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REVIEW ARTICLE

Degradation of organic pollutants and microorganisms from wastewater using different dielectric barrier discharge configurations—a critical review

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Abstract The growing global drinking water crisis requires the development of novel advanced, sustainable, and cost-effective water treatment technologies to supplement the existing conventional methods. One such technology is advanced oxidation based on dielectric barrier discharge (DBD). DBD such as single and double planar and single and double cylindrical dielectric barrier configurations have been utilized for efficient degradation of recalcitrant organic pollutants. The overall performance of the different DBD system varies and depends on several factors. Therefore, this review was compiled to give an overview of different DBD configurations vis-a-viz their applications and the in situ mechanism of generation of free reactive species for water and wastewater treatment. Our survey of the literature indicated that application of double cylindrical dielectric barrier configuration represents an ideal and viable route for achieving greater water and wastewater purification efficiency.

Keywords Wastewater treatment · Organic contaminants · DBD · Plasma · Electrode geometry · Ecosystem

Introduction

Water sustains all life and needs to be preserved from pollution in order to maintain public health and ecologies. The lack of sufficient, sustainable sources of clean drinking water has been linked to focuses such as global climate change, industrialization, overpopulation and agricultural practices. While there is growing concern about the persistent global water crisis due to these factors, the available potable water is often not completely suitable due to the presence of low quantities of persistent chemicals that are potentially harmful to humans and other living organisms (Boithias et al. 2014; Bokhale et al. 2014). Increased industrial and high-tech activities have contributed to improving gross domestic products and the standard of living. Nevertheless, industrialization has contributed to the deterioration of water quality via the discharge of untreated wastewater containing high organic loads, thereby endangering the natural equilibrium in the environment. It is important to mention that water becomes a waste when it has been undesirably polluted by both organic and inorganic contaminants, bacteria and other microorganisms, industrial effluent or any component that might modify its initial quality (Ibrahim 2012). In addition, Ellis (2004) revealed different constituents of wastewater namely proteins, carbohydrates, fats, oils and trace amounts of priority pollutants, surfactants and emerging contaminants. Wastewater originates from many sources, which include municipal, agricultural and industrial sources (Ibrahim 2012). Municipal wastewater is generated as a result of liquid waste discharged by domestic residences, households and septic tank leakages. The study conducted by Ibrahim (2012) revealed that municipal wastewater usually contains various contaminants including colony-forming units (CFU)/millilitre of coliform organisms, faecal streptococci, protozoan cysts and virus particles. Studies have shown that many pharmaceuticals are also contained in municipal wastewater (Marc et al. 2005). Also, industrial wastewaters are predominantly effluents produced via industrial activities that include food processing, dyeing factories, iron and steel industry, mines and quarries among others. Industrial wastewater generated from the metal processing

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industry, mines or chemical industries contain toxic metals, organic and inorganic compounds as well as chlorinated by-products (Ellis, 2004). In textile industries, several organic synthetic dyes used for material colouration are major contributors of organic pollutants in industrial wastewater. The discharge of untreated coloured wastewater containing organic pollutants into the environment did not only damage the aesthetics of nature but also affect the aquatic species (Martynas et al. 2013). This industrial wastewater has a very unpleasant odour, high pH, strong colour, high chemical oxygen demand (COD), biochemical oxygen demand (BOD) and total organic carbon (TOC) and contains other soluble substances (Hussaini et al., 2013). Different wastewater treatment processes such as physical, chemical and biological methods have been explored either as pre- or posttreatment steps to remove colour and reduce COD, BOD and TOC. The efficiency of these methods varies. Biological treatment for instance cannot remove biologically recalcitrant, inhibitory and toxic pollutants. Other methods such as ozonation, air stripping, coagulation/flocculation, reverse osmosis, ultrafiltration and chlorination may produce toxic disinfection by-products (DBP) that are genotoxic, mutagenic and carcinogenic to human health (Gultekin and Ince, 2009). Chemical coagulation and flocculation use large amounts of chemicals and produce sludge that contains hazardous materials; thus, sludge discarding remains problematic. Adsorption also produces toxic sludge which needs disposal in solid waste repositories (Maletz et al. 2013). Moreover, in these processes, the pollutants are merely being transferred from one phase to another without necessarily being decomposed (Kasprzyk-Hordern et al. 2009; Maletz et al. 2013). The application of chemical oxidation for the removal of environmental toxicants is considered more expensive due to the formation of intermediate products. Aside from this, the toxicity level of the partially metabolized compounds remains an issue as the transformation products are often more toxic than the parent compounds and as such resistant to further chemical decomposition (Kasprzyk-Hordern et al. 2009). The conversion of these intermediate products into harmless inorganic compounds requires more energy, long reaction times and use of expensive chemical oxidants such as ozone and others (Malik et al. 2001). Other treatment processes may be hindered by economics and wastewater characteristics (Vujevic et al. 2004; Yijun and Muqing 2013). Due to the systemic failure of conventional techniques designed to address such issues, it is of utmost importance to reduce the concentration of these toxicants to a tolerable level using appropriate technologies in order to comply with the stringent environmental laws. Some of which have been established while some need to be further developed in order to degrade emerging pollutants in wastewaters (Yijun et al. 2013).

Recently, advanced oxidation processes (AOPs) such as direct ozonation, UV photolysis, high voltage electrical discharges, heterogeneous photocatalysis, cavitation, electrochemical oxidation, Fenton and photo-Fenton processes have been established and proved to be applicable not only in the degradation of organic pollutants but also in their total mineralization as well (Vujevic et al. 2004). Some of the above-mentioned processes have also been used as pretreatment in order to minimize the concentration of toxins such as pesticides, surfactants, colouring matter, pharmaceuticals and endocrine-disrupting chemicals that impede biological wastewater treatment methods. Among the AOPs, DBDs have been used as pre/posttreatment method or in combination with other techniques for water/wastewaters treatment (Valinčius et al. 2012). However, there is little or no information on the use of the optimized DBD system as a single technology for wastewater treatment. Thus, optimization of the DBD system at ambient conditions could result in a promising advanced oxidation technology for complete treatment of water/wastewaters. This review focuses specifically on dielectric barrier electrohydraulic discharge (DBD) systems as a typical advanced oxidation process and provides information on the state of wastewater treated using DBDs. The overview of plasma technology, DBD configurations and their applications and the mechanistic pathways for the production of the free reactive species in the DBD process are also covered in this review.

Water treatment processes

The elimination or inactivation of organic pollutants is a problematic challenge for the drinking water industry. The conventional disinfection approach may not always be suitable since international regulations stipulate that new pathogens have emerged, and previously unknown disinfection by-products have been identified. Processes such as coagulation/ sedimentation, granular media filtration and chlorination have been used for years to reduce microorganisms in water and wastewater. Recently, membrane filtration, ozonation and UV irradiation have also been recognized as effective techniques for achieving microbial inactivation. According to Igawa et al. (2011), ozone is an economical clean, simple and efficient oxidation agent that is broadly used in industry. Likewise, ozone is commonly utilized for oxidative cleavage of a carbon–carbon double bond in organic synthesis, thus showing the significance of an addition-type oxidation of an alkene and its transformation in organic synthesis. Historically, ozone came into use as a drinking water disinfectant around 1906 in France. From that time, ozonation has been adopted in several facilities in Europe (Rice 1985). Initially, ozone was used as a primary or sole disinfectant and as an oxidant to regulate the flora, odour and colour and to reduce the manganese and iron content of drinking water. With the improvement in the engineering sector, ozone has become widely used in flocculation of suspended particles on the surface of waters.

Ozone has attracted scientific attention for many reasons. Firstly, it was used to reduce the utilization of free chlorine in water treatment processes. Literature supports that for years, free chlorine has been used not only as disinfectant but also as a powerful oxidant especially in North America. However, its utilization results in the production of by-products such as trihalomethanes (THMs), which Lin and Shih-Wen (2000) and Backer et al. (2000) proved to be harmful to human health. In recent times, chloramination (the combination of free chlorine and ammonia) has been widely used as an alternative to free chlorine in flocculation of suspended particles on the surface of waters. Water treatment by chloramination was considered as the most popular alternative disinfection process since chloramines are free from THMs. Unfortunately, chloramines are weak oxidants; therefore, stronger oxidants, such as ozone and chlorine dioxide, were early established as substitutes for the chlorine treatment process. Apart from the fact that ozone was more efficient compared to chlorine, ozone still shows its utility as a more powerful coagulant than chlorine (Prendiville et al. 1986). Furthermore, the decomposition of ozone results in the production of more potent radical intermediates than ozone itself. Prendiville et al. (1986) also argued that since ozone is an unstable gas, it has to be generated where it can be used. Cold plasma discharge, usually called corona discharge (CD), has been identified as the most suitable technique to generate ozone. In the CD method, ozone is formed by decomposition of diatomic oxygen O_2 according to the following equations:

$$O_2(\text{Corona Discharge}) \rightarrow O^{\bullet} + O^{\bullet} \quad (1)$$

$$O^{\bullet} + O_2 \rightarrow O_3 \quad (2)$$

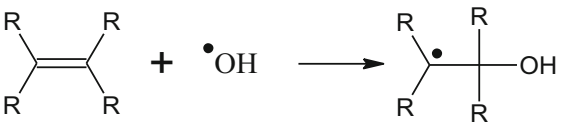
Recently, Locke et al. (2006) and Panicker (2003) reviewed the cold plasma technique used to generate ozone. This included the expansion of the following parameters: generators that operate in a resonant frequency range and modifications of the tube design which therefore require an advanced electronic system to control current. Bhattacharyya et al. (1995) proved that although it has been established that ozone is an effective oxidant towards hazardous organic pollutants, a single-phase ozonation system has limitations such as low ozone solubility, low ozone stability and a lack of selective oxidation potential. Therefore, it is crucial to mention that ozone should be combined with other agents or processes for an effective water and wastewater treatment rather than ozonation alone. These agents include hydrogen peroxide, UV radiation, metallic catalysts, such as reduced iron, and ultrasound. These combinations are usually referred to as advanced oxidation processes (AOPs). The literature review indicates that a new generation of these methods is being technologically developed to reduce energy consumption, operational cost and infinitely enhance the degradation efficiency so that these processes can hopefully meet future regulations associated with organic pollutants and the microbiological quality of water (Movahedyan et al. 2009).

