

New insights about the electrochemical production of ozone

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Abstract

Ozone is a rather attractive oxidant for wastewater treatment and water disinfection, because it is very efficient in the oxidation of anthropogenic refractory pollutants and in the killing of pathogens and, in addition, it does not generate any hazardous waste during its use. For this reason, its generation has been constantly sought in an effective way, focusing on obtaining high concentrations of ozone at the lowest possible cost. In the recent years, it has been found that electrochemical production of ozone may show advantages over conventional corona discharge generation, since this technology may reach high ozone productions without the necessity of applying very high voltages, feeding oxygen or pure air or dissolving the ozone into the liquid water or wastewater to be treated. However, it is still at early development stage with many promising results and many important handicaps and, because of that, there is still a long way to reach the high technology readiness levels (TRLs) needed to complete its value chain. Equipment considerations (including the type of anodes and electrochemical cells) and operation conditions (including electrolyte formulation, temperature, and current density) are the key points that need to be understood in order to increase efficiently the TRL. The recent novelties in the state of the art of the research are summarized in this work.

Keywords

Ozone; electro-ozonizers; anode; electrolyte

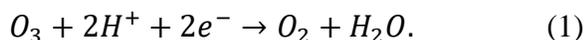
Highlights

- Electro-ozonizers are promising alternative to conventional ozonizers
- Outstanding influence of electrode material and electrolyte
- New cells with improved ozone production capacity
- High number of applications of electro-ozonizers

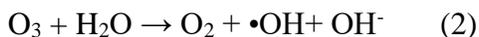
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1. Introduction

Ozone (O_3) is a powerful oxidant, with an outstanding oxidation potential (2.076 V vs SHE) that it is only surpassed by fluorine and several radical species [1]. It is considered eco-friendly because no harmful by-products are formed during its use, in contrast with other highly oxidizing compounds like chlorine. Thus, during oxidation processes ozone is transformed into O_2 and H_2O (Eq. 1) and when it reacts with the organic species the oxidation process proceeds throughout the oxygenation of the pollutants up to their mineralization, leading typically to less harmful species [2,3] than other oxidation technologies.



It was first identified by Schönbein, who observed that the electrolysis of water produced an peculiar odor identical to that perceived from an electric arc [4]. From the chemical point of view, it is a triatomic molecule with three oxygen atoms, a gas density of 2.144 g L^{-1} at 0°C and a boiling point of -112°C at atmospheric pressure [5]. The solubility of the gas in aqueous solution is low, fitting well to the Henry's Law with an equilibrium constant (H) that depends strongly on the composition of the liquid. As an example, at 298.2 K, it ranges from $0.440 \text{ kPa m}^3 \text{ mol}^{-1}$ in saline solutions of sodium sulfate to $0.064 \text{ kPa m}^3 \text{ mol}^{-1}$ potassium chloride, with values of $0.11 \text{ kPa m}^3 \text{ mol}^{-1}$ in sodium chloride and $0.182 \text{ kPa m}^3 \text{ mol}^{-1}$ in aqueous solution of calcium nitrate [6]. This molecule is highly unstable and decomposes into pure oxygen with a short half-life, which depends importantly on the conditions of temperature and pressure [7]. Thus, the half-life of ozone dissolved in water at neutral pH is 30 minutes at 15°C and it decreases down to 15 minutes at 25°C and to 8 minutes at 35°C [8]. Stability also depends on pH, being higher at pHs below 6.0 and decreasing importantly above this pH, because of the formation of hydroxyl radicals according to eq 2, whose rate increases with pH, becoming almost instantaneous at pH 10.0 [9].



The hydroxyl radical is a much stronger oxidizing agent than molecular ozone (oxidation potential of 2.76 V vs 2.076 V for O_3) and because of that, it is non-selective and very

unstable with an extremely short average lifetime [10]. Opposite, molecular ozone is more selective and preferentially attacks double bonds (e.g. olefins and aromatic systems) or amines [11–16]. Depending on operation conditions, dosing of ozone may lead to the formation of these radicals or not, helping to explain the outstanding oxidation capacity and the very different behaviors observed, when comparing performance of ozonation at different pHs. The contribution of each pathway also depends on other factors such as ozone dose and scavenging capacity of wastewater matrix and, even, it may change during the oxidation process [17]. Because of the much lower change in conditions, oxidation by molecular ozone is typically the primary pathway in the disinfection process, while in the oxidation of organic species, both pathways are important to explain the experimental results observed during the ozonation [18].

