysis during phenol degradation for initial phenol = 5 ppm. (a) Background TOC value of DWG water, (b) comparison between "After discharge" and "During discharge" cases, and (c) Effect of initial pH in only "During discharge" case.

Table 1 | Phenol degradation using mixture water

| Time (days) | Phenol removal (%) | |
	A	B
1	18	24
2	22	26

A: $NO_2^- - N = 1 \, mM$, $NO_3^- - N = 2 \, mM$.
B: $NO_2^- - N = 1 \, mM$, $NO_3^- - N = 4 \, mM$.

phenol concentration used is 5 ppm with initial adjusted pH values of 3, 7 and 10.

All the results have the similar efficiency for TOC level confirming almost the same kind of reaction intermediates and end products in both cases. Complete oxidation means mineralization otherwise the presence of harmful and toxic by-products of almost the same nature as that of the parent compound. It should be remarked, that the theoretical TOC level of all phenol solutions is different than the measured TOC value. This difference is about 1 mg/l in all cases and probably due to some background TOC value of the DWG water (Figure 7(a)) which might be due to the presence of some alkalinity inducing substances, eluted matters from the acrylic reactor or a few unknown radicals in the DWG water.

Reaction kinetics and reaction rate constant for phenol degradation in DWG system during discharging

Reaction kinetics and reaction rate constant is evaluated at pH = 10 for phenol degradation in the DWG system during discharging with initial phenol concentration of 5 mg/l. In most of the cases the reaction kinetics for phenol degradation is first order, so by assuming first order reaction kinetics, 'k' value of about $0.0233 \, min^{-1}$ is obtained and coefficient of determinant (R^2 value) is 0.9949.

The ozonation of phenol follows different kinetic regimes according to the pH of the water. Researchers have calculated different values of the reaction rate constant for ozonation of phenol with both first and second-order reaction kinetics resulting in different units of reaction rate constant, k, both per time and per mole per second. Further more, these k values are both pH and temperature dependent and the pH dependency of the total rate

during and after discharging has almost the same efficiency for TOC removal.

For comparison between the DWG system during and after discharging one hour "After discharge" water is compared with one hour "During discharge" system as shown in Figure 7(b). Initial phenol concentration used is 5 ppm with initial adjusted pH = 7. Furthermore, TOC values are compared for only the DWG system having different initial pH values as shown in Figure 7(c). Initial

constants is well known. In fact the total reaction-rate constants of phenolic compounds increase over a wide range of pH values by a factor of 10 per pH unit.

The apparent first-order rate constant for the ozonation of phenol declines by increasing the initial phenol concentration (Jiangning Wu *et al.* 2000), and 'k' values of $0.0166 \, min^{-1}$ and $0.0573 \, min^{-1}$ are calculated for 10 mM and 3 mM of initial phenol concentrations respectively at pH of 8. Comparing with the ozonation of phenol, the DWG system has a lower reaction rate constant for the same initial phenol concentration and this difference is most probably due to different pH and temperature conditions.

BPA degradation with horizontal flow type DWG system

Major species produced during the reaction

Figure 8 represents changes of nitrite and nitrate concentration when 5 ppm BPA solution at initial pH value of 3 is discharged in the DWG system.

During BPA degradation concentrations of two major species, nitrite and nitrate, produced in the DWG system are about 20 and 100 mg/l respectively as shown in Figure 8. These concentrations are higher than nitrite and nitrate produced in the DWG system when phenolic solutions were discharged in the DWG system as it is clear from Figure 3 where nitrate and nitrite concentrations are only about 35 and 11 mg/l respectively after one hour discharging time.
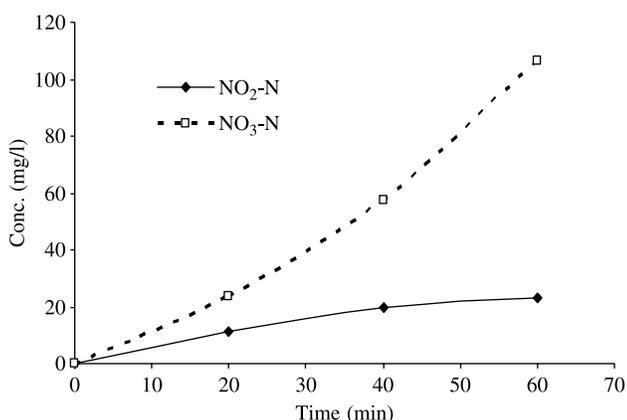
In the case of phenol degradation the DWG system used was the vertical flow system but in the case of BPA degradation the horizontal flow DWG system was used. The higher production of nitrite and nitrate might be due to a better discharging ability of the horizontal flow system than the vertical flow system and also due to the air cooling system used in the horizontal flow type DWG system as compared to the water cooling system used during phenol degradation.

