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REVIEW ARTICLE

Review of the methods for determination of reactive oxygen species and suggestion for their application in advanced oxidation induced by dielectric barrier discharges

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Abstract
Advanced oxidation processes (AOPs) particularly non-thermal plasmas based on electrical discharges have been widely investigated for water and wastewater treatment. Dielectric barrier discharges (DBDs) generate large amounts of selective and non-selective reactive oxygen species (ROS) such as ozone, hydrogen peroxide, atomic oxygen, superoxide molecular anions and hydroxyl radicals, having been proved to be efficient for water decontamination among various forms of electrical discharge systems. The detection and quantification methods of these oxygen species in non-thermal plasmas have been reviewed. However, their application in dielectric barrier discharge has not been well studied. It is therefore imperative to summarise the various detection and quantification methods for oxygen-based species determination in AOPs, aqueous systems and non-thermal plasma processes. Thereafter, reviewed methods are suggested for the determination of ROS in DBD configurations to understand the consumption trend of these oxidants during treatment of water effluents and to evaluate the performance of the treatment reactor configuration towards the degradation of targeted pollutants.

Keywords AOPs · DBD · Quantification · Measurement · Reactive oxygen species

Introduction

For decades, the decontamination of polluted water by advanced oxidation processes (AOPs) gained a lot of attention worldwide. The principal goal of AOPs is the generation of strong non-selective hydroxyl radicals that destroy target contaminants, apart from these contaminants, UV light and other molecular and ionic species are also produced. For instance, non-thermal plasma (NTP) advanced oxidation technologies have been proved to generate various reactive oxygen species (ROS) among which O_3, H_2O_2, $O_2^{\cdot-}$, O·, OH, etc. that directly or indirectly oxidise water pollutants. Hence, NTP AOPs have proven to be adequately effective in water and wastewater treatment in the past decades (Bruggeman et al. 2016, Vanraes et al. 2016; Foster 2017).

Though the detection and quantification methods of oxygen species in non-thermal plasma AOPs and aqueous systems have been reviewed to some extent (Bruggeman and Leys 2009; Shih and Locke 2010; Locke and Shih. 2011, Bruggeman et al. 2016), their coherent summary is imperative to understand the consumption trend of these oxidants during treatment of water effluents and to evaluate the performance of the treatment reactor configuration towards the degradation of targeted pollutants. This review presents different detection and quantification methods widely employed in literature to measure the concentration of oxygen-based species in aqueous media and further suggest reviewed methods useful for the determination of ROS in double cylindrical dielectric barrier discharge. The worldwide scarcity of freshwater resources is often attributed to continuous industrialisation and urbanisation processes, a consequence of population growth, deforestation and unlimited pollution (Gilmour and Madhumita Ray 2012). The United Nations (UN) in collaboration with

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some researchers (Gilmour and Madhumita Ray 2012) insisted that constructive policies based on sustainable use of freshwater need to be endorsed to reach global pertinent demands. Gilmour and Madhumita Ray (2012) reported that protection of water resources, management of water resources and the expertise of water recovery from diverse effluents will ensure a durable sustainability of uncontaminated water supply. Persistent organic compounds usually referred to as emerging contaminants (EC), endocrine disrupting compounds (EDCs) such as pharmaceuticals and personal care products (PPCP) have been detected in numerous water runoffs and aqueous media (Onesios et al. 2009; Li et al. 2012). These toxins and their degradation intermediates are continuously being released into the aquatic environment either through untreated or partially treated discharges which consequently affect human health and raise environmental concerns (Kidd et al. 2007). In addition to these, the existence of micropollutants in aquatic environment demonstrate the failure of water management based on water resources protection and reuse from various municipal and industrial wastewater sewages. Conventional water treatment methods, often termed as secondary biodegradation techniques, have not been able to eliminate completely these toxins as they were not designed for such categories of pollutants. Some conventional methods such as activated charcoal and reverse osmosis claim to produce satisfactory water quality, but in reality only transfer and convert the pollutants from one phase to another, hence necessitating the demand for further treatment processes. Recently, advanced oxidation processes focussing on the in situ production of non-selective hydroxyl radicals have been recognised as prospective technologies for water and wastewater treatment (Abdelmelek et al. 2011). Apart from the non-selective OH radicals produced, other molecular and ionic reactive species such as O_3, H_2O_2, $O^{\cdot}$, $O_2^{\cdot-}$, etc. are also generated in plasma systems and often considered as $OH^{\cdot}$ precursors. The common AOPs documented in literature include direct ozonation, UV photolysis, UV photo catalysis, Fenton and photo-Fenton reactions, sonolysis, ozone sonolysis, catalytic oxidation, supercritical water oxidation or wet oxidation, radiolysis, ultrasonic irradiation and high-voltage electrical discharges all of which have been used to oxidise organic pollutants into CO_2, water and harmless organic and inorganic species (Wu et al. 2011; Iqbal et al. 2013). Some research studies report that the cost and insufficient information about the subsequent water quality often limits the applicability of these effective technologies at a large scale (Gilmour and Madhumita 2012), while the performance of these technologies are often dictated by various parameters, such as pollutant concentration, toxicity, degradation and mineralisation efficiency of pollutants as well as the amount of reactive species produced in the systems. Recently, dielectric barrier discharge (DBD) has been identified as an attractive AOP because on its own, DBD generates UV light and high reactive species including O_3, H_2O_2, $O^{\cdot}$, $O_2^{\cdot-}$, etc. with or without any chemical addition (Magureanu et al. 2015; Mouele et al. 2015). Therefore, their combination renders DBD a potential treatment technique for water and wastewater remediation. This review focuses on various methods used to detect and quantify reactive oxygen species produced either in AOPs or in other aqueous systems. Since it has been documented that DBD systems directly depend on reactor configurations, the performance of DBD reactor could be dictated by the amount of reactive species generated and hence contribute to large production of OH radicals. These methods can relatively be applied in particular systems as various quantification techniques for ROS species in non-thermal plasma systems, and other aqueous systems have been developed taking into consideration that the selection of the appropriate method might depend on availability, affordability and operational costs.

Ozone quantification methodologies via advanced oxidation processes

Ozone, considered as a protective natural agent forming the well-known ozone layer, is recognised as a toxic pollutant for living organisms (Iliadis et al. 2013). Its accurate determination in aqueous environments may be challenging.

The choice of detection and quantification of ozone in aqueous systems may depend on the type of AOP used for ozone generation, the instruments and their accuracy. Recently reported ozone measurement techniques are based on instrumental, chemical reactions, chemiluminescent and colourimetric properties (Metzger 2009).

Instrumental methods for the determination of ozone concentration

Measurement of ozone in the liquid phase

The ozone analysis investigation using electrochemical means have been reported by Johnson et al. (1967). Johnson and coworkers described the basic electrochemistry process of ozone measurements on gold and platinum electrodes in aqueous media. On the other hand, Smart et al. (1979) investigated the reduction of dissolved ozone on gold electrodes while Stanley et al. (1979) studied the measurement of ozone using amperometric sensors. The study conducted by Uchiyama et al. (1993) supported the lowest detection limits of ozone in water to about 0.5 ppb using an amperometric carbon electrode. Besides, various studies (Kim et al. 2000; Miyata et al. 2000) reported that ozone concentration could be determined at higher parts per billion and parts per million using semiconducting oxide films. However, cross sensitivities in these technologies are problematic and could be overcome by a combination of sensors with multivariate calibration (Mitrovics et al.