Associated to the outstanding oxidizing capacity of ozone, there are many applications. Table 1 summarizes, as relevant examples, the most important aspects of two reviews which point out the outstanding importance of this oxidant in industrial processes related to the dairy and the agri-food industries.

Table 1. Reviews showing examples of the application of ozone in industry

Review	Topics covered	Main conclusions
Use of ozone in the dairy industry: A review (2016) [2]	<p>Benefits of ozone usage in food processing</p> <p>Inactivation of microorganisms and microbial products by ozonation</p> <p>Use of ozone in dairy processing</p> <p>Wastewater treatment in dairy processing</p>	<p>Due to its high oxidation potential, ozone has outstanding antimicrobial properties that make it attractive for the industry. It manages to eliminate fungi, viruses, bacteria, and mycotoxins, degrading them or lowering their bioactivity. Ozone has been widely used in disinfection in food processing, where it is replacing chlorine, showing advantages such as the prevention in the formation of harmful residues and the easiness of its generation on site, which in turn, reduce transport and storage costs. Within the food industry, ozone is widely used for cleaning equipment, as it manages to remove residues more efficiently than other cleaning methods.</p> <p>The challenges of ozone in this area are: determination of optimal doses and contact times, improvement of ozone gas generation systems to achieve greater purity and higher concentration while minimizing costs, and clarifying the effects of ozone on the sensory and nutritional properties of the foods.</p>

<p>Ozone as a novel emerging technology for the dissipation of pesticide residues in foods—a review (2020) [19]</p>	<p>Ozone and its half-life</p> <p>Pesticide degradation in water</p> <p>Full scale application of ozone</p> <p>Impact of ozonation on quality of agro-products</p>	<p>Ozone has been used to remove pesticides from fruits and vegetables, however a drawback of this application is how to achieve a good distribution of ozone on the surfaces of vegetables and fruits which can efficiently oxidize pesticides. In addition, it has been shown that ozone can change the properties of food.</p> <p>The efficiency of the degradation of pesticides in water by ozonation depends on various operating parameters such as the pH of the water, the ozone concentration, and the contact time.</p> <p>Ozone continues to be an attractive disinfection alternative both at the food level and in water treatment, since there are no regulations on its use and it is preferred over other disinfectant agents as it does not leave harmful residues</p>
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As seen, ozone behaves as a very attractive process disinfectant and it has partially replaced the widely-used chlorine (when a residual disinfectant is not required), not only because it does not leave harmful residues but also because it can be generated in situ, reducing storage and transport operations. It is also used in the treatment of the wastes generated in industry. In this context, the most well-known applications of ozone are in this field, where it is not only used in the treatment of water and wastewater but also in the treatment of gases, as pointed out in several recent reviews, such as those shown in Table 2.

Table 2. Reviews showing examples of ozone application in environmental remediation

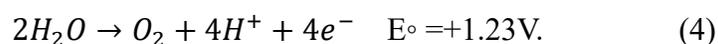
Review	Topics covered	Main conclusions
<p>Application of ozone for the removal of bisphenol A from water and wastewater – A review (2013) [20]</p>	<p>Treatment of BPA by ozone and formation of by-products</p> <p>Estrogenicity of BPA after ozone application</p>	<p>Ozone has reached degradation efficiencies of 70-100% for bisphenol A. However, formation of hazardous byproduct has been found to be an important problem</p>
<p>A review on photocatalytic ozonation used for the treatment of water and wastewater (2015) [21]</p>	<p>Photocatalytic ozonation</p> <p>Application of photocatalysts to photocatalytic ozonation reactors</p> <p>Economic aspects of photocatalytic ozonation.</p>	<p>The coupling of ozone with photocatalysts improves the degradation efficiencies of organic compounds in the water, allowing to reach mineralization. To achieve a good degradation efficiency, it is necessary to use the appropriate photocatalyst and irradiation source and to find the optimal ozone concentration. The deposition of photocatalyst on inert substrates is a good option, trying to avoid the increase in costs of filtration of the photocatalyst after treatment.</p> <p>This treatment shows limitations for the application in the wastewater treatment, as corrosive pH conditions are required and the presence of chemical substances that can be</p>