BPA degradation in DWG system during discharge

In the case of the DWG system during discharging two different initial concentration BPA solutions in distilled water i.e. 5 and 10 ppm at different pH values i.e. 3 and 10 respectively were injected in the DWG machine for one hour (Figure 9).

Different initial pH values were selected to find the optimum initial pH value and optimum initial BPA concentration for maximum efficiency of the DWG system for BPA degradation. Basic pH adjusted by adding dilute sodium hydroxide and acidic pH achieved by adding dilute sulfuric acid. BPA degradation is almost about 80% for both solutions with different initial pH values i.e. acidic and basic.

Intermediate analysis is performed by GC-MS to find out the reaction intermediates and end products. The quality of all the intermediates is not very high so it is very difficult to speak exactly about the reaction mechanism. The possible intermediates were 1-Dodecanol, 2-Heptenal, 1-Decanol, 1,1-Dioctyloxyoctane and many others. Due to the very poor quality of all these intermediates and complex reaction
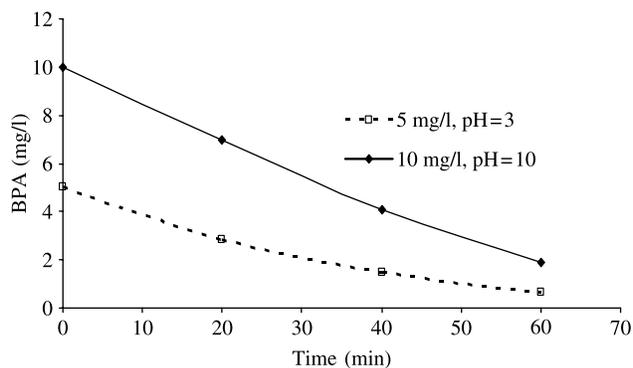

Figure 8 │ NO₂ and NO₃ production in DWG system during discharging of BPA solutions.

Figure 9 │ BPA degradation in DWG system during discharging at different pH and various initial concentrations.

mechanisms it is quite difficult at this stage to speak about the exact reaction mechanism of BPA degradation.

BPA degradation comparison among DWG system during and after discharging and mixture water

Additional test was performed for comparison purposes to find out which system is working best towards BPA degradation. 5 ppm BPA is selected at pH = 3 and mixture water used was NO_2-N = 1 mM and NO_3-N = 4 mM. Distilled water was injected in the system for one hour and then 5 ppm BPA was added in this discharged water in the case of "After discharge" process while in the case of "During discharge" BPA added distilled water is injected in the DWG system.

Figures 10 and 11 represents the comparison among different systems used in this research for BPA degradation. Comparison is carried out for one hour because it is very difficult for the DWG system to be operated for more than one hour. In the case of the DWG system after discharge, degradation efficiency is higher at acidic pH and with higher initial BPA concentrations. In the case of mixture water, degradation efficiency is higher with higher initial BPA concentrations and using mixture water with less concentration of nitrate. It is obvious that the DWG system is much more efficient during discharging than after discharging and mixture water. This higher efficiency of the DWG system during discharging and mixture water towards BPA degradation might be due to the contribution of high electrical energy, ozone, OH radical and other oxidants produced in the DWG system during discharging. Furthermore, the DWG system after discharge is more efficient than mixture water due to some oxidants and radicals in "After discharge" water which are absent in mixture water.

Comparison of TOC removal among DWG system during and after discharging and mixture water

During the degradation of BPA solutions, the TOC level has been measured every 15 minutes during one hour. The DWG parameters are V = 100 V and I = 4 mA.