Advanced oxidation processes

AOPs focus on using the hydroxyl radical as primary nonselective oxidant of organic pollutants. Such processes often result in a complete mineralization of organic molecules into CO_2, water and harmless inorganic substances (Legrini et al. 1993). Literature shows that organic toxins such as pesticides, surfactants, colouring matter, pharmaceuticals and endocrine-disrupting chemicals have already been treated in wastewater using advanced oxidation techniques (AOTs). In addition, these methods have also been used in pretreatment processes aimed at reducing pollutant concentrations that impede biological wastewater treatment processes (Stasinakis 2008). AOPs have been described as water treatment procedures that involve an input of energy (which could be chemical, electrical or radiative) into the water matrix to produce strong oxidizers in situ. According to Carla et al. (2013), the principal function of AOPs is the in situ production of chemical reactive species such as O_3, H_2O_2, HO·, HO_2· and O^1 (D). This is because, after fluorine (*F*2, *E*o=3.03 V), ·OH radicals have been identified as the most effective oxidants in decomposing organic compounds into CO_2, water and inorganic salts due to the high standard reduction potential of ·OH (*E*o=2.8 V), compared to those of atomic oxygen (*E*o=2.42 V), ozone (*E*o=2.07 V), hydrogen peroxide (*E*o=1.78 V) and per hydroxyl radical (*E*o=1.70 V) (Cheng et al. 2007). Hydroxyl radical attack occurs by abstraction of the hydrogen atoms (Eqs. 3 and 4), followed by electrophilic addition of ·OH (Eqs. 4 and 5), electron transfers (Eq. 5) and radical-radical reactions (Eqs. 5 and 6) (Vujevic et al. 2004).

$$HR + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \quad (3)$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \quad (4)$$



… (5)

$$RX + {}^{\bullet}OH \rightarrow RX^{\bullet +} + OH^{-} \quad (6)$$

$$2OH^{\bullet} \rightarrow H_2O_2 \qquad k = 5.3 \times 109\ \text{L mol}^{-1}\text{s}^{-1} \quad (7)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad k = 2.7 \times 107\ \text{L mol}^{-1}\text{s}^{-1} \quad (8)$$

Conversely, the oxidizing species play a specific role towards organic pollutants. Active species, such as hydrogen peroxide, have been proved too weak to degrade azo dyes alone at normal conditions of temperature and pressure (Selma, 2007). Furthermore, aromatic azo dyes are very stable when exposed to ozone; the reactivity of these compounds with ozone is very low compared to an olefinic or azomethine group (Galindo et al. 1999). Thus, electrohydraulic discharge

(EHD) that produces a combination of all these reactive oxidizing species has emerged as a powerful alternative for wastewater remediation. The most common techniques classified under AOPs and that are reported in literature are presented in Table 1. For decades, most of these processes have been the subject of investigations for the degradation of organic pollutants in drinking water and wastewater treatment. In recent research studies, the Water Framework Directive of the European Commission has considered the following biorecalcitrant pesticides: alachlor, atrazine, chlorfenvinfos, diuron, isoproturon and pentachlorophenol as priority hazardous substances. Literature shows that photo-Fenton/ozone (PhFO) and TiO_2-photo catalysis/ozone (PhCO), both combined systems, have been used as advanced oxidation processes for the degradation of these organic compounds. Even though photo-Fenton reaction and TiO_2 photo catalysis are not part of the current study, their use as common advanced oxidation processes had to be mentioned. In 2005, Farre et al. demonstrated that when PhFO and PhCO are applied respectively, the degradation process of the different pesticides occurs through oxidation of the organic molecules by means of their reaction with generated OH radical which follows a first and zero-order kinetics. Additionally, Farre et al. (2005) investigated the total organic carbon (TOC) reduction of the different pesticides in aqueous solutions using these two advanced oxidation processes, together with conventional ozone+UV techniques. Results showed that best pesticide mineralization were obtained when PhFO was applied. The aqueous pesticide solutions became detoxified with the use of this advanced oxidation process, except in the case of alachlor and atrazine aqueous solutions after 2 and 3 h of treatment, respectively, where no detoxification was achieved at the experimental conditions used in their work. Based on literature information, artificial light or solar energy has been used in different photochemical processes for the degradation of pesticides (Kochany et al. 1994). Chiron et al. (2000) demonstrated that complete degradation of the pesticides is rarely achieved with such degradation processes since it requires long treatment periods. Therefore, Legrini et al. (1993) advised that an additional homogenous or heterogeneous oxidant could be used to improve the degradation power of photochemical oxidation process.

Recently, Walid and Al-Qodah (2006) combined advanced oxidation processes with biological treatment processes to remove both pesticides and then reduce the chemical oxygen demand (COD) load from aqueous solutions. The study showed that O_3 and O_3/UV oxidation systems could remove 90 and 100 % of the pesticide deltamethrin, respectively, in a period of 210 min. It was found that the combination of O_3 and UV radiation enhanced pesticide degradation and the residual pesticide reached zero in the case of deltamethrin. Research results also revealed that at a pH value greater than 4, the combination of O_3 and UV could reduce COD up to 20%. In addition, the degradation of pesticides and the removal of COD in the combined O_3/UV system followed pseudo-first-order kinetics and the parameters of this model were assessed. In addition to this, Walid and Al-Qodah (2006) investigated the application of biological treatment to remove the bulk COD from different types of feed solutions. It was found that O_3/UV system removed more than 95 % of COD. Several other AOPs have been used to lower COD of industrial and municipal wastewater, containing organic compounds

Table 1 Common advanced oxidation procedures (AOPs) reported in literature

Processes	Authors
O_3/H_2O_2	(Selma 2007)
O_3/UV, UV/TiO_2 and UV/TiO_2/O_3	(Farre et al. 2005; Walid and Al-Qodah 2006)
UV/H_2O_2	(Madhu et al. 2009; Iqbal et al. 2013)
TiO_2/UV and TiO_2/UV/H_2O_2	(Wu and Chern 2006; Madhu et al. 2009)
O_3/UV/H_2O_2	(Selma 2007)
TiO_2 nanotubes/UV/O_3	(Selma 2007)
$O_3/TiO_2/H_2O_2$ H_2O_2/UV/O_3/TiO_2	(Selma 2007)
H_2O_2/O_3/Fenton's reactions	(Selma 2007; Wilhelmus 2000)
UV/Ag-TiO_2/O_3	(Wu et al. (2011)
Sonolysis	(Stasinakis 2008)
Ozone sonolysis	(Stasinakis 2008)
Catalytic oxidation	(Stasinakis 2008)
Supercritical water oxidation or wet oxidation	(Wilhelmus 2000)
Radiolysis	(Wilhelmus 2000; Lukeš 2001)
Ultrasonic irradiation	(Wilhelmus 2000; Lukeš 2001)

(Stasinakis 2008). Some of these compounds are primary constituents of organic dyes/azo dyes. On the other hand, the textile-processing industry is affecting the environment, by the release of heavily polluted wastewaters which largely contain organic azo dye compounds. Biological treatment methods have been chosen by Walid and Al-Qodah (2006) due to their reduced operational cost and because they are well known as being environment friendly. Literature highlighted that photocatalytic degradation of pollutants in the presence or absence of air is the most reasonable biological treatment strategy (Harrelkas et al. 2008). Their study showed that in the absence of air (anaerobic), azo dyes and other types of dyes such as anthraquinone, phthalocyanine and triphenylmethane could be decolourized. In the presence of air, aromatic amines from azo dye cleavage could be mineralized and other types of dyes could be removed by adsorption and biodegradation. However, Van der Zee and Villaverde (2005) discussed that it is impossible that all aromatic amines can be degraded and that the complete removal of other types of dyes is questionable. Furthermore, some of the future challenges (decrease of operational cost, adoption of strategies for processes integration) were also discussed (Stasinakis 2008). These limitations therefore lead research to concentrate on combining biological treatment of dye-containing wastewaters with other methods such as adsorption on solids (activated carbon, natural products such as agro wastes), coagulation-flocculation and most importantly advanced oxidation processes (AOPs). Systems such as UV-hydrogen peroxide (Daneshvar et al. 2005; Baldrian et al. 2006), ozonation (Farre et al. 2005) and O_3/UV/H_2O_2 (Selma 2007) have been extensively described in literature as advanced oxidation processes and have demonstrated great detoxification efficiency. The latter advanced oxidation processes are the principal driving force of dye oxidation in the present EHD system. Despite the fact that all advanced oxidation techniques have been used to treat water/wastewater, the operational conditions, separation problems and mostly the cost of some of these processes have been considered as limiting factors for these technologies. Therefore, electrical discharges, among which dielectric barrier discharges, have emerged as novel and promising techniques for water/wastewater treatment.