1998; Sauter et al. 2000). An amperometric detector for atmospheric ozone monitoring was described by Huang and Dasgupta (1997), and the device was employed in absorption in a liquid electrolyte phase for electrochemical reduction. Penrose et al. (1995) conducted the direct amperometric detection of ozone at a gas electrode using a commercially available gas sensor. The authors reported that traditional amperometric gas sensors are usually based on porous poly (tetrafluoroethylene) with a working electrode deposited on the one side and in contact with an internal electrolyte solution. An alternative electrode configuration involving ion-exchange technology also referred to as solid-polymer electrolyte membrane (SPE) was developed by (Schiavon et al. 1990a, b). The authors emphasised that SPE carrying an electrode on the front side is used as an extension of the liquid phase and is directly exposed to the sample gas. A similar electrode type was already described by Xie et al. (1998) for ozone sensing. Additionally, Hodgson et al. (2000) and Knake et al. (2001) conveyed that for a series of electroactive species, high sensitivities with low detection limits in parts per billion were achieved as compared to 200 ppb recorded previously. In this regard, Knake and Hauser (2002a) investigated the sensing of ozone using an ion-exchange membrane-based electrode aiming at improving the lower limit of detection. The authors insisted that sensitivity is a critical issue in amperometric sensors that needed to be considered. Alternatively, Knake and Hauser (2002a) showed that electrochemical methods based on the reduction of ozone at solid electrodes could be a possible means of monitoring the amount of ozone. Based on this, Nakagawa et al. (2001) and Awad and Ohsaka (2004) confirmed that the open-circuit potential and the measure of the thermal heat of decomposition have been extensively considered as practicable principles for ozone quantification. Ozone concentrations have been monitored by spectroscopic methods or semiconductor sensors Sauter et al. (2000) and Parrish and Fehsenfeld (2000).

Measurement of ozone in the gas phase

For decades, sensors based on semiconducting oxide films have been developed for direct determination of ozone in gas phase at higher parts per billion and parts per million range (Doll et al. 1998; Kim et al. 2000). Meanwhile, Doll et al. (1998) and Lee et al. (1999) showed that the response limit in semiconductor sensors is constricted and usually falls in the range of 0–250 ppb. Additional ozone gas sensing, using a biosensor concept, such as a polymer degradation impedimetric sensor based on solid-state redox polymer electrolytes has also been studied (Maruya et al. 2009; Maruo et al. 2010).

Even though the techniques described above and summarised in Table 1 are consistent and used for ozone quantification, their applicability is often limited by their high cost and lack of feasibility which usually necessitates integration of air pumps. Similarly, Doll et al. (1998) and Lee et al. (1999) claimed that nitrogen oxide gases resulting from air pump systems may cause serious interference during sensing or quantification of ozone gas. Gołkowski et al. (2012) studied a hydrogen-peroxide-enhanced non-thermal plasma effluent for biomedical applications. In their study, direct frequency comb absorption spectroscopy was used to assess the concentrations of ozone (O_3) and other oxygen and nitrogen reactive species. The oxidation-reduction potential electrode probe (ORP) has been utilised not only to measure ozone concentration but various oxidisers and disinfectants including chlorine, chlorine dioxide and peroxides (Metzger 2009). The author confirmed that this technique is mostly used in disinfection of pools and spas and is limited by interferences caused by water turbidity, which may decrease the ORP readings below the expected ones. According to Metzger (2009), other ozone measurement techniques include the use of an electrochemical cell which involves passing ozone over a working membrane that converts it into oxygen. In turn, the oxygen level is determined by an oxygen-sensitive cell. This procedure was claimed to be constant and feasible for the determination of the amount of ozone in a process. Its disadvantages however are related to the cost and maintenance of the equipment. Consequently, the development of practical, applicable and cost-effective techniques for quantification of ozone in aqueous and non-aqueous media was a subject of numerous research studies in the past decades.

Chemiluminescent and colourimetric methods

Among diverse ozone instrumental measurement techniques reported in literature (Ben-Jebria et al. 1990; Hodgson et al. 2000), gas-phase chemiluminescence technique has been the most broadly used analytical method for detection and measurement of ozone at lower concentration. Consequently, numerous chemiluminescence procedures for ozone determination have been proposed, yet cross sensitivities, lack of feasibility, maintenance and high costs limit practical applications (Watanabe et al. 2010; Nakadoi 2016). For these reasons, the development of simple, feasible and economical methods for ozone measurement is still of great interest. A number of colourimetric measurement methods based on colour reactions shown in Table 1 were subsequently explored for quantification of O_3. For instance, Lodge (1988) and Pearson (1990) state that the oxidative interaction of ozone with various molecules usually leads to excited species that radiate when returning to their ground state with the authors showing that Ethylene–O_3 reaction can be used for ozone measurement. Alternatively, Helaleh et al. (2002) and Franklin et al. (2004) affirmed that nitrites can also be oxidised to nitrates by ozone (NO–O_3 CL reaction). In this process, the authors claimed that dosimeters (filters coated

Table 1 Categories of methods used for the quantification of ozone

Type	Approach	Ozone phase	Detection limit	Authors
Instru-colourimetric methods + colour reaction mental methods	Amperometric	Liquid/gas	≈ 0.5 ppb	Uchiyama et al. 1993; Huang and Dasgupta 1997; Penrose et al. 1995
	Gas sensors	Gas	0.1 ppb	Doll et al. 1998; Lee et al. 1999; Kim et al. 2000; Maruya et al. 2009; Maruo et al. 2010
	Ion-exchange membrane and electrochemical cell	Liquid/gas	200 ppb	Xie et al. 1998; Schiavon et al. 1990a, b; Hodgson et al. 2000 and Knake et al. 2001
	Direct frequency gold electrode	Liquid	–	Smart et al. 1979, Knake and Hauser 2002a, b
	Indigo blue method, malonic acid + UV-vis spectroscopy techniques	Liquid	40 ppb	Barder and Hoigne 1982; Takayanagi et al. 2003; Metzger 2009; Tichonovas et al. 2013 and Massima 2014
	Iodometric method (conversion of iodide to iodine, starch-iodide)	Liquid	5 ppb	Yimit et al. 2002 and Li et al. 2008
Chemical reactions	N, N-diethylp-phenylenediamine (DPD) method	Liquid	21 ppb	Franklin et al. 2004; Metzger 2009
	$NO–O_3$ CL reaction	Gas	0.1 ppb	Helaleh et al. 2002
Chemiluminescent methods	Ultraviolet (UV) absorption, ethylene–O_3 reaction, various dyes (alkaline chromotropic acid)	Liquid	0.1 ppbv	Lodge 1988 and Pearson, 1990
pH metric	Ozone + unbuffered KI solution	Liquid	0.11 ppb	Stergiou et al. 2010a, b

with nitrites) should be used in such a way that the quantity of nitrates formed on the dosimeter is directly proportional to ozone concentration. Aside this, Li et al. (2008) mentioned that ultraviolet absorption is also a viable method to measure ozone concentration in both air and in water effluents with low turbidity and negligible dissolved-solid content. Moreover, Metzger (2009) proposed the use of N, N-diethylp-phenylenediamine (DPD) method as an alternative means of measuring ozone concentrations even though this technique was developed for common measurement of disinfectants such as chlorine, bromine and iodine. The N, N-diethyl-phenylenediamine method could therefore be used to quantify ozone in the absence of the aforementioned halogen disinfectant species. Even though the iodometric method for ozone determination in aqueous systems already was mentioned by Yimit et al. (2002) and Li et al. (2008), also known as pH-metric determination of ozone, it was further explored by Stergiou et al. (2010b). In this process, Stergiou and co-workers (2010b) emphasised that measurement of ozone was based on spotting the pH increase due to the reaction of ozone in an unbuffered potassium iodide (KI) solution. Previous works have shown that when the initial KI of pH 7.00 was set at a slight pH increase, about 0.01 pH-units corresponded to 2.3×10^{-9} M of the reacting ozone. The uncertainty of this method is related to the fact that the pH deviations from the ultimate neutral pH could have been due to the presence of acidic or basic impurities as mentioned by Stergiou et al. (2010a). Nevertheless, the estimated pH changes and those experimentally obtained for particular ozone quantities were compared. Apart from these, the indigo method developed by Barder and Hoigne (1981) has been used to determine ozone concentration in aqueous media. The indigo technique is based on the analysis of a coloured mixture consisting of a few millilitres of sample with indigo reagent solution using UV-VIS spectrophotometer at a wavelength of 600 nm. Takayanagi et al. (2003) stated that various dyes and related molecules interact with ozone either in solution or in solid-phase and generate bleached matrixes. In addition, Takayanagi et al. 2003 reported that ozone quantification involving the reaction of alkaline chromotropic acid with ozone occurs quickly with a high degree of sensitivity, where the limit of detection (LOD) was estimated to be about 40 parts per trillion by volume (pptv). Metzger (2009) reports the indigo blue method has been widely accepted as an adequate ozone measuring technique.