From TOC analysis it is clear that the DWG system after discharge is more efficient than the DWG system during discharging and mixture water. TOC removal efficiency in
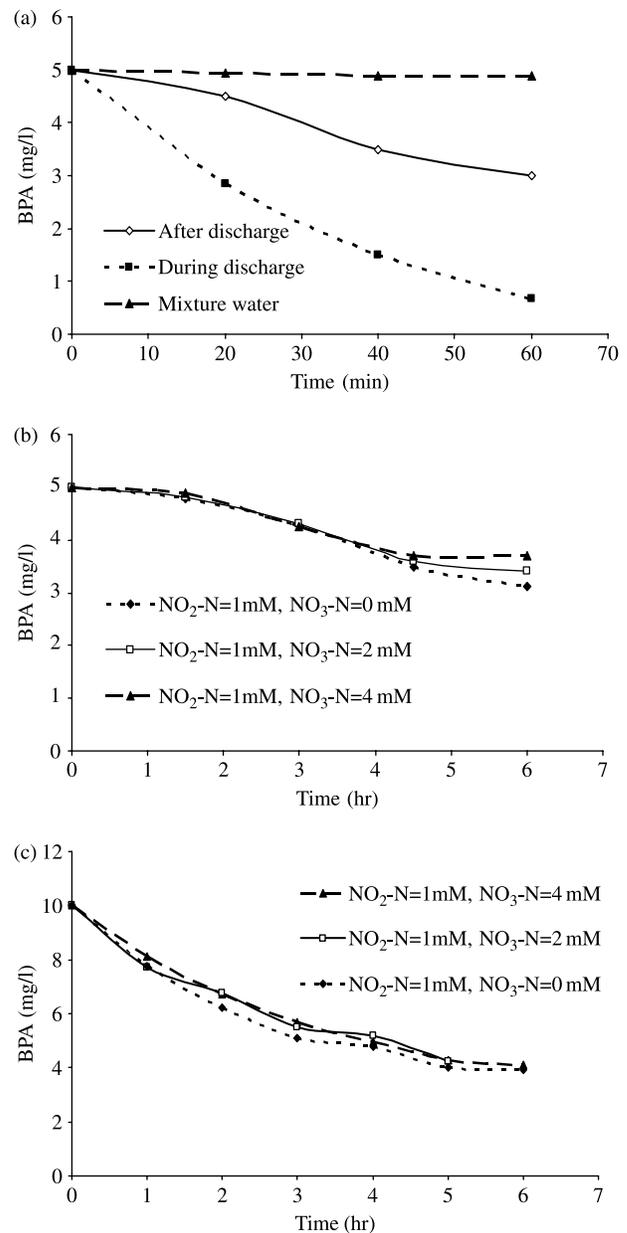

Figure 10 | BPA degradation comparison among (a) DWG system during and after discharging and mixture water, and with different nitrate concentration in case of mixture water for (b) 5 ppm BPA and (c) 10 ppm BPA.

the case of the DWG system after discharging is almost 50% after one hour mixing of DWG water with BPA while in the case of the DWG system during discharging TOC level decreases about 20–40% after one hour discharging of BPA solutions in the DWG machine. In mixture water TOC level remains constant although BPA degradation increases as it is clear from degradation data. This might be due to the fact
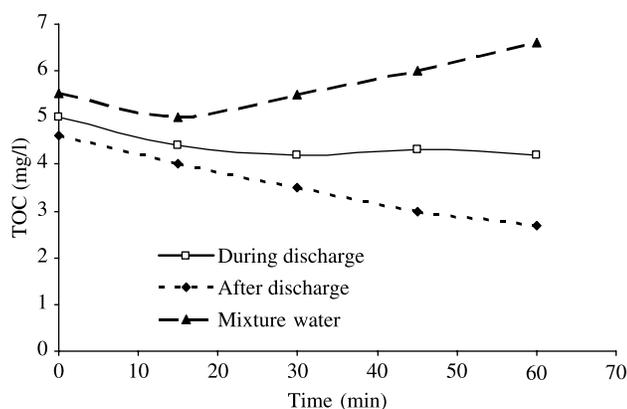
Figure 11 | TOC removal during BPA degradation in DWG system during and after discharging and mixture water at pH = 3 and initial BPA concentrations = 5 mg/l.

that some intermediates remain in the solution for observed range of analysis.

Again it should be remarked, that the theoretical TOC level of BPA solution is different from the measured TOC value. This difference is due to some background TOC value of DWG water (Figure 7(a)) which might be due to the presence of some alkalinity inducing substances, eluted matters from acrylic reactor or a few unknown radicals in the DWG water.