Liquid phase electrical discharge: electrohydraulic discharge

Even though application of electrical discharge on the surface of water in water and under water has been studied for many years, electrical discharge processes in liquid phase have mostly been explored in recent years for various purposes including water treatment (Chang et al. 2010), sterilization and decomposition of organic compounds (Yamatake et al. 2007 and Angeloni et al. 2007).

Depending on the electrode configuration, electrohydraulic discharge involves the submersion of two electrodes in water. The high voltage and ground electrodes both immersed into the solution initiate a plasma channel that is characterized by both chemical and physical properties (Chang et al. 2010). Electrohydraulic discharges (above, under or directly in aqueous medium), involving the generation of plasma, have been recognized to be effective at degrading and removing a number of organic pollutants such as phenols (Sun et al. 2000; Lukes et al. 2002), trichloroethylene Sahni (2006) and organic dyes (Sato et al. 2000) from water and wastewater. Yet, the study of plasma and mostly its effect on the decomposition of organic pollutants remains an open field for research.

Depending on the amount of energy input and supplied voltage and current range in the system, Chang (2008) and reported that electrohydraulic discharge can be divided into four different categories. These include pulsed corona electrohydraulic discharge (PCEHD) or pulsed spark electrohydraulic discharge (PSEHD) which use high voltage or low current discharges with energy per pulse of about 1 J/pulse or 10 J/pulse, respectively. In the case of pulsed arc electrohydraulic discharge (PAEHD) and the pulsed power electrohydraulic discharge (PPEHD) systems, a higher current discharge is used. The PAEHD system uses energy of about 1 kJ/pulse with a few kilovolts, whereas larger energy per pulse with higher voltages is required for the PPEHD system.

Plasma technology

Plasma is often categorized as the fourth state of matter besides solid, liquid and gaseous states that are commonly known (Valinčius et al. 2012). Plasmas are generally ionized gases that consist of electrons, positive and negative ions and neutral species (Valinčius et al. 2012). These gases either ionize completely (100 %) or are somewhat ionized (with low values between 10–4 and 10–6). Moreover, Sturrock (1994) identified two other groups of plasmas such as low temperature plasmas (≤50,000 K) and high-temperature or fusion plasmas (50,000–106 K). Nehra et al. (2008) equally classified plasmas into two categories. The first category is the one in which the active species (electrons, ions and neutrals) have the same temperature and is usually referred to as thermal equilibrium plasmas, in the case of fusion plasma ($Te \approx Ti \approx Tn$ 106 K). Whereas in the second category known as non-thermal/equilibrium plasma, the aforementioned species have different temperatures in such a way that electrons are considered to have a higher temperature (10,000–50,000 K) than that of heavy ions and neutrals, hence ($Te \gg Ti$, with $Ti \approx Tn$). Furthermore, the authors emphasized that plasma can be classified based on pressure. Based on this, Valinčius et al. (2012) wrote that the gas discharge plasmas can be classified into local thermodynamic equilibrium (LTE) and non-LTE plasmas. As for LTE plasma, the high pressure induces many collisions in the plasma and therefore leads to a significant

energy interchange between the plasma species. On the other hand, the low gas pressure in non-LTE plasma leads to few collisions and hence different temperatures of plasma species due to poor energy exchange.

As earlier mentioned, in equilibrium plasma, electron temperature (Te) is generally equal to ion temperature (Ti) or thermodynamic gas temperature (Tg). However, in non-equilibrium plasma, (Te) largely exceeds (Tg) and the temperature of heavy particles. Valinčius et al. (2012) also found that in non-equilibrium plasma, the number of electron is often reasonable in the bulk region of plasma and becomes significant towards the centre of the dense volume. Based on this background information, the plasma concepts are briefly summarized and presented in Table 2.

A few years ago, Nehra et al. (2008) argued that low-pressure discharge plasmas play a significant role in fundamental research, the microelectronic industry and material technology. The use of air to generate these plasmas in numerous configurations makes these technologies extremely expensive and time-consuming. Apart from this, the amount of their corresponding activated particles is small. Therefore, there is an urgent need to develop new plasma sources which could maintain the properties constant and operate unchangeably at atmospheric pressure. Non-thermal plasma generated at 1 atm presents operational and economic advantages which have led to the development of multiple plasma sources that have been employed in the industries. Based on these claims, great attention has been given to atmospheric non-thermal plasma (ANTPs) due to their substantial industrial advantages compared to low-pressure discharge. A decade ago, Mark and Schluep (2001) reported that non-thermal atmospheric plasma (NTP) offers a number of advantages for environmental control and protection such as dry cleaning operations as well as processing of chemical waste streams.

Apart from these advantages of NTP highlighted by Mark and colleagues, Nehra et al. (2008) reported that non-thermal atmospheric plasma may be obtained by a variety of electrical discharges including micro hollow cathode discharge, corona discharge, atmospheric pressure plasma jet, one atmospheric uniform glow discharge, dielectric barrier discharge (DBD), plasma needle and gliding arc discharge presenting crucial technological applications. The common characteristics of these plasma sources based on plasma properties have been summarized by Nehra et al. (2008) and are presented in Table 3.

Over the last few years, plasma treatment has widely attracted scientists' attention as an alternative method of cleaning water. This is due to the production of UV radiation, shock waves and mostly highly reactive species such as O_3, H_2O_2, and ·OH that oxidize the pollutant and mineralize it into CO_2, H_2O and simpler inorganics. Besides, electrode configurations in the aforementioned electrical discharge reactors also play a crucial role in the treatment of polluted water. In fact, most electrode arrangements in these water/wastewater technologies have failed to meet the expectations of significantly cleaning polluted water. Therefore, electrode configuration is a key parameter to differentiate electrical discharges from one another. For instance, several electrode configurations summarized by Gupta (2007) and presented in Figs. 1 and 2 have been explored in corona electrohydraulic discharge reactors. In these configurations, the powered tipped anode is directly in contact with the discharged gas and the polluted liquid. This usually results in electrode etching and corrosion. In addition, in corona discharge, active species result from streamers produced at the tip of the conductive anode. This could therefore slow down/limit the production of oxidizing species responsible for the degradation of organics and microbes. Therefore, the development of a novel reactor configuration with different electrode arrangements is of great importance to overcome the dilemma of water pollution. The choice of dielectric barrier discharge (DBD) over corona discharge and other types of electrical discharges lies in plasma properties proposed by Nehra et al. (2008) and presented in Table 2. In addition, the presence of one or more dielectric barriers in DBDs facilitates a fair distribution/dispersion of high energetic electrons (charges) on the surface of the whole electrode and therefore increasing micro discharge density along the anode surface. Other than the plasma generated inside the discharge zone, UV, shock waves as well as ozone are produced. In DBD, the charges are dispersed along the anode rod. This increases the yield of reactive species in the DBD reactor which improves the rate of decomposition of the pollutant. Based on these benefits of DBDs,

Table 2 Classification of plasma

Plasma	State	Example
	Low temperature plasma	
Thermal plasma (quasi-equilibrium plasma)	$T_e \approx T_i \approx T_g \leq 2\times10^4$ K $n_e \geq 10^{20}$ m	Arc plasma, plasma torches, RF inductively coupled discharges
Non-thermal plasma (non-equilibrium plasma)	$T_e >> T_i \approx T_g = 300 \ldots 10^3$ K $n_e \approx 10^{10}$ m^{-3}	Glow, corona, direct barrier discharge, atmospheric pressure plasma jets, hollow cathode discharges, electron beams, microwave and etc.

Source:(Valinčius et al. 2012)

Table 3 Plasma properties of atmospheric discharge schemes

Parameters	Corona discharge	DBD	APPJ	Atmospheric glow MHCD
Method and type	Sharply pointed electrode	Dielectric barrier cover on electrode	RF capacitively coupled	DC glow with micro hollow cathode electrode
Excitation	Pulsed DC	AC or RF	RF 13.5 MHz	DC
Pressure (bar)	1	1	1.013	1
Electron energies (eV)	5 variables	1–10	1–2	–
Electron density (cm^3)	10^9–10^{13}	≈10^{12}–10^{15}	10^{11}–10^{12}	–
Breakdown voltage (kV)	10–50	5–25	0.05–0.2	–
Scalability and flexibility	No	Yes	Yes	Yes
T_{max} temp, T (K)	Room	Average gas Temp (300)	400	2000
Gas		N_2+O_2+NO Rare gas/rare gas halides	Helium, argon	Rare gas, rare gas/rare gas halides

Source: Nehra et al. (2008)

MHCD micro hollow cathode discharge, *APPJ* atmospheric pulse plasma jet

various DBD reactor/electrode configurations have been developed. The common DBD configurations described in literature are introduced in the following two figures showing the structure of the DBD systems.