The interference encountered in this method showed that the presence of H_2O_2 in the system might slightly bleach the indigo reagent and hence give unexpected and undesired readings. Metzger (2009) also suggested that this limitation could be overcome by analysing the ozone-indigo adduct in less than 6 h after the addition of indigo reagent. If the interference is caused by the presence of halogen chlorine, the author suggested that this could be alleviated by addition of malonic acid. Similar studies on ozone quantification were conducted by Tichonovas et al. (2013) and Massima (2014) during treatment of water and wastewater by the dielectric barrier discharge systems. Besides indigo procedures, instrumental methods such as electrochemical cell, gas sensor amperometric, and ion-exchange membrane direct frequency comb, etc. have also been used as efficient methods for

quantification of O_3 in aqueous environments. The possible interferences and variation of half-life of ozone in different water schemes as well as analysis and sampling times make the measurement of ozone in water very problematic. The choice of monitoring method and sampling mode will determine the desired accuracy levels and may minimise the operating cost of the experimental task.

Quantification of hydrogen peroxide in AOPs

Among various reactive oxygen species, Hydrogen peroxide (H_2O_2) is widely known as an active antimicrobial agent with various applications including bacterial spores and viruses with a negligible poisonousness effect (Von Woedtke et al. 2004). Its quantification in aqueous non-thermal plasma systems has been widely investigated. The main benefit behind cold plasma remains the generation of reactive oxygen species such as O_3, H_2O_2, O_2^{-}, O_2^{-}, $OH^{\cdot}$, etc. which massively contributes to the destruction of hazardous compounds (Bruggeman and Leys 2009). Hence, depending on the cost, the feasibility, the availability and the efficiency, reactor configuration also remains a crucial parameter in cold plasma treatment technologies. Hence, the quantification of H_2O_2 in non-thermal plasma studies has been conducted. For instance, during the aqueous decolouration of Methylene blue in an electrical discharge plasma reactor, Benetoli et al. (2011) quantified H_2O_2 using vanadate method which involves the reaction of vanadate ion and hydrogen peroxide leading to the formation of a red solution of peroxovanadium (V) cation ($\lambda_{max} = 456$ nm) as shown in Eq. (1):

$$VO_3^{-} + 4H^{+} + H_2O_2 \rightarrow VO_2^{3+} + 3H_2O \quad (1)$$

Recently, Joshi et al. (2011a) showed that oxidative stress induce peroxidation of fatty acid membrane which in turn yields products that lead to significant detrimental changes in prokaryote and eukaryote cells.

The authors claimed that reactive oxygen species are the crucial controllers as they prove to cause lipid peroxidation in *Escherichia coli*. In the study conducted by Joshi et al. (2011a), various ROS, among which is H_2O_2, were quantified using amplex ultrared reagent (AUR), a highly specific ultrasensitive fluorescent molecular probe with an intense fluorescent (emission/excitation spectra of 530 nm/590 nm) specifically sensitive to detect H_2O_2 in aqueous media (Gough et al. 2009).

Besides, Yost and Joshi (2015) investigated the inactivation of *Escherichia coli* by oxidative DNA damage with non-thermal treated phosphate-buffered saline (PBS). In their study, Yost and Joshi measured the amount of hydrogen peroxide in each sample using a commercially available hydrogen peroxide detection kit (National Diagnostics, Atlanta, GA), following a well descriptive protocol. In addition to these, Vyhnánková et al. (2014) used a direct current (DC) pinhole discharge configuration to investigate the influence of electrode material on the production of H_2O_2 where several electrode materials including graphite, aluminium, stainless steel, platinum, copper, titanium-zinc and brass were used to evaluate their effects on hydrogen peroxide generation. Similarly, Gołkowski et al. (2012) developed a non-thermal plasma dielectric barrier discharge system for decontamination, sterilisation and medical applications in which a direct frequency comb absorption spectroscopy was used to determine accurate concentrations of oxygen-based species mainly ozone (O_3) and hydrogen peroxide (H_2O_2). In addition to this, interferences due to measurement of various ROS using the same equipment might occur, hence limiting the practicability of this method. Furthermore, Klavarioti et al. (2009) and Cheng et al. (2007a, b) reported that H_2O_2 is a primary source of hydroxyl radicals. Lukeš (2001) endorsed that H_2O_2 can be used as a quantitative parameter to assess the discharge efficiency; hence, its quantification is of great importance for optimisation processes. In this regard, a colourimetric technique known as Eisenberg method for hydrogen determination was earlier proposed by (Eisenberg 1943; Uher et al. 1991). In effect, the Eisenberg process involves the measurement of hydrogen peroxide concentration using a specific titanium reagent. In this process, titanium ions contained in titanium (IV) oxysulphate/sulphuric acid solution reagent selectively interacts with hydrogen peroxide forming a yellow complex of pertitanic acid (Eq. (2)) which is stable for at least 6 h.

$$Ti^{4+} + H_2O_2 + 2H_2O \rightarrow TiO_2.H_2O_2 + 4H^{+} \quad (2)$$

Since the initial concentration of H_2O_2 is proportional to the absorbance of the complex solution measured at 407 nm, a simple UV-VIS measurement can be used to estimate hydrogen peroxide concentration (Vyhnánková et al. 2014). The Eisenberg technique has gained great attention and has been used worldwide to measure H_2O_2 concentration in aqueous media. This is due to its affordability and feasibility. For instance, the descriptive steps of this method estimating the concentration of H_2O_2 produced in dielectric barrier discharge configuration during degradation of Methylene blue dye were well explored by Massima (2014). Various techniques can be used for H_2O_2 determination in aqueous media, but their efficacy may depend on their feasibility, availability and operational costs of the equipment.

Quantification of singlet oxygen and superoxide anion in aqueous systems

The determination of singlet oxygen ($^1O_2$) in advanced technologies has been attempted in few studies. For instance, Di Mascio and Sies (1989) quantified singlet oxygen generated