CONCLUSION AND RECOMMENDATIONS

DWG technique is a novel technique to produce oxidants. HNO_2, ozone and some other radicals can be the main factor in oxidizing matters, but there is a need to study the effects of unknown products and various radicals.

In the case of phenol degradation the DWG system used was a vertical flow system but in the case of BPA degradation a horizontal flow DWG system was used. Three processes i.e. DWG system during and after discharging and mixture water were used for BPA degradation and mineralization during BPA degradation.

Nitrite and nitrate, produced in the horizontal flow DWG system are higher than nitrite and nitrate produced in the vertical flow DWG system used for phenol. The higher production of nitrite and nitrate might be due to better discharging ability of the horizontal flow system than the vertical flow system and also due to an improved cooling system used in the horizontal flow type DWG system.

(1) The lower the initial phenol concentrations, the higher the degradation rates approached. Best results at basic pH because the contribution of radical way increased with pH. The DWG system during discharging has the ability to degrade phenol more than the DWG system after discharge or mixture water of nitrite and nitrate. Phenol degradation is only 3–7% by using mixed water, which confirms the contribution of other oxidants produced in the DWG system during and after discharging except nitrite or nitrate for phenol degradation and these might be high electrical energy, ozone, OH radical and other oxidants.

(2) From the intermediate analysis it is clear that more products are produced for the phenol degradation at low pH and high initial phenol concentrations. The only intermediate that is confirmed is ortho-nitro-phenol although there are some other intermediates but these are not confirmed. Almost the same intermediates or end products are found in the DWG system during and after discharging and mixture water.

(3) TOC almost remains the same for one hour of treatment DWG system during and after discharging showing the production of intermediates without complete mineralization. However the TOC results can be improved by increasing the reaction time. Reaction order is 0.8 and the reaction rate constant is $0.0233 \, \text{min}^{-1}$ for phenol degradation using the DWG system during discharging.

(4) BPA degradation is almost about 80% using the DWG system during discharging for both acidic and basic solutions. The DWG system is much more efficient during discharging than after discharging and mixture water for BPA degradation. This higher efficiency of BPA degradation might be due to the contribution of high electrical energy, ozone, OH radical and other oxidants produced in the DWG system. Furthermore, the DWG system after discharging is more efficient than mixture water.

(5) The DWG system after discharging has a higher TOC removal efficiency than the DWG system during discharging and mixture water which is about 50% after one hour as compared to the DWG system during discharging which has a TOC removal efficiency of 20–40%. The reason for this fact is the higher

concentration of different intermediates produced in the case of the DWG system during discharging than after discharging. TOC level remains constant when mixture water is used, although the BPA degradation shows intermediate reaction products in the solution for the observed range of analysis.

Based on the results of this trial, a number of recommendations can be made as to future research into the treatment of organic compounds in water using this innovative DWG System. Firstly, investigations should be carried out to determine the effect of low pH on the degradation of various compounds. Secondly, the maximum concentration of any compound that can be effectively treated should be determined, and finally, the addition of a supplemental base source to improve the performance of the DWG system by maintaining the pH of the discharged water should be investigated. Increase of temperature due to high energy should also be considered and a proper cooling system to maintain the temperature must be provided.

The favorable degradation efficiency of both phenol and BPA using the DWG system during and after discharging justify the continuation of this system for water treatment; topics of interest may be described as follows. Optimization of the reactor/electrode configuration can be achieved by increasing the contact area between the target compound solution and the discharges. Also an investigation of pH and temperature control may result in even higher oxidizer production efficiency. Continuous flow application, scale-up possibilities and process stability should be studied. The identification of unresolved oxidation products needs to be improved by application of Gas Chromatography / Mass Spectrometry.

An investigation of using oxygen as a feed gas instead of natural air is also a vital future research objective to eliminate the effect of nitrite which is produced in the DWG system when natural air is used for discharging. Thus the degradation efficiency can be improved and also the mineralization could be achieved with no harmful intermediates or end products. Provision of anoxic zone can also improve the efficiency of treatment by nitrite and nitrate removal.

Application of the DWG in the water reuse area and in hybrid systems could be the future concern based on the justified results of this research.

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