In Fig. 2, the reactor described by Gupta (2007) was positioned vertically and the dead volume in the chamber was eliminated by a cylindrical Teflon block on the bottom and an oil paraffin layer on the top to avoid electrical breakdown in air.

Structure, characteristics and configurations of the dielectric barrier discharge

Mark and Schluep (2001) characterized dielectric barrier discharges (DBDs) as specific and silent AC electrical discharges providing durable thermodynamic, non-equilibrium plasma at reasonable atmospheric temperature and pressure. Based on the discharge properties and the various possibilities in configurations, different DBDs names like barrier discharge, silent discharge, ac-discharge, normal pressure glow discharge, ozonizer discharge and display discharge are often used to denote DBD (Valinčius et al. 2012). Their studies highlighted that DBDs are usually formed in configurations consisting of two electrodes (anode and cathode) whereby one or both metal electrodes are normally protected with layers having a high insulating (dielectric) constant such as pyrex, quartz and ceramic that separates them from a gas layer (single dielectric). Otherwise, the dielectric can also be positioned between electrodes to separate two gas layers (double dielectric). Valinčius et al. (2012) also proved that DBD is a non-equilibrium discharge that can be operated at ambient conditions with the main goal being the long-term generation of ozone. In this regard, Nehra et al. (2008) proposed that the difference between a traditional and a DBD discharge relies on the fact that in traditional discharge, electrodes are directly in contact with the discharge gas and plasmas. This consequently leads to premature electrode etching and corrosion during the discharge process. However, in DBDs, the electrode (anode and cathode) is separated from the discharge gas by one or more dielectric layers thus reducing or eliminating electrode etching and corrosion, as presented in Figs. 3, 4, 5 and 6.

In addition, glass, quartz, ceramics and polymers are usually used as common dielectric materials. The distance between electrodes (gap) varies noticeably from a few millimetres to several centimetres. Furthermore, Lopez (2008) and Valinčius et al. (2012) indicated that the dielectric limits the amount of charges transported by a single micro discharge (micro plasma) over the entire electrode surface area. Furthermore, Konelschatz et al. (1997) claimed that non-equilibrium plasma conditions of DBD are presented in a simpler way compared to those of other types of discharges such as electron beam, low-pressure discharges and pulsed high-pressure corona discharges. This aspect therefore gives DBD the possibility of being scaled up from the laboratory scale to industrial conditions. According to Lopez (2008) and Nehra et al. (2008), DBD cannot be performed using DC but can be operated at high voltage alternating current (AC) due to the capacitive coupling of dielectric which requires an alternating voltage to drive a displacement current.

A decade ago, Kogelschatz et al. (2003) demonstrated that ionization of the discharged gas, also called breakdown, occurs in the region between the two electrodes in a DBD reactor at a sufficient high voltage. In this process, the charges accumulated on the surface of the dielectric layer discharge somewhere else on the exterior of the insulator. Hence, plasma generation is maintained if the continuous energy source delivers a corresponding degree of ionization, preventing the recombination route that leads to the destruction of the discharge. During the discharge of the accumulated particles, an energetic photon, whose frequency and energy correspond to the type of gas used is emitted and fills the discharge gap.

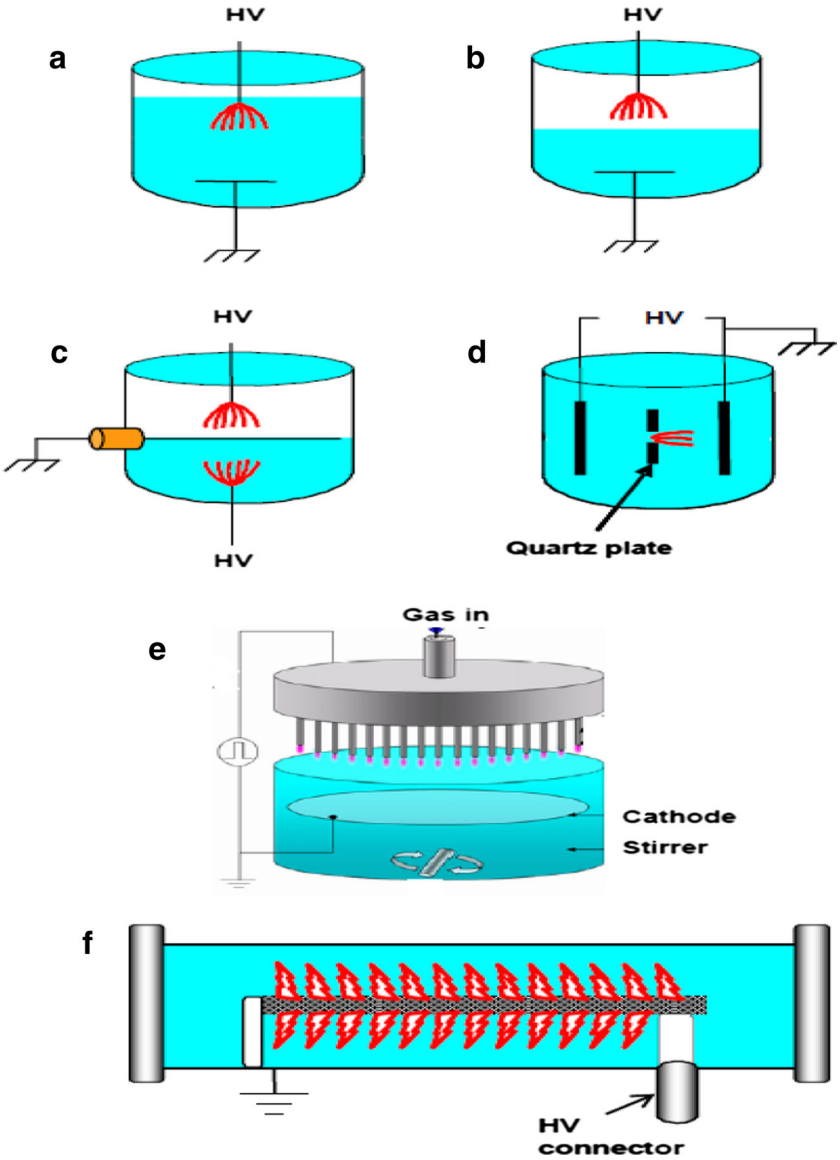


Fig. 1 Different configurations for the initiation of streamer discharges in water. **a**) Point plane geometry for liquid phase corona discharges. **b**) Point plane geometry for glow discharge initiation in the gas plenum above the water. **c**) Hybrid geometry for simultaneous streamer discharge initiation in the water and in the gas plenum. **d**) Streamer discharge originating from a diaphragm. **e**) Multi-pin reactor configuration. **f**) Coaxial pulsed underwater corona reactor with anode covered by a porous ceramic layer, (Gupta 2007)

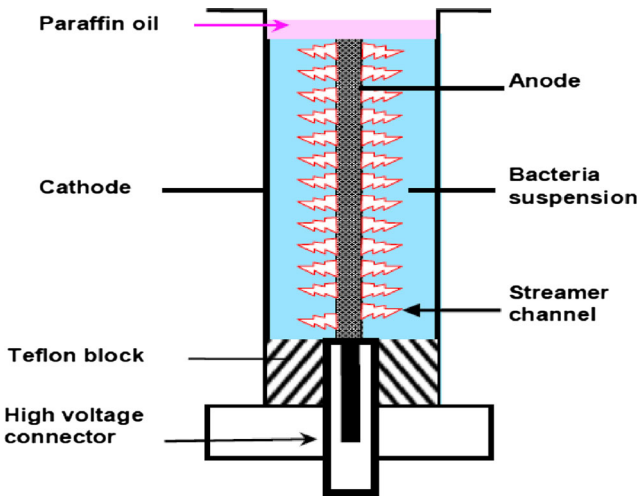


Fig. 2 Schematic of the modified corona reactor for microbiological (Gupta 2007)

Kogelschatz and colleagues also showed that numerous configurations can be used to induce DBD. Some of these include parallel plates (planar) separated by a dielectric or cylindrical and coaxial plates with a dielectric tube between them. The common DBD configurations reported in literature are presented in Fig. 7.

Furthermore, Mark and colleagues clarified that the creation of DBDs is characterized by the production of a huge amount of short lifetime micro discharges induced by the continuous current flow in the system. The study also proved that the dielectric barrier conformation supplies a self-ending electrical discharge regardless of the applied voltage wave shape. Their paper also highlighted that in the absence of a barrier / insulator, with gas pressures of about one atmosphere and a gas discharge gap of limited millimetres, only a few localized intense arcs would develop in the gas gap between the powered metal electrodes.