by thermolysis of the water-soluble endoperoxide of 3, 3′-(1, 4-naphthy1idene) dipropionate ($NDPO_2$) or from hypochlorite/H_2O_2; the trapping of $^1O_2$ produced from $NDPO_2$ or from hypochlorite/H_2O_2 was monitored by using the water-soluble disodium salt of anthracene-9, l0-diyldiethyl disulphate (EAS) that yielded the endoperoxide ($EASO_2$) as the specific oxidation product. In this process, the reactivity of EAS towards $^1O_2$ was expressed by its beta ($_\beta$) value, representing the concentration of the available trapped $^1O_2$. This methodology hinges on previous reports by Foote (1976). The result of the studies showed that the beta value of the $EASO_2$ generated with $NDPO_2$ was estimated to be 7.7×10^{-3} M and 8×10^{-3} M with hypochlorite/H_2O_2. These values were lower when the generation of $^1O_2$ from $NDPO_2$ or hypochlorite/H_2O_2 was performed in deuterium oxide (D_2O). A similar study based on detection and trapping of singlet oxygen using EAS in biological aqueous media was conducted by Mano et al. (2014). In their research, the presence of singlet oxygen was evidenced by the energy transfer process from triplet excited ketone species to [^{18}O]-labelled triplet molecular oxygen $\left[^{18}O_2\,\Sigma_g^-\right]$ through the detection of [^{18}O]-labelled O_2 ($^1\Delta_g$) [$^{18}O_2{}^1\Delta g$)]. In the trapping process of $^{16}O_2$ (^1D_g) and $^{18}O_2$ (^1D_g) using the anthracene-9, 10-diyldiethane-2, 1-diyl disulphate disodium salt spin trap, the resulting adduct endoperoxide (EAS^xO^xO, where $x = 16$ or 18) was examined by high-performance liquid chromatography coupled to electrospray ionisation tandem mass spectrometry (HPLC-ESI-MS/MS). Even if the chemical probes required in these aforementioned methods are available, the affordability of the HPLC-ESI-MS/MS analytical equipment could limit the applicability of these techniques in quantification of $^1O_2$ during water and wastewater treatment. Apart from EAS used as spin trap of $^1O_2$ in aqueous systems, singlet oxygen was also trapped using the compounds 2, 2, 6, 6-tetramethyl-4-piperidinol (TMP) (Brame et al. 2014). Comparable studies were already conducted by Maruya et al. (2009) and Liao et al. (2013) in which the authors highlighted that spin traps interacted with $^1O_2$ and formed spin adducts which were identified by their EPR spectrum. In this case, Brame et al. (2014) showed that TMP was oxidised when interacting with singlet oxygen to form 2, 2, 6, 6-tetramethyl-4-piperidinol-N-oxyl radical (TMPN), which could similarly be identified by EPR spectroscopy. Further trapping of singlet oxygen in photodamage of photosystem II in the cyanobacterium synechocystis PCC 6803 was performed by Rehman et al. (2013) using histidine-mediated chemical trapping process. The results of their study showed that the rate of O_2 uptake, measured by a standard Clark-type electrode, was improved in the presence of deuterium oxide with increased $^1O_2$ lifetime.

Further trapping of singlet oxygen investigated by Wu et al. (2012a) also studied the electron spin resonance (ESR) of different reactive oxygen species including hydroxyl radical ($OH^{\cdot}$), superoxide anion radical ($O_2^{\cdot-}$) and singlet oxygen ($^1O_2$) produced in aqueous plasma microjet (PMJ) system. Since these active species have a short life span, their measurement was improved by ESR using spin-trap reagents, namely 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP), respectively. In their study, the authors used L-histidine (L-His), and 3(10-(2-carboxy-ethyl)-anthracen-9-Y)-propionic acid (ADPA), respectively. In that regard, the concentration of $^1O_2$ and $^{\cdot}OH$ in plasma process was estimated by comparison of PMJ ESR spectra with those of different concentrations of commercial TEMPO in the same experimental conditions. Literature sustained that 2, 2, 6, 6-tetramethylpiperidine has extensively been used as a chemical probe to trap $^1O_2$ in aqueous media (Mano et al. 2014) whereby the resulting spin adduct TEMPO usually displays a triplet ESR spectrum with similar peak intensity. Hence, the addition of the conventional L-His, spin trap of $^1O_2$ into the system resulted in progressive decrease of ESR signal intensity which demonstrated the presence of $^1O_2$ in the system. In addition to this, the influence of $^1O_2$ on the generation of TEMPO signal was verified by adding ADPA along with TEMP into the system before plasma treatment process as a typical quencher of $^1O_2$ (Wu et al. 2012a). As a result, the reduction in TEMPO intensity signal proved the presence of $^1O_2$ in the system as expected. In order to determine the concentration of $^1O_2$ in the system, the authors prepared different concentrations of commercial TEMPO referred to as $TEMPO_{[ref]}$ which was analysed using ESR spectroscopy. The resulting ESR signals were double integrated and plotted versus $TEMPO_{[ref]}$ concentrations. The linear plot obtained was used as a standard to estimate the concentrations of TEMPO formed in the treated water. As for superoxide anion ($O_2^{\cdot-}$), due to its short life span, its quantification in aqueous solutions is not well established in the literature. Wu et al. (2012a) attempted the measurement of $O_2^{\cdot-}$ using electron spin resonance assisted with spin-trap reagents, 5, 5-dimethyl-1-pyrroline N-oxide. In their investigation, the authors showed that DMPO could spin trap O_2^- or its conjugate acid HOO, yielding the spin adduct DMPO-OOH which showed 12 consecutive peaks in ESR spectrum (Buettner 1987). Wu et al. indicated that the reaction rate between DMPO and $O_2^{\cdot-}$ (10^2 $M^{-1}S^{-1}$ at pH 7) was lower than that of DMPO with $^{\cdot}OH$ (10^9 $M^{-1}S^{-1}$) (Finkelstein 1980). Moreover, their study also highlighted that the spin adduct DMPO-OOH formed, likely decomposed into DMPO-OH, hence making the direct measurement of $^{\cdot}O_2^-$ with DMPO more difficult (Buettner 1987). Furthermore, Wu and coworkers discussed that O_2^- can also react with protons in water to yield H_2O_2 often referred to as self-dismutation. The H_2O_2 formed further dissociates into $^{\cdot}OH$ which represents the main targeted non-selective reactive species in water treatment units aiming at the decomposition of organic pollutants. Thus, $^1O_2$ and $O_2^{\cdot-}$ quantification methods described above showed that the following analytical combinations

EAS-ESI-MS/MS, TMP-EPR/TMP and TEMP-ESR, DMPO-ESR were proved effective methods for the quantification of $^1O_2$ and $O_2^{\cdot-}$ in aqueous systems. The use of sophisticated and expensive equipment employed in these techniques such as ESR/EPR spectroscopy could however limit their applicability (Wu et al. 2012a).

Quantification of OH radical in aqueous systems

Advanced oxidation processes (AOPs) commonly converge towards the production of highly reactive and non-selective hydroxyl radicals ($HO^{\cdot}$) that initiate oxidation processes (Sedlak and Andren 1991). Compared to ozone and chlorine, hydroxyl radical is favoured for oxidation reactions and does not present harmful effects on the treated effluents (Cheng et al. 2003). Hence, quantification of the generated OH radicals is very crucial not only to optimise the AOPs systems but to understand their characteristic features (Quiroz et al. 2014). In this regard, a number of measurement techniques have been developed among which electron spin resonance spectroscopy, chemiluminescent methods and spectrophotometric methods including fluorescent and non-fluorescent chemical probes have been explored for the determination of $HO^{\cdot}$ in aqueous media. The research publications on the different methods of assessing the reactive oxygen species (ROS) generated in vitro within reaction volume are enormous (Franclemont and Thagard 2014; Badmus et al. 2016). However, the selected methods are expected to be sensitive because most of the radicals produced in AOPs have a very short life span (10^{-9} s). Furthermore, in most of the techniques, the choice of stable chemical compounds with high reactivity as dosimeter with a sensitive and selective electrochemical determination is considerably important (Diez et al. 2001).