		contained in real wastewater can inhibit the oxidation process.
Application of ozonation for pharmaceuticals and personal care products removal from water (2017) [22]	<p>Ozonation for microcontaminants removal</p> <p>Single and catalytic ozonation combined with hydrogen peroxide, light, and ultrasounds</p> <p>Integration with other conventional processes.</p> <p>Comparison between ozonation, reverse osmosis and powdered activated carbon for water reclamation processes</p>	<p>Ozonation is a suitable alternative for the treatment of emerging pollutants contained in water since it can be carried out at suitable pressure and temperature conditions. This technology can oxidize by ozone or hydroxyl radicals formed during treatment.</p> <p>The integration of ozonation with various technologies shows an improvement in the mineralization of emerging pollutants. The use of catalysts has been shown to increase degradation efficiencies, but their use in wastewater treatment is still limited. The H₂O₂/ O₃/ UV treatment shows good prospect for industrial application as cost can be reduced using solar energy. The critical point of this process is to find the optimal dose of H₂O₂ that does not inhibit the oxidation power.</p> <p>Ozonation shows advantages over membrane filtration and powdered activated carbon (PAC) in water purification as it requires a lower cost per kWh m⁻³. However, the presence of toxic intermediaries can be a disadvantage of ozonation, mineralization can be increased with the integration of post-ozonation technologies.</p>
Catalytic ozonation for water and wastewater treatment: Recent advances and perspective (2020) [23]	<p>Catalytic ozonation</p> <p>Application for the degradation of toxic organic pollutants</p>	<p>Ozonation has been studied for the treatment of wastewater obtaining good results in terms of degradations reached. However, water with toxic by-products can be obtained because of the low mineralization attained. Integration of ozone with various technologies can improve its efficiency but not necessarily its applicability at an industrial level, so it is required to optimize these processes.</p> <p>The use of catalysts promotes the decomposition of ozone into hydroxyl radicals, improving mineralization capability. Catalytic ozonation needs to be optimized to be applied in water treatment. Catalysts synthesis is usually very expensive or complex, so it is necessary to develop stable, economical, and reusable catalysts.</p>
Flue gas treatment with ozone oxidation: An overview on NO _x , organic pollutants, and mercury (2020) [24]	<p>Principles of ozone oxidation</p> <p>NO_x control by ozone oxidation</p> <p>Volatile organic compounds controlled by ozone</p> <p>Industrial application of simultaneous removal of SO₂ and NO_x by ozone</p>	<p>Further work should be made regarding the ozonation of atmospheric pollutants. It is necessary to develop catalysts with high stability and selectivity, the generation of ozone with less energy consumption.</p> <p>It is necessary to forward research towards VOCs removal.</p> <p>A great advantage of ozone oxidation is that the residual oxygen in the combustion gases can also be used as an auxiliary oxidant.</p>

Over the years, the ozone has been generated by different methods. Usually, the technology most widespread for ozone generation is the production from ambient air or pure oxygen, in an electrical discharge chamber or by ultraviolet irradiation. Unfortunately, these methods waste a very important percentage of energy inside processes. This fact, together with the low solubility of ozone in water, become the real bottleneck for a more extended application [25–27]. For that reason, the search of alternatives, including the electrochemical generation, is a topic of the major interest nowadays.

2. Fundamentals of electrochemical ozone generation

Ozone is produced electrolytically by oxidation of water (Eq. 3) [28] as it was demonstrated using radiotracer techniques [29]. This reaction competes with the oxygen production (Eq. 4) with a lower redox potential. Because of that, to promote the formation of the triatomic molecule, strategies such as working with electrodes exhibiting high anodic overpotential for the oxygen evolution reaction [30–33] or applying rather large current densities should be applied.



It is also important the choice of a suitable electrolyte and the temperature, because of their influence on the stability of the produced ozone [28,34,35]. Key advantages of the electrochemical technology, as compared with the conventional technologies [36], are (1) the much lower voltages required, which reflects on lower energy production costs [27,37–40] and (2) the production of ozone directly into the liquid, which skips out the typically poorly-efficient and slow dissolution of the ozone gas (produced in conventional methods) into the liquid where it is used [41,42]. Table 3 shows a compilation of some reviews focused on the electro-generation of ozone, which highlight all the aspects and parameters that influence on the capability of reaching high ozone concentrations.