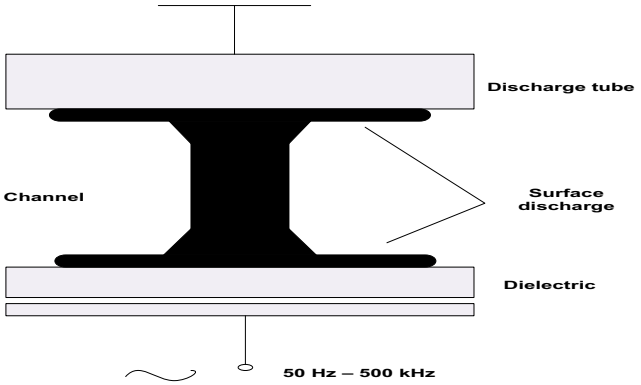


Fig. 3 Single planar dielectric electrode configuration (Lopez 2008)

However, in the presence of the dielectric layer between the conductive electrodes with an AC voltage of about 1–100 skV and a frequency of a few or several hertz, a significant amount of plasma is created by an important number of micro discharges in the gas discharge zone (Nehra et al. 2008; Mark and Schluep 2001). Whereby, each micro discharge is regarded as a source of non-thermal plasma characterized by energetic electrons that produce extremely reactive free species in the plasma region. As earlier mentioned, in non-thermal plasma, species such as electrons, ions and neutrals have different temperatures and hence different kinetic energies. Thus, in the case of DBD, electrons having the highest energy initiate the formation of active species such as O_3, H_2O_2 and mostly free radicals including O(1D), $O(^3P)$, OH· and H· from the gaseous feeds such as O_2 and air which free radicals are immediately used to decompose the contaminants.

Application of DBD configurations: degradation of organic pollutants using DBD plasma

The aforementioned advantages of DBD over the conventional plasma technologies have attracted attention and are reported in various studies. Various studies on treatment of water/wastewater using single dielectric electrode configuration have been conducted. Very recently, Reddy et al. (2014) used a cylindrical single dielectric barrier catalytic non-thermal plasma reactor (Fig. 8) for mineralization of endosulfan in aqueous medium for the treatment of pesticide contaminated water. Indeed, in their study, an advanced oxidation process was developed by combining non-thermal plasma with cerium oxide catalysts for the mineralization of a model pesticide endosulfan from aqueous medium. The single dielectric electrode configuration presented in Fig. 8 shows that the endosulfan solution was mixed with air in the gas discharge gap and therefore exposed to micro discharge plasmas generated on the inner electrode (first dielectric quartz). The study showed that incorporation of cerium oxide catalysts into the DBD reactor significantly improved not only the conversion but also increased the degree of mineralization of the pollutant. This was evidenced by total organic carbon and infrared spectroscopy analysis. Joshi and Shrivastava (2011) reported that oxidative stress induces membrane lipid

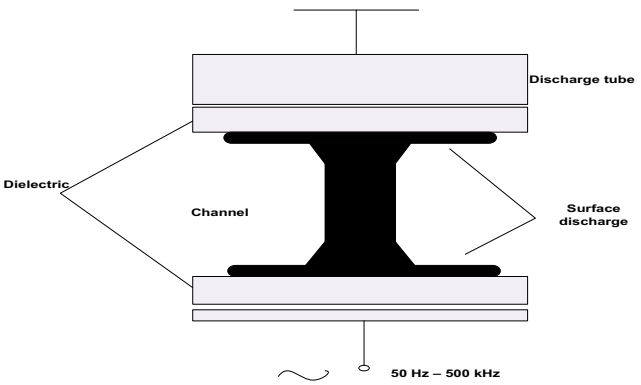


Fig. 4 Double planar dielectric electrode configuration (Lopez 2008)

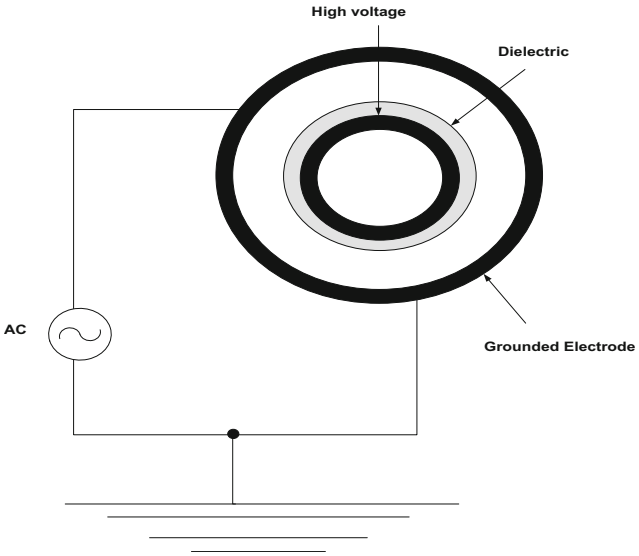


Fig. 5 Cylindrical single dielectric electrode arrangement Nehra et al. (2008)

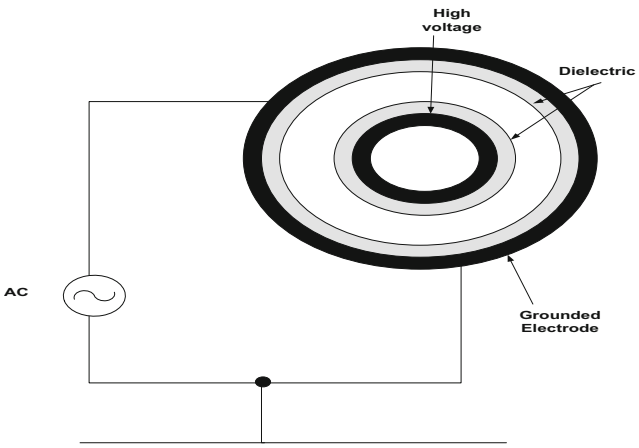


Fig. 6 Cylindrical double dielectric electrode arrangement (Nehra et al. 2008)

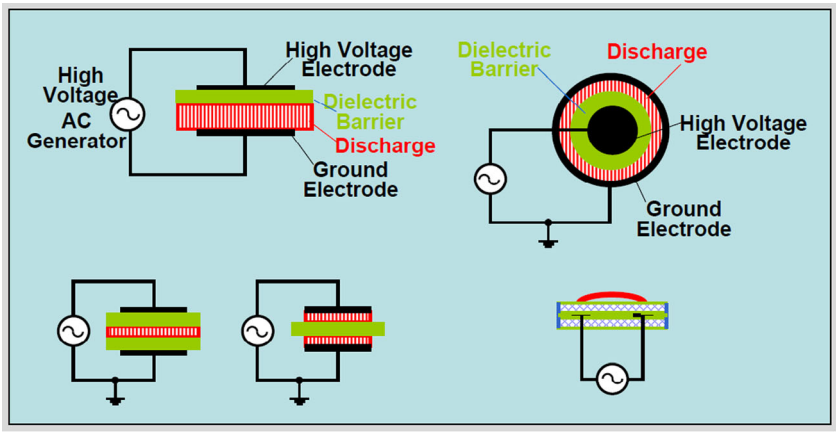


Fig. 7 Common dielectric barrier discharge configurations with one or two dielectric barriers (Kogelschatz et al. 2003)

peroxidation, which leads to the production of detrimental substances causing oxidative modification in cells, leading to cell death.

Based on this claim, Joshi and Shrivastava (2011) successfully applied non-thermal plasma using a floating-electrode dielectric barrier discharge (FE-DBD) technique for rapid inactivation of bacterial contaminants in normal atmospheric air. The study proved that reactive oxygen species (ROS) such as singlet oxygen and hydrogen peroxide-like species were the main regulator oxidative species in the oxidative stress process. These oxidizing agents were also suspected to be responsible for the lipid peroxidation in *Escherichia coli*. In the same vein, Reddy et al. (2013) investigated the plasma-induced methylene blue degradation using dielectric barrier discharge. In their study, dielectric barrier discharge at the gas water interface was used as an advanced oxidation process for the oxidative degradation of dye-contaminated wastewater. Mark and Schluep (2001) proved that DBD can be used to degrade volatile organic compounds (VOCs) as their emission into the atmosphere can cause adverse effects on human health such as photochemical smog formation. In that regard, Mark and Schluep (2001) used a single DBD to generate gas-phase free radicals such as O (1D), O (^{3}P), and OH at low temperature (293 K) to decompose pollutants such as benzene. The results showed that a near complete decomposition of benzene (>99%) was reached in both wet and dry gas streams. Apart from environmental and industrial applications, DBD has also been employed in the medical sector. For example, Arjunan et al. (2012) noted that vascularization is very important for tissue engineering and wound healing. They highlighted that non-thermal plasma, principally DBD, as a source of reactive oxygen species (ROS), has been frequently used for medical applications such as sterilization, malignant cell apoptosis and blood coagulation. In addition, Mastanaiah et al. (2013)