Electron spin resonance spectroscopy

Electron spin resonance is one of the most reliable methods for ROS determinations based on the principle that the electron is a particle which spins around its axis and possesses magnetic moment like any tiny bar magnet (Atkins and De Paula 2009). It aligns itself parallel or anti parallel to the external magnetic field by the explanation of quantum mechanics. The energy difference between the two alignments is dependent on the external applied field. A second weaker alternating magnetic field operating at a microwave frequency and targeting the main field can destabilise the alignment if it is equal to precession frequency. The quanta of incidence microwaves induced transitions between the two states of the unpaired electron in ESR (Atkins and De Paula 2009). For non-magnetic substances, chemical bonding involves pairing of electrons which move from one atom to the other but the presence of unpaired electrons in ROS and other paramagnetic substances results in resonance at the instance of applied magnetic field and incidence microwave radiation. Spin traps such as nitroso compounds phenyl tert-butylnitrone (PBN) or 5, 5-dimethyl-1-pyrroline-1-oxide (or a spin label such as oxygen molecule) can react with the OH radical to generate a spin adduct which is easily detectable in ESR spectroscopy (Cheng et al. 2007a, b). The ESR is a reference technique for OH radical determination (Hoebeke et al. 1997; Cheng et al. 2003). The combination of ESR with DMPO was already employed by Hoeben et al. (1999b) during pulse corona discharge (PCD). However, these authors did not obtain any DMPO-$OH^{\cdot}$ adduct because the PCD decomposed the spin trap. Consequently, an alternative probe, coumarin-3-carboxylic acid (CCA) fluorescence was used to determine OH radicals; however, the presence of the probe in water caused a high background compared to that of the fluorescent sample. This therefore made quantification of OH radicals very difficult. In addition to these, dimethyl sulphoxide (DMSO) has been used as a chemical probe by Steiner and Babbs (1990) for $^{\cdot}OH$ quantification in Fenton reaction and during irradiation of H_2O and photolysis of H_2O_2. Furthermore, the measurement of OH radicals using dimethyl sulphoxide and 2, 7-DNPH has also been conducted by Obradović et al. (2015) and Li et al. (2015). The ESR technique coupled with chemical probes and spin traps is very effective but requires expensive instrumentation, high detection limits as well as operational complexities which constitute a serious limitation to the determination OH species in aqueous media.

The chemiluminescent method is usually an acceptable technique for determination of ROS due to its simplicity, sensitivity, lower detection limit and wider linear range (Li et al. 1999). Previous studies showed that ROS can be detected by the measurement of luminescent-generating substances (Tosi and Hamedani 1992; Li et al. 1999) such as luminal (used in $O_2^{\cdot-}$ quantification) and lucigenin (used in H_2O_2 quantification). A rapid method of OH radical detection has been reported by Tosi and Hamedani (1992), using indoyl-glucuronide as a probe in an ultra-weak chemiluminescent analyser. Phthalhydrazide is another hydroxylation probe which reacts with OH radicals to give luminescent products that can be easily quantified by a photo counting techniques (Backa et al. 1997). Backa et al. (1997) showed that chemoluminescent adduct mostly resulted from the reaction of OH radical with phthalhydrazide because reaction with other oxidants did not yield chemoluminescent products. Thus, the chemiluminescent method is rapid and specific for the determination of OH radical. However, literature presents little information on the availability and the cost of the analytical equipment. The determination of OH radicals has also been carried out by Qiu et al. (2015) during the kinetic modelling of the Electro-Fenton process (E-Fenton). In their investigation, a "trip-

and-trigger" technique was used to quantify OH radicals generated in the E-Fenton process. As described by Miller et al. (2011) and He et al. (2014), the "trip-and-trigger" method involved the reaction of E-Fenton-generated ·OH with phthalazine (Phth) to form 5-hydroxy-2, 3-dihydro-1, 4-phthalazinedione (Phth-OH·), a chemiluminescing product. Likewise, literature presents little information about the disadvantages of this technique.

In summary, the two categories of techniques, (electron spin resonance spectroscopy and chemiluminescent method) used in OH radical quantification in aqueous media reviewed above have been clarified and shown in Table 2. The reviewed data in Table 2 shows that a few ESR and chemiluminescent methods employed for the determination of OH radicals are feasible and applicable. However, literature presents little information on their affordability and in some cases only, the instrumental equipment required in this regard. These problems therefore could limit their applicability in the quantification of OH radicals in aqueous media.

Spectrophotometric methods

Wu et al. (2012a) reported that quantification of ·OH radicals in AOPs has been a research challenge due to the short lifetime of these species; thus, numerous ·OH measurement methods have been developed (Wang et al. 2003; Cheng et al. 2003); among these are spectrophotometric methods that involve monitoring the intensity of the absorbed, fluorescence or transmitted light after passing through the sample solution (Wang et al. 2003; Cheng et al. 2003). At a certain wavelength of maximum absorbance, the concentration of the solution could be determined from the calibration curve obtained from known concentrations of the substance (Steiner and Babbs 1990; Montgomery et al. 1995). This principle has been used in the determination of OH radicals or hydrogen peroxide formed in an AOP by selecting the active reagent for reaction with the radical or peroxide formed during the process to give a product with known maximum absorbance on the spectrophotometer (Wang et al. 2003; Cheng et al. 2003). The stability and specificity as well as possibility of separating the product formed must be considered in the choice of chemical dosimeter (Wang et al. 2003; Cheng et al. 2003). Since the equipment is affordable and easy to operate, UV-VIS spectrophotometer and fluorescent spectroscopy can be used to estimate hydroxyl radical concentration (Peralta et al. 2014).

In studying the kinetics of pyrite-induced ·OH formation through rates of hydroxylation, Fisher et al. (2012) used amino acid phenylalanine (Phe) to synthesise three isomers of tyrosine (Tyr)—ortho-, meta-, and para-Tyr. The results of this study showed that Phe was almost converted to Tyr, and the reaction rate of the produced Tyr with ·OH radicals was similar to that of Phe. In addition to this, the study proved that the decomposition of Phe followed a pseudo-first-order kinetics,

Table 2 Electron spin resonance (ESR) spectroscopy and chemiluminescent methods used for OH quantification in aqueous media

Type	Approach	Instrument equipment	Detection limit	Feasibility/applicability	Affordability	Authors
Electron spin resonance (ESR) spectroscopy	• Phenyl tert-butylnitrone (PBN) or 5, 5-dimethyl-1-pyrroline-1-oxide (DMPO)	ESR spectroscopy	–	Applicable but DMPO-OH adduct was not obtained because DMPO was decomposed by the PCD system	Uncertain and ESR equipment might be expensive	Cheng et al. 2007a, b; Hoeben et al. 1999a
	• Dimethyl sulphoxide (DMSO); DMSO + 2, 7-DNPH	ESR spectroscopy	(0.05–1.0) M	Very effective but operationally complex and requires high detection limit	Uncertain and ESR equipment might be expensive	Steiner and Babbs 1990; Yang et al. 2015
Chemiluminescent methods	• Indoyl-glucuronide probe	Ultra-weak chemilumines cent analyser	≈ 0.1 nM	Feasible and applicable	Uncertain	Qiu et al. 2015
	• Phthalhydrazide	Uncertain	1.0 pM	Rapid and specific for the determination of DMPO-OH radical	Uncertain	Backa et al. 1997
	• Trip-and-trigger phthalazine (Phth + ·OH) yielding Phth-OH	Uncertain	(7.2–12.2) mM	Applicable	Uncertain	Qiu et al. 2015

highlighting that ·OH concentration decreased during decomposition of Phe with time and significantly increased with the formation of Tyr. It was therefore inferred that Phe is a convenient probe that can be used to measure the amount of ·OH and can be utilised for similar applications with other minerals. Alternatively, Joshi et al. (1995) used a combination of a probe (phenol) and a scavenger (carbonate ions) to establish the rate of formation of hydroxyl radicals; proving that the variation of carbonate ions concentration induced to different solution conductivities impeded the generation of ·OH radicals.

Fricke dissymmetry is a simple and direct method for radical determination and has shown to directly measure the $OH^{\bullet}$ or HO_2 as well as peroxide H_2O_2 radicals. However, it might not be applicable for separate determination of radical because of its lack of specificity (Jana and Chatterjee 1995). The principle of this method focussed on the oxidation of 1 mM Fe II in the presence of (0.8 N) sulphuric acid to the blue colour of Fe III that was spectrometric ally determined.