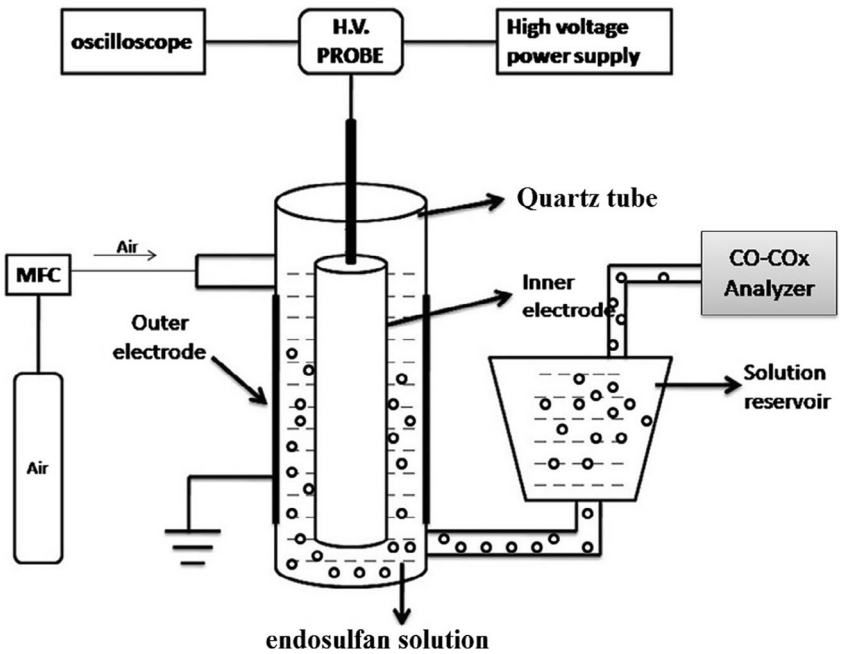


Fig. 8 Single dielectric barrier discharge experimental setup for the treatment of endosulfan in aqueous medium (Reddy et al. 2014)

claimed that sterilization by plasma is faster, less toxic and multipurpose compared to traditional sterilization methods. By using a low temperature, atmospheric, single dielectric barrier discharge surface plasma generator, the authors achieved greater sterilization (elimination of different bacteria) in shorter periods of time compared to conventional sterilization techniques.

Apart from the single DBD, double DBD has also been used in several different fields such as the environmental, industrial and health sectors. In the double dielectric configuration, the two conductive electrodes are protected by two insulating layers (dielectrics). The discharge zone between the inner and the outer dielectric quartz is a source of highly reactive species produced via the interaction between air and the highly energetic electrons widely dispersed on the surface of the anode in the inner quartz tube. The resulting free radicals in the air gap are directly circulated into the polluted solution to induce the oxidation process. In the same way that the single dielectric barrier discharge has been explored in various fields, several experiments have also been performed with the double dielectric barrier discharge. For instance, Rong et al. (2014) applied a cylindrical double dielectric barrier discharge (DBD) reactor (Fig. 9) as an advanced oxidation process for the degradation of diclofenac in aqueous medium. The outcomes of their study showed that at specific conditions (power 50 W and a pH of 6.15), a concentration of 10 mg/L diclofenac was completely removed within 10 min. These authors also affirmed that the presence of Fe^{2+} in the liquid phase promoted the decomposition of diclofenac.

Atmospheric pressure dielectric barrier discharge plasma jet. In their experiment, *Bacillus subtilis* and *Escherichia coli* planted in two media (agar and filter papers) were exposed to after-glow plasma generated by a double dielectric barrier discharge (DBD) plasma jet generator in open air at a temperature between about 30 and 80 °C. For the bacteria planted in agar medium, the results showed that after 5 min of treatment, the effective area of inactivation was much larger than the plasma jet and increased with the plasma treatment time. In the case of the bacteria seeded in the filter paper, the results indicated that significant inactivation was obtained when adding reactive gases such as oxygen and hydrogen peroxide vapour compared to noble gases.

In the DBD configuration used by Rong and colleagues in 2014, the inner insulator tube of the reactor was made of quartz but the outer dielectric layer was a plexi-glass tube. In addition to the tube material, the configuration had two air flow distribution tubes. This might be beneficial for even distribution of bubbles in the bulk solution, but the configuration design would be very complex. Moreover, in some DBD configurations, the reactor can be placed and moved out of the treatment vessel. This means that the double dielectric configuration can easily be scaled up to treat the desired volumes of the pollutants. In DBDs, electrode/reactor configuration is a very crucial parameter for treatment of effluents. The literature cited in the paragraphs above showed that the cylindrical single dielectric configuration can be employed in various applications. Likewise, the cylindrical single and double barrier has also been widely utilized in water/wastewater treatment technologies. In most studies using DBDs processes, various pollutants and bacteria have been used as model contaminants and microorganisms as shown in Table 3.

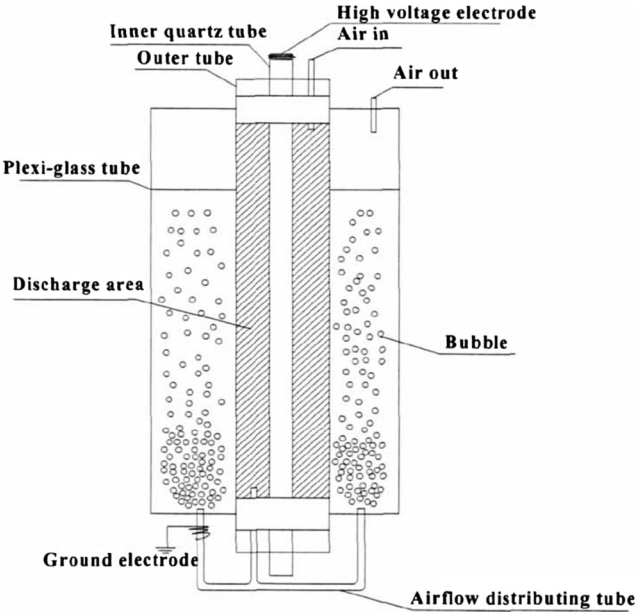


Fig. 9 Cylindrical double DBD experimental setup (Rong et al. 2014)

Advantages of single/double cylindrical dielectric barrier discharge

Smirnov (1977) summarized plasma properties as a conductive fluid containing the same number of positive and negative charge carriers. The authors further demonstrated that the fundamental property of plasma is based on the existence of an electric and magnetic field which perhaps is the driving forces behind the processes. Panicker (2003) submitted that different types of gas ionization occurred during plasma processes especially when air is used as a feeding gas for the production of the plasma. Thus, several ionizations were noticed among which are, particle impact ionization, photo or irradiative ionization and electric field ionization. These ionization categories are discussed below:

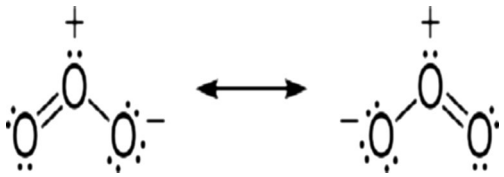


Fig. 10 Resonance structure of ozone (Vatistas 1987)

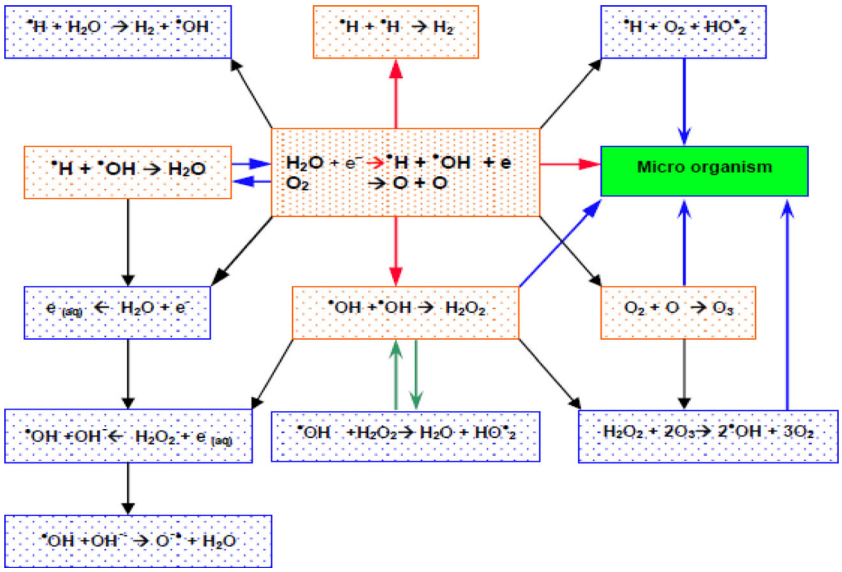


Fig. 11 Chemical reactions occurring in electrohydraulic discharges based on plasma process (Gupta 2007)

Particle impact ionization Particle impact ionization is a phenomenon in which particles, predominantly electrons or ions, strike atoms and make them lose or gain a charge depending on the amount of transmitted energy during collision. In fact, the transferred energy has to surpass the ionization energy (Ei) of the atom (Panicker 2003). During electron impacts, an atom can absorb an electron and the absorbed electron can excite the outermost electrons of the atom until it becomes ionized if continuously provided with enough energy. Furthermore, this type of ionization probably occurs in regions bounded by strong electric or magnetic fields where the particles are usually accelerated. In cases where the electrons produced during ionization have high energy, a secondary ionization can be induced. Smirnov (1977) and Panicker (2003) explained further that ions can also be accelerated and interact with atoms and ionize them. Since ions are heavier species their acceleration requires an extreme amount of energy in the presence of a strong electric and magnetic field. Nuclear reactions are often used for ion acceleration and ionization of gases. However, this approach is not usually safe.