Numerous measurement methods for ·OH quantification have been developed, among these, non-fluorescent probes such as phenylalanine, benzoic acid, salicylic acid (SA) and the esterification of aspirin. Various fluorescent spin traps have been described for the determination of ·OH in aqueous media. In the case of non-fluorescent probes, salicylic acid with high reactivity (5×10^9 M^{-1} S^{-1}) was used as HO· scavenger (Chang et al. 2008) and concentrations of the hydroxylated 2, 3-dihidroxybenzoic acid and 2, 5-dihydroxibenzoic acid proportional to that of hydroxyl radicals were separated by high-performance liquid chromatography (HPLC) and detected electrochemically with UV spectrophotometer (Milne et al. 2013; Peralta et al. 2014). Furthermore, Peralta et al. (2014) stated that the use of the aforementioned chemical probe is applicable. However, sophisticated analytical equipment is needed for identification of scavengers' reaction products. Even though most of the previously cited probes are accurate in ·OH quantification, the complexity and the operation cost of the equipment usually limit their applicability. In contrast, several fluorescent probes such as aminophenyl fluorescamine (APF), amplex ultrared and dichlorofluorescein (DCFH) and two radical species including proxyl fluorescamine and tempo-9-ac have been evaluated for the quantification of hydroxyl radicals formed in two different solutions, one containing ferrous iron and the other suspended pyrite particles (Cohn et al. 2008). The results of Cohn's work showed that APF, amplex ultrared and DCFH had similar reactivity towards hydroxyl radicals. However, DCFH and amplex ultrared lacked specificity because they were claimed to react not only with reactive oxygen species other than hydroxyl radicals but with another highly nitrogen reactive species, peroxynitrite. Consequently, the authors proved that due to its sensitivity and selectivity, APF was the most appropriate scavenger of OH radicals. In addition to this, coumarin scavenger as shown in Eq. (3) has been widely utilised for measurement of OH concentration in aqueous media (Ji et al. 2013; Sun et al. 2014).

$$\text{Coumarin } (C_9H_6O_2) + 2\,{}^{\cdot}OH \rightarrow \text{hydroxycoumarin } (C_9H_6O_3) + H_2O \quad (3)$$

Subsequently, Maezono et al. (2011) established that the fluorescence intensity of 7-hydroxycoumarin could be estimated using a multi-channel spectrometer with an optical fibre cable. Besides, coumarin could not accurately measure the HO· due to its very low stability (Maezono et al. 2011). Furthermore, the authors suggested that the disadvantages encountered in coumarin trapping technique could be overcome by increasing the amount of scavenger in the experimental reactor until the concentration of 7-hydroxycoumarin is stabilised. Similarly, Sahni (2006) performed quantification of hydroxyl radicals using chemical probes DMSO and disodium salt of terphthalic acid (NaTA), advocating for the use of dimethyl sulphoxide and disodium salt of terphthalic acid as chemical probes due to high rates of reaction with hydroxyl radicals generating products that could easily be identified by fluorescence and UV-vis spectroscopy. In the same vein, the reaction of DMSO with hydroxyl radical yields methane sulphinic acid and methyl radical although in most hydroxyl radical measurement techniques, quantification of methane sulphinic acid or the subsequent products methane sulphonic acid and sulphate anions has been adopted. The applicability of this method however is limited by the presence of multiple by-products. To overcome this limitation, an alternative approach based on quantification of the methyl radical or its subsequent oxidation product formaldehyde was favoured. Sahni (2006) emphasised that fluorescence spectroscopy could be used to quantify formaldehyde. The fluorescence spectrometry method using terephtalic acid is very specific for the measurement of the OH radical. The 2-hydroxyl terephthalic acid (HTA) formed as a consequence of the reaction between the hydroxyl radical and TA shown in Fig. 1 has peak intensity at wavelength 425 nm (Badmusa et al. 2016). The fluorescent equipment applied in this technique is often available and hence could be used for OH radical determination. In total, spectrophotometric methods for the quantification of OH radicals described above have been clearly summarised and presented in Table 3. Based on the feasibility/applicability and affordability aspects, techniques presented in Table 3 showed that amino acid phenylalanine probe, 5, 5-dimethyl-1-pyrroline-1-oxide, disodium salt of terphthalic acid are convenient probes used in combination with UV-vis or fluorescence spectroscopy for the quantification of OH radical in aqueous media. These could be followed by salicylic acid and aminophenyl fluorescamine probes even though analytical equipment required for these methods are costly.

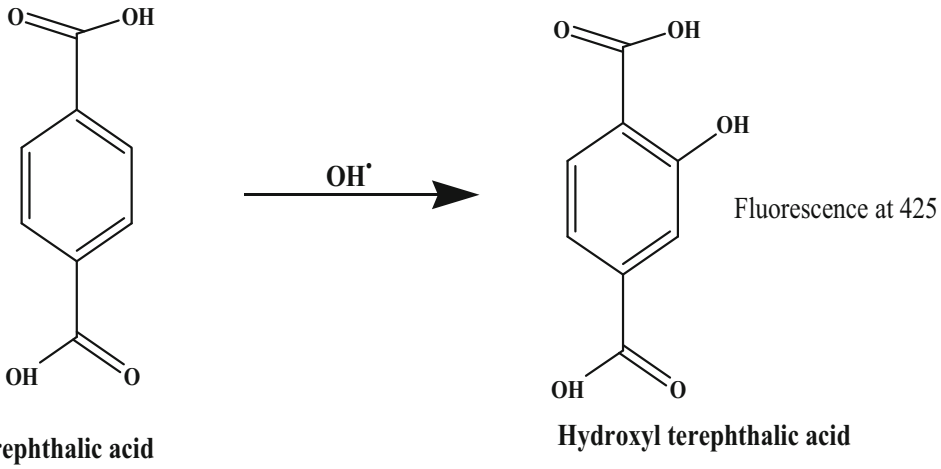


Fig. 1 Reaction of terephthalic acid (non-fluorescent) with OH radical yielding the fluorescent 2-hydroxyl terephthalic acid (HTA) (Montesinos et al. 2015; Badmusa et al. 2016)

Determination of oxygen-based species in dielectric barrier discharges

Reactive oxygen species have been widely quantified in various AOPs and their determination in non-thermal plasma systems documented (Bruggeman et al. 2009; Shih and Locke 2010; Locke and Shih. 2011). In fact, non-thermal plasma processes include various electrical discharges such as corona discharge, glow discharge, pulse arc discharge, dielectric barrier discharges (DBDs), etc. that are different from one another by their electrode configurations. In the case of non-thermal plasma technologies based on DBDs, Kogelschatz et al. (1997) and Mouele et al. (2015) showed that reactor configuration as presented in Fig. 2 is a critical parameter in DBD processes that needs to be considered for efficient production of non-selective OH radicals that largely contribute to the degradation process.

Among the common DBD configurations, single and double planar (Fig. 2a, b) or single and double cylindrical dielectric barrier discharges (Fig. 2d, e) have been reported (Gupta 2007; Nehra et al. 2008). Although most DBD configurations have been used in water treatment (Mark and Schluep 2001; Marotta et al. 2011; Reddy et al. 2014; Magureanu et al. 2013; Magureanu et al. 2015; Hamdan and Cha 2016), double cylindrical dielectric barrier discharge (DCDBD) configuration described in Fig. 3 could be a more favourable and convenient electrode arrangement for decontamination of water effluents (Tijani et al. 2013; Rong et al. 2014; Massima 2014). This is due to the fact that in DBDs, the high-voltage electrode is protected at least by one dielectric material that not only limits the amount of charge transported by single microplasma but distributes the microplasmas over the entire electrode surface area and minimises risks of electrode corrosion, thus ensuring long operating reactor time. Non-thermal plasma configurations based on DBDs generate a huge amount of free radicals as shown in Fig. 3. These oxidising agents directly or indirectly oxidise organic pollutants into dissolved CO_2, H_2O and simpler entities.