Photo or irradiative ionization In passive or irradiative ionization, Panicker (2003) mentioned that photons of high energy can ionize atoms provided that the amount of energy associated with photon is greater than that of the atom. Gamma rays, X-rays and ultraviolet rays are often applied in such process. The UV radiations generated in the DBD plasma reactor scatter in different directions and diffuse in the bulk solution and hence irradiate molecular and ionic species present in the polluted solution.

Electric field ionization Electric field ionization involves the circulation of gas (such as air) between the ionized electrodes (anode and ground electrodes). In this process, depending on the polarity of the electrode, atoms or molecules brought in contact with the surface of the metal electrodes loose or gain charges. In order to initiate ionization, the density of the electric field has to be as high as possible. Another essential parameter necessary for rapid ionization is electrode geometry. Indeed, electric fields around sharp materials and metallic surfaces with low radii of curvature are stronger than around rounded frames. However, when particles such as oxygen approach an electrode highly surrounded by a strong electric field, it gets ionized before reaching it. The degree of ionization drops with the decrease in the electric field intensity. The electric field ionization is easily generated and controlled in the laboratory. Also different electrodes geometries with various conformations can be designed and varied for specific tasks.

Formation of UV light and reactive species in the DBD system In plasma processes, the highly energetic electrons impact with neutral molecules such as O_2 and N_2 in the air gap region and excite these molecules to higher energy levels (Eqs. 9 and 11). The relaxation of the excited molecules (O_2* and N_2*) to their lower energy states (Eqs. 10 and 12) according to Jiang et al. (2014) leads to the emission of the UV light that shines around the whole anode electrode and is propagated in all directions within the bulk solution.

$$N_2 + e- \rightarrow N_2^* + e- \text{excitation} \quad (9)$$

$$N_2^* \rightarrow N_2 + hv \text{ relaxation} \quad (10)$$

$$O_2 + e- \rightarrow O_2^* + e- \text{excitation} \quad (11)$$

$$O_2^* \rightarrow O_2 + hv \text{ relaxation} \quad (12)$$

This process has been widely observed during the photodecomposition of organic pollutants. This view was expressed

Table 4 Different dielectric barrier discharges systems for water and wastewater treatment

Compound	Type of DBD	Voltage	Main oxidizing species	Degradation / mineralization percentage	pH	Treatment time (min)	Degradation intermediates	Analytical techniques	References
Dye alizarin red (AR)	Double hybrid gas- liquid dish DBD	8 kV	Ozone	99.73	8.4	40	Glyoxylic acid and vinyl formate	UV-vis spectrometry, colorometric method, TOC and GC-MS	Xue et al. (2008)
Dye fluorescein-4-isothiocyanate (FITC)	Single planar DBD	6.5 kV	H_2O_2 and O_3	35	5.7	20	Undefined	UV-vis spectrometer, colorimetric method using titanyl reagent and indigo solution, respectively	Baroch et al. (2008)
Styrene	Single wire-tube DBD	3.6–16 kV	O_3	–	–	120–180	–	–	–
Endosulfan	Cylindrical NTP-double DBD+CeO_2	1–40 kV	O_3 and H_2O_2	NTP alone Conversion 82 % Mineralization 15 % NTP-CeO_2 Conversion 94 % Mineralization 48 %	–	60	–	UV-vis spectroscopy TOC, spectrophotometry quantification of the per titanic acid	Reddy et al. (2014)
Methylene blue	Cylindrical NTP-double DBD+$NaSO_4$, Fe^{2+}	14–18 kV	O_3 and H_2O_2	O_3 alone 75 % DBD reactor 95 %	–	25	–	UV-vis spectroscopy CO, COx and NOx analysis (Siemens Ultramat 23) TOC	Reddy et al. (2013)
Azo dye (methylene orange)	NTP-Single DBD	Undefined	O_3 and H_2O_2	92 %	5.01	20	–	UV-vis spectroscopy, colorimetric method using titanyl reagent and indigo solution, respectively, ICS, COD	Jiang et al. (2012)
Methylene blue	Single planar DBD	22 kV	O_3, $\cdot O_2$, OH, H_2O_2	99.75 %	5.33	40	Phenyl thiophene	UV-vis spectrometer, iodometry, UV-vis spectroscopy, GC-MS, FT-IR, ICS, OES	Huang et al. (2010)
Azo dye Orange II	Single cylindrical DBD	13.4–23.3 kV	O_3, H_2O_2 and $OH^{\cdot}$	90 %	5.3–3.58	60	–	UV-vis spectroscopy, TOC and HPLC	Mok et al. (2008)
Reactive azo dyes	Single coaxial DBD+H_2O_2 +Fe^{2+}	17 kV	O_3, H_2O_2 and OH	90–97	5, 7 and 9	24 h	–	UV-vis spectroscopy, Colorimetric method with titanyl sulphate	Jović et al. (2013)
Indigo Carmine	Spraying DBD	30 kV	O_3, H_2O_2 and OH	95 %	–	30 min	–	Undefined	Wang et al. (2008)
Danube water	Single coaxial DBD	18 kV	O_3, $\cdot O_2$, OH, H_2O_2	Undefined	–	40 min	–	Iodometric method, Indigo colorimetric method and COD	Kuraica et al. (2004)
E. coli in culture water	Single cylindrical DBD	25 kV	$O^{\cdot}$, OH, O_3	90–99 %	–	–	–	OES and TDS	Hernández-Arias et al. (2012)
Gram-negative *E. coli* and gram positive *S. aureus*	Double planar DBD	1–30 kV	O_3, $O^{\cdot}$, OH	100 %	–	7–10 s	–	TEM and optical density	Yue et al. (2008)
Escherichia coli, *Bacillus subtilis* and *Pseudomonas aeruginosa*	Double planar DBD	11 kV	O_3, $O^{\cdot}$, OH	99.99 %	–	70 s	–	OES and SEM	Choi et al. (2006)
vegetative bacterial and yeast cells, *Geobacillus stearothermophilus* spores	Multi-electrodes planar DBD	1–100 kV	O_3, $O^{\cdot}$, OH	≥6 log reduction	–	2–20 min	–	–	Mastanaiah et al. (2013)
Escherichia coli	Single floating-electrode (FE)-DBD	15 kV	O_3, $\cdot O_2$, OH, H_2O_2	90–95 %	–	30–90 s	–	SEM, chemical probes (SOSGR, AUR, etc.)	Joshi and Shrivastava (2011)
Textile dyes in wastewater	Single dielectric DBD	30–50 kV	O_3, $\cdot O_2$, OH, H_2O_2	95 %	7–8	300 s	–	UV–Vis, FT-IR, toxicity test	Martynas et al. (2013)
HCN in water	Single coaxial DBD	1–20 kV	O_3, $\cdot O_2$, OH, H_2O_2	92–99 %	11	100 min	–	GC-NPD	Maria et al. (2013)
Veterinary antibiotics	Single coaxial DBD	–	O_3, $\cdot O_2$, OH, H_2O_2	60–90 %	–	–	–	–	Kim et al. (2013)

by Willberg et al. (1996) and Joshi et al. (2013) who independently observed that when an organic compound (C) is illuminated by UV light, it gets promoted to an excited state (C*) and instantly falls back to the ground state (C) due to its short lifetime (10–9 to 10–8 s). During relaxation of the compound, the decomposition of the molecules occurs and new species become evident as shown in Eq. (13).

$$C + hv \rightarrow C^* \rightarrow \text{products} \quad (13)$$

Additionally, Peyton and Glaze (1988) and Anpilov et al. (2001) stated that, besides the photo-degradation of organic molecules, UV light also plays an important role in the dissociation of ozone and hydrogen peroxide and hence enhanced the production of OH in the plasma treatment process. Furthermore, the generated OH radicals attack and decompose the target pollutants. Therefore, in the DBD system, the UV light is generated in the discharge gap as a result of the collision between highly energetic electrons and the neutral O_2 and N_2 molecules from the dry air.

Ozone formation and properties (oxygen-based species) Several species of oxygen and nitrogen are formed during the plasma process induced by the decomposition of air via electrical discharge (Wilhelemus 2000). Among the oxygen species, ozone (O_3) is identified as an allotrope of oxygen and remains the principal molecule responsible for the decomposition of the target organic contaminants (Jiang et al. 2014). According to Jiang et al. (2014), O_3 is usually produced via the exposure of oxygen to electrical discharge in the air gap zone of a DBD plasma reactor and circulated within the bulk solution with a continuous flow of dry air and current both in contact. These strongly oxidizing O-based species exhibit crucial chemical properties. Ullmann (1991) and Kirk and Othmer (1996) showed that O_3 is a strong oxidizing agent with an oxidation potential of E_0=2.08 V. Also, Glaze (1987) stated that ozone mainly reacts with chemical compounds through three different routes. The author considered ozone as an electron transfer acceptor that can oxidize metal ions or an electrophile that induces the oxidation of phenol and other stimulated aromatics. Then ozone can act as a dipole addition reagent when added to carbon–carbon multiple bonds. Gurol and Vatistas (1987) affirmed that the electrophilic characteristic of ozone is due to the presence of the positive charge on oxygen atom leading to resonance structures as shown in Fig. 10.