Even though a limited number of procedures for measurement of O_3, H_2O_2 and $^{\cdot}OH$ in DBDs during decomposition of organic pollutants have been developed (Wu et al. 2012a; He et al. 2014), literature still presents little information on subsequent quantification of $O^{\cdot}$ and $O_2^{\cdot-}$ in most DBD configurations though they have been measured in other aqueous systems, mostly during inactivation of biological contaminants such as bacteria using several techniques. While O_3 has been proved to be selective towards organic pollutants (Glaze 1986), H_2O_2 as a well-known disinfectant species has been shown as one of the major precursors of OH radicals which in turn are non-selective and hence oxidise the target pollutants ideally into CO_2 and H_2O and inorganic salts (Kirk and Othmer 1996; Zimmer 2013). Mouele et al. (2015) showed that DCDBD reactor configuration presented in Fig. 3 could efficiently be used to degrade organic pollutants and microorganisms. The authors sustained that DCDBD system produces various reactive oxygen species (ROS) among which O_3, H_2O_2, $^{\cdot}OH$, $O^{\cdot}$, $O_2^{\cdot-}$ etc. that form a chemical cocktail that potentially destroys contaminants. However, literature presents limited information on measurement of these species in DCDBD configuration. Therefore, depending on the availability of analytical equipment and chemical probes, the various techniques reviewed in this text could be used to quantify ROS in DCDBD reactor configuration. This would give a better understanding not only on their production mode and their reactivity towards pollutants but for the optimisation of electrical discharges such as DBDs designed for water and wastewater decontamination.

Summary of quantification of reactive oxygen species

The various quantification methods for the determination of ROS species in AOPs and other aqueous media reviewed in this text and summarised in Tables 1, 2 and 3 showed that indigo, titanyl sulphate and terephtalic acid methods coupled

Table 3 Most common spectrophotometric methods used for quantification of OH radicals in aqueous media

Approach	Analytical equipment	Feasibility/applicability	Detection limit	Affordability	Authors
Amino acid phenylalanine (Phe) probe/pyrite-induced ˙OH	Fluorescence/UV-vis spectrophotometry	Feasible and applicable	0.01–30 μM	Affordable	Fisher et al. 2012
Probe phenol probe + scavenger (carbonate ions)	Fluorescence spectrophotometry	Not feasible	> 0.54 μM	Affordable	Joshi et al. 1995
Fricke dosimetry (1 Mm Fe II +(0.8 N) sulphuric acid/blue colour Fe III	Fluorescence spectrophotometry	Applicable but lack of specificity	≈ 10 mM	Affordable	Jana and Chatterjee 1995
Salicylic acid (SA)	HPLC and UV spectrophotometer	Feasible and applicable	≈ 0.2 μM	Complex and expensive analytical equipment	Milne et al. 2013; Peralta et al. 2014
Florescent probes: aminophenyl fluorescamine (APF), amplex ultrared, dichlorofluorescein (DCFH), proxyl fluorescamine and tempo-9-ac	Fluorescence spectrophotometry	All applicable, APF was the best except DCFH and amplex ultrared lacked of specificity	–	Affordable but fluorescence instrument could be costly	(Cohn et al. 2008)
Coumarin fluorescent scavenger	Fluorescence spectrophotometry	Very difficult to apply because of the high background caused by this probe in water	≈ 2.06 pM	Affordable	Hoeben et al.1999a, Zhang et al. 2013; Sun et al. 2014a, b
Chemical probes 5, 5-dimethyl-1-pyrroline-1-oxide (DMPO), disodium salt of terphthalic acid (NaTA), analysed by UV-vis or fluorescence spectroscopy respectively	Fluorescence/UV-vis spectrophotometry	Both applicable. TA is very specific for ˙OH while DMPO could be limited by multiple by-products that could be alleviated	(0.18–0.22) pM	Affordable	Montesinos et al. 2015; Badmusa et al. 2016
Non-thermal plasma in contact with water	EPR analysis using DMPO spin-trap probe	feasible	(2.9–18.3) μM	Affordable	Gorbanev et al. (2016)
Various non-equilibrium atmospheric pressure plasmas	EPR/ESR, LIF, etc.	Applicable	≤ 0.06 fM	Affordable	Lu et al. (2016)
Pulsed corona plasma	Optical emission Spectroscopy	Applicable	≈ 0.08 M	Affordable	Shin et al. (2000)
Atmospheric pressure bioplasma jet	Optical emission spectroscopy	Applicable	≤ 4.32 μM	Affordable	Hong et al. (2012)
Water-argon arc plasma jet	Optical emission spectroscopy	Applicable	(0.3–0.74) mM	Affordable	Mašláni and Sember (2014)
	Absorption measurements				
Non-thermal atmospheric pressure plasma jet	Ultraviolet absorption spectroscopy	Applicable	(4.98–34.87) μM	Affordable	Kim et al. (2014)
Plasma-initiated ultraviolet (UV) photolysis	Optical emission spectrum measured by CCD spectrometer with optical fibre	Applicable	(1.66–69.74) μM	Affordable	Attri et al. (2015)
	Laser-induced fluorescence (LIF)				
Atmospheric pressure helium plasma jet	Laser-induced fluorescence	Applicable	≤ 19 nM	Affordable	Yonemori and Ono (2014)

Table 3 (continued)

Approach	Analytical equipment	Feasibility/applicability	Detection limit	Affordability	Authors
Argon RF plasma jet	Laser-induced fluorescence	Applicable	≈ 0.83 M	Affordable	Vorac et al. (2013)
Atmospheric pressure RF plasma jet	Laser-induced fluorescence spectroscopy	Applicable	≈ 0.04 M	Affordable	Xiong et al. (2012)
Pulsed discharges on the surface	Laser-induced fluorescence	Applicable	(0.08–8.56) μM	Affordable	Kanazawa et al. (2011)
Transient plasma and mechanism of flame ignition and propagation in quiescent methane–air mixtures	Laser-induced fluorescence	Applicable	< 0.22 μM	Affordable	Cathey et al. (2008)
Pulsed Discharge in Ar/H_2O	Laser-induced fluorescence	Applicable	≈ 4.98 μM	Affordable	Tochikubo et al. (2004)
Pulsed corona discharge	Laser-induced fluorescence	Applicable	≤ 0.17 mM	Affordable	Ono and Oda (2002)

with UV-vis and fluorescent spectroscopy are identified as the most convenient, feasible, applicable and affordable measurement techniques for determination of O_3, H_2O_2 and OH radicals in AOPs or any other aqueous systems. It is noteworthy to mention that attempts using chemical spin traps alone or in some cases, coupled with other advanced techniques to quantify atomic oxygen and superoxide anions in aqueous media were unsuccessful (Wu et al. 2012b; Liao et al. 2013). Various studies have shown that active species such as superoxide ions and atomic oxygen are generated in plasma processes, but little information on atomic oxygen and superoxide quantification is provided (Jiang et al. 2014; Mouele et al. 2015). This could be attributed to the fact that these two species have been found more likely to behave as short-lived intermediates as they contribute to the production of long-lived species such as O_3 and H_2O_2 (Ullmann 1991; Kirk and Othmer 1996). Studies confirmed by Wu et al. (2012b) documents that, though produced in plasma technologies, it could be possible that these short-lived radicals are totally transformed into $^{\cdot}OH$ via Haber–Weiss reactions when catalysed by Cu^{+} as shown in Eqs. (4)–(7). The highlighted disadvantages limit the quantitative analysis of solutions subjected to non-thermal plasma generation.

$$2\,{}^{\cdot}O_2^{-} + 2H^{+} \rightarrow H_2O_2 + O_2 \text{ (Self dismutation)} \quad (4)$$

$$H_2O_2 + Cu^{+} \rightarrow {}^{\cdot}OH + OH^{-} + Cu^{2+} \text{(Fenton reaction)} \quad (5)$$

$$Cu^{2+} + {}^{\cdot}O_2 \rightarrow Cu^{+} + O_2 \text{ (Oxidation and reduction)} \quad (6)$$

$${}^{\cdot}O_2^{-} + H_2O_2 \rightarrow {}^{\cdot}OH + OH^{-} + {}^{1}O_2 \text{(Haber–water reaction)} \quad (7)$$