In addition to this, the authors concluded that the chemical instability of ozone leads to its decomposition through mechanistic reaction chains resulting in the production of OH radicals as shown in Equations 14 and 15 (Gurol and Vatistas 1987).

$$O_3 + OH^{\bullet} \rightarrow O_2 + HO_2^{\bullet} \quad (14)$$

$$HO_2^{\bullet} + O_3 \rightarrow OH^{\bullet} + 2O_2^{\bullet} \quad (15)$$

Moreover, Ullmann (1991), Kirk and Othmer (1996) and Lide (1999) proved that at room temperature, ozone is able to oxidize water molecules to hydrogen peroxide. This was supported by Glaze (1987) and is presented in Eqs. 16 and 17.

$$H_2O_2 \rightarrow H^+ + H_2O^- \quad (16)$$

$$O_3 + H_2O^- \rightarrow {}^{\bullet}O_2^- + {}^{\bullet}OH + O_2 \quad (17)$$

As earlier mentioned, the UV light produced in the DBDs systems is diffused in the aqueous solution and irradiates the O_3 dissolved in the polluted water. In this regard, Atkinson and Carter (1984) substantiated further that UV radiation with a wavelength of $\lambda \leq 310$ nm can dissociate O_3 into singlet oxygen and oxygen molecules. The singlet oxygen with a life time of about 4.4 μs can react with water yielding hydroxyl radicals which eventually recombine to form H_2O_2 (Atkinson and Carter 1984). Some dissociative chemical reactions of O_3 are presented in Eqs. (18–20).

$$O_3 + h\nu \rightarrow O(^1D) + O_2(1\Delta g) \lambda \leq 310 \text{ nm} \quad (18)$$

$$O(^1D) + H_2O(g) \rightarrow 2OH \quad (19)$$

$$O(^1D) + H_2O(l) \rightarrow H_2O_2 \quad (20)$$

Hydrogen peroxide Assuming that dry air contains small traces of hydrogen, therefore the generation of OH radicals in the plasma zone might be possible Zimmer (2013). However, the diffusion of these powerful reactive species (diffusion distance 6×10^{-9} m) from the plasma region to the bulk zone of the target contaminant is very insignificant, Roots and Okada (1975). Therefore, the formation of long-lived, active, molecular species such as hydrogen peroxide in the bulk solution is necessary. Ullmann (1991) and Kirk and Othmer (1996) highlighted that hydrogen peroxide that is usually considered as the recombination product of hydroxyl radicals has a reduction potential of E_0=1.76 V in acidic medium and is inactive with some organic compounds than its reactants. However, its presence in the water treatment processes is of great importance. Because H_2O_2 apart from its oxidizing properties substantially contributes to the synthesis via dissociation, photolysis and metal-based catalytic reactions of various other oxidizing reactive species such as OH and HO^{2-} in the polluted solution (Jiang et al. 2014). Lide (1999) also confirmed that in plasma processes, about 213 kJ/mol (2.2 eV) is required to break the OH–OH bond during decomposition of H_2O_2 by pyrolysis. The authors submitted that hydrogen peroxide is unstable at high concentrations and has the ability to oxidize and reduce itself at room temperature. Lide (1999) also affirmed that the decomposition of concentrated hydrogen peroxide is an exothermic process that releases about 98.3 kJ/mol. Furthermore, Moeller (1957) confirmed that hydrogen peroxide is a weak acid with a dissociation constant pKa=11.75. The chemical reactions based on the formation

and decomposition of H_2O_2 are listed in Eqs. (21–24) (Wilhelemus 2000).

$$H_2O \rightarrow H + OH \quad (21)$$

$$H + O_2 \rightarrow HO_2 \quad (22)$$

$$HO_2 + OH^- \rightarrow O_2^- + H_2O \quad (23)$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \quad (24)$$

Based on the aforementioned facts from literature, the hydrogen peroxide species are expected to be mostly produced in the bulk of the polluted solution being treated in the EHD system.

Formation of HO· radicals and their reactions Most advanced oxidation processes (AOPs) reported in literature as water treatment techniques are based on the production of hydroxyl radicals (Lukeš 2001). These powerful free reactive species are highly reactive, nonselective and responsible for the decomposition of various organic and inorganic molecules into harmless compounds. Indeed, Sangster (1971) noted that there are three different ways through which OH radicals reacts with organic and inorganic compounds. These include abstraction of a hydrogen atom (Eq. 25), electrophilic addition to double/triple bonds (Eq. 26) and electron transfer (Eq. 27) (Gogate and Abdullahi 2004a; Gogate and Abdullahi 2004b)

$$OH^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \quad (25)$$

$$OH^{\bullet} + R_2C = CR_2 \rightarrow R_2(OH)\,C{-}CR_2\cdot \quad (26)$$

$$OH^{\bullet} + RX \rightarrow XR^{\bullet +} + OH{-} \quad (27)$$

Indeed, the aforementioned theoretical che.mical reactions established for the production of powerful oxidants in EHDs has been summarized by Gupta (2007).

Summary of the DBD reactor configurations On the whole, most dielectric barrier discharge studies elaborated in this section involve chemical additions (Nehra et al. 2008; Madhu et al. 2009; Joshi and Shrivastava 2011; Heon et al. 2012). The double cylindrical dielectric barrier electrohydraulic discharge (DB–EHD) system, however, requires few or no chemical additives. So without adding any chemical, the DBD system could be a suitable technique of decomposing/degrading organic contaminants such as dyes at ambient conditions. Jin-Oh and Mok (2009) attempted exploration of the double cylindrical DBD plasma reactor. However, in their study they used azo dye as a model contaminant, with addition of H_2O_2 and O_3 in the system. Apart from this, their study only investigated the effect of a few parameters on the degradation of dye pollutant. In their paper, dielectric barrier electrohydraulic discharge was identified as an improved advanced oxidation technology over other conventional electrical discharges by showing its benefits in water/wastewater treatment. Indeed, the following advanced oxidation techniques, H_2O_2/UV, O_3/UV and the combination (H_2O_2/UV/ O_3) employed in the DBD plasma reactors are the source of the diverse active species shown in Fig. 11 that are responsible for the degradation of organic pollutants as well as the inactivation or sterilization of microorganisms. From the literature review, numerous mechanistic pathways for the formation of reactive species have been suggested by various authors (Prendiville et al. 1986; Tarr et al. 2003; Hayashi et al. 2000).

It is known that DBD is widely used to eliminate organic pollutants from water and wastewater; however, reactor configurations, electrode material and geometry and the type of pollutant in DBD processes differ from one study to another (Bian et al. 2009; Magureanu et al. 2012; Iqbal et al. 2013). Moreover, Magureanu et al. (2012) and Bian et al. (2009) used reactor configurations involving several high voltage electrodes in parallel as well as catalysts to enhance the degradation efficiency of pollutants.

Apart from this, the dielectric barrier electro hydraulic discharge (DBD), also referred to as liquid electrical discharge, is characterized by its physical and chemical parameters such as shock waves, UV radiations and reactive species including OH., H_2O_2, O_3, O· etc. resulting mainly from dissociation of water molecules and oxygen gas by UV light (Iqbal et al. 2013). To recall, decolourization and degradation are two different aspects usually highlighted in treatment of water and wastewater effluents. While decolourization refers to colour removal of a specific pollutant such as dye as a result of the destruction of its chromophoric form, degradation indicates how much organic carbon of the contaminant has been removed. Since the literature reviewed above showed that several DBD-based water/wastewater treatment technologies have been developed, the efficiency of any treatment system could be evaluated by its capability of achieving a high percentage of these two parameters simultaneously. Nevertheless, some configurations would achieve these two parameters separately. A very few authors in the literature have investigated the decolouration or decomposition of organic pollutants such as dyes using cylindrical DBD plasma reactors as shown below in Table 4. Therefore, this review highlights the efficiency of the DBDs plasma reactor systems through a description and by providing details on the formation of free radical species that are responsible for sterilization of microorganisms as well as the destruction and mineralization of the pollutants into harmless organic and inorganic by-products.

Conclusion

The literature reviewed on DBDs has shown that high degradation or removal efficiencies of contaminants were achieved with different reactor configurations. However, it can be noticed that in most of these investigations, chemical additives were used. Likewise, the additions of chemical species in

traditional or novel treatment methods often result in unwanted by-products that are non-degradable and whose removal is usually challenging. Apart from this, only a few parameters such as pH and conductivity have been investigated in these studies during the degradation of the target pollutants. In addition, none of these studies dealt with the full optimization of the DBD system for water and wastewater treatment. Failure to fully optimize the various configurations used in these studies might be the reason for not achieving the complete desired decontamination of polluted waters. Therefore, it would be recommended that irrespective of the electrode geometries, the effect of various parameters such as physical, chemical, electrical and reactor configuration on the degradation of the target compound should be fully studied in order to achieve the desired decomposition of persistent organic toxins at optimum conditions.

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