The detection and accurate measurement of atomic oxygen and superoxide have been attempted mostly in biomedicine. However, their determination during treatment of water and wastewater effluents contaminated by toxic organic compounds discloses little information (Calderon and Roberfroid 1995; Sonntag 1987; Rehman et al. 2013). The complexities presented by the use of chemicals, the cost, and unavailability of sophisticated equipment could limit effective measurements in systems other than biomedicine media. Furthermore, based on detection and trapping process previously elaborated, it could be inferred that short-lived species such as $^{1}O_2$ and $^{\cdot}O_2^{-}$ are mostly produced in medicinal and biomedicine systems where they have been proved to be more active in processes such as lipid peroxidation of bacteria (Joshi et al. 2011b; Joshi et al. 2015). In contrast, trapping of these short-lived species in the treated contaminated water samples is challenging where they have been proved to contribute mostly to production of long-lived species such as ozone and hydrogen peroxide (Ullmann 1991; Kirk and Othmer 1996). Based on non-thermal plasma technologies, Kogelschatz et al. (1997) and Mouele et al. (2015) showed that reactor configuration is a crucial parameter in DBD that needs to be considered for efficient production of non-selective OH radicals that largely contribute to the degradation process. Among the common DBD configurations, single and

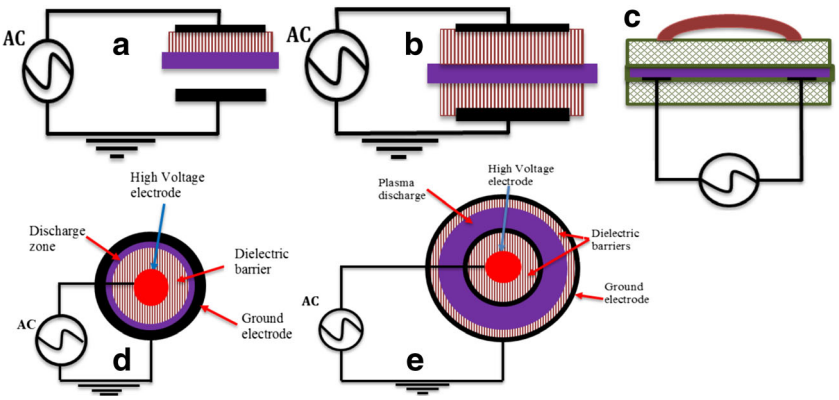


Fig. 2 Dielectric barrier discharge electrode configurations used in water and wastewater treatment (Kogelschatz et al. 1997; Nehra et al. 2008; Mouele et al. 2015)

double planar or cylindrical dielectric barrier discharges have been reported (Gupta 2007; Nehra et al. 2008). In addition, double cylindrical DBD configuration has been solicited as a convenient electrode arrangement for decontamination of water effluents. This is due to the fact that in double cylindrical DBD, high-voltage electrode is protected at least by one dielectric material, minimising risks of electrode corrosion and thus ensuring long operating reactor time. ROS in these configurations have partially been quantified. For instance, a few procedures for measurement of O_3, H_2O_2, $^{\cdot}OH$ in DBD during decomposition of organic pollutants have been developed (Wu et al. 2012b; He et al. 2014). Likewise, literature presents little information on subsequent quantification of $O^{\cdot}$ and $O_2^{\cdot-}$ in DBD configurations though they have been measured in aqueous systems other than DBDs, mostly for inactivation of biological systems such as bacteria using several techniques.

The measurement processes of ROS reviewed also shows that O_3, H_2O_2 and $^{\cdot}OH$ have been widely quantified during aqueous decomposition of organic pollutants in AOPs such as non-thermal plasma or in other systems using different techniques (He et al. 2014; Wu et al. 2012b). While O_3 has been proved to be selective towards organic pollutants (Glaze 1986), H_2O_2 as a well-known disinfectant species has been shown as one of the major precursors of OH radicals which in turn are non-selective and hence mineralise the target pollutants ideally into CO_2 and H_2O (Kirk and Othmer 1996; Zurich and Zimmermann 2011). Recently, Mouele et al. (2015) showed that double cylindrical dielectric barrier discharge reactor configuration could efficiently be used to degrade organic pollutants and microorganisms. The authors sustained that DBD system produces various reactive oxygen species that form a chemical cocktail that potentially destroys contaminants. Likewise, literature presents limited information on subsequent quantification of these species in double cylindrical DBD configuration. Therefore, depending on the availability of analytical equipment and chemical probes, the various techniques reviewed in this text could be used to quantify ROS in double cylindrical reactor configuration. This would give a better understanding

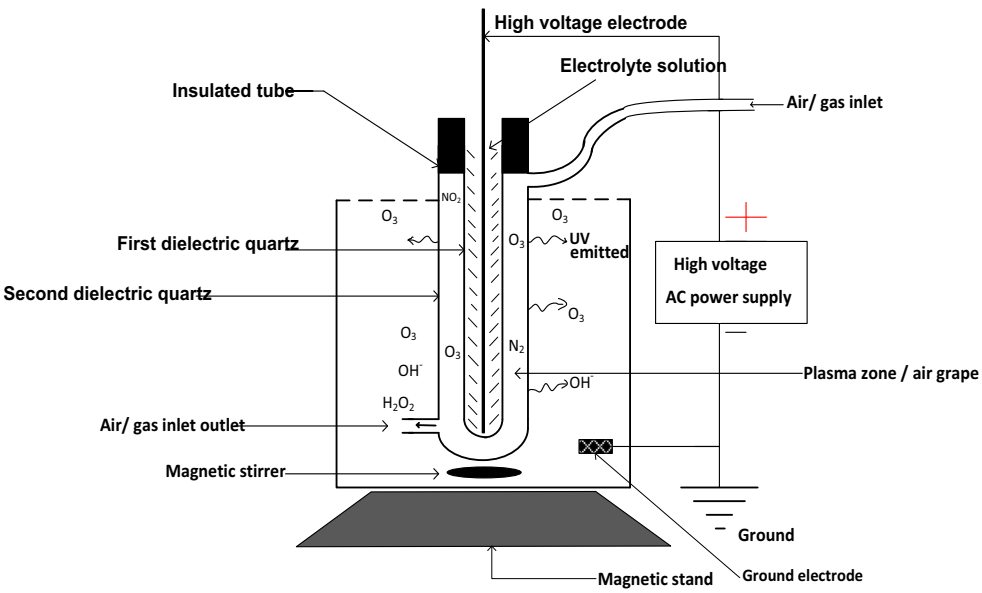


Fig. 3 Free reactive oxygen species produced in double cylindrical dielectric barrier discharge (DCDBD) configuration and the effect on pollutants (Massima, 2014)

not only on their production mode and their reactivity towards pollutants but for the optimisation of electrical discharges such as DBDs designed for water and wastewater treatments.

Conclusion

Extensive literature review has showed that reactive oxygen species have been widely quantified in various applications using different methods. However, there has been little information on subsequent measurement of ROS in non-thermal plasma based on dielectric barrier discharge. This review shows that O_3, H_2O_2 and OH have largely been quantified through degradation of organic contaminants in aqueous media. Conversely, the determination of $^1O_2$ and $O_2^{\cdot-}$ was mostly conducted in biological systems during water disinfection. The double cylindrical dielectric barrier discharge reactor configuration could effectively putrefy organic toxins and microbes from water and wastewater. Therefore, the measurement techniques mentioned in this paper could be used to successively determine ROS such as O_3, H_2O_2, $^{\cdot}OH$, $O^{\cdot}$ and $O_2^{\cdot-}$ under the double cylindrical DBD system. The quantification of these species in the proposed configuration is crucial to gain insight, not only about the production cycle but to also understand their reactivity towards contaminants.

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