Table 3. Reviews focused on the electrochemical ozone generation

Review	Topics covered	Main conclusions
<p>Anodic Materials for Electrocatalytic Ozone Generation (2013) [26]</p>	<p>Traditional ozone production method is corona discharge to air or pure oxygen.</p> <p>The electrocatalytic ozone generation method is to oxidize water to ozone on the anode. It is well known that water is more favorable to be oxidized to oxygen than ozone, because the oxygen evolution occurs under a much lower anodic potential than that for ozone evolution as.</p> <p>Anodic materials.</p>	<p>The generation of ozone by electrocatalysis, achieves a high concentration of ozone in the gas and the liquid phases.</p> <p>Materials for electrolytic ozone generation must have a high oxygen evolution potential to prevent oxygen evolution and be stable to strong anodic polarization in the electrolyte (Pt, DSA, Au, Pd, PbO₂, SnO₂, diamond and carbon vitreous).</p> <p>BDD and the Nickel Antimony Doped Tin Dioxide Electrode can reach a current efficiency of more than 30% under mild experimental conditions. However, these two types of electrodes also have a high cost or a short service life.</p> <p>Further anodic materials evaluation should be made to improve the efficiency of ozone decay under conditions that will increase its stability.</p>
<p>The Electrochemical Generation of Ozone: A Review (2013) [40]</p>	<p>Advantages of electrochemical generation of ozone.</p> <p>Electrochemical cell configuration and anode materials</p> <p>Membrane Electrolyte Assembly (MEA)-based cells employ a solid polymer electrolyte (SPE) membrane (typically Nafion) as the electrolyte, with the anode and cathode being pressed tightly against the membrane</p> <p>Effect of temperature and current density</p>	<p>The electrochemical generation of ozone have many advantages such as low voltage operation, high concentrations of ozone in the gas and liquid phases with high current efficiency, no need for gas feeds of any description and simple system design.</p> <p>The MEA configuration offers great promise for the electrochemical production of ozone.</p> <p>To inject ozone directly into water requires the use of MEA-based, zero gap cells. Currently it is employed Nafion as the polymer electrolyte membrane. The use of this type of membrane limits the application in actual wastewater because of the blocking of the membrane cause by Ca²⁺ and Mg²⁺ and the slow down produced by the Na⁺ ions that replace protons as the mobile species in the Nafion. This problem may be overcome by the development of membranes that can reject multiply charged cations</p>
<p>Electrochemical generation of ozone in a system with a solid polymer electrolyte (2016) [43]</p>	<p>Comparative between UV radiation, corona discharger and anodic oxidation of water</p> <p>Effect of current density on electrogeneration of ozone</p>	<p>UV (low ozone concentration and high value of specific energy expenditure kW h kg⁻¹ O₃), CD (better concentration of ozone than UV and lower value of specific energy expenditure kW h kg⁻¹ O₃, mass transfer problems)</p> <p>Anodic oxidation (high ozone concentration, high value of specific energy expenditure kW h kg⁻¹ O)</p> <p>The solid polymer electrolyte (SPE) system allows to discard the use of hazardous liquids as electrolytes. However, their application can be limited if components of the water can damage the membrane (e.g. ions such as Ca²⁺ and Mg²⁺ may block the sulfo groups through which proton transport occurs).</p>

		The anode most used and with which high efficiencies were reached in ozone production was PbO ₂ . Its application in wastewater treatment is limited by lead toxicity. BDDs have high activity and selectivity and good stability but require very high energy consumption for the process. The study of anodic materials for the generation of ozone continues to be one of the keys to its production.
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From these works, it can be concluded that efficiency in the electro-generation of ozone depends mainly on the equipment and operation conditions used. Regarding the first, the anode composition and the electrolyzer technology should be considered as the primary items. With respect to the second, the more relevant inputs seem to be the operation current density and temperature, and a suitable formulation of the electrolyte used. Details about all these points are going to be discussed in the next sections of this Review.

3. Equipment for the electrolytic production of ozone

The study of anodic materials and the design of cells should focus on finding low-cost materials that can improve the efficiency of ozone production under conditions that increase ozone stability. Table 4 shows design parameters of several of the most recent works focused on the development of electro-ozonizers and highlights the great variability of cell technologies and electrodes materials applied.

Table 4. Equipment used for the electro-ozonation process

Type of cell	Anode	Reference/year
Divided cell (SPE)	PbO ₂ /Pt	[44] 2006
Divided cell (SPE)	Si/TiO _x /Pt/TiO _x	[45] 2009
Conventional three-electrode cell	PbO ₂ /Pt	[30] 2010
Divided cell (SPE)	Pt-TaO _y	[46] 2015
SPE filter-press reactor	OFM-PbO ₂	[39] 2016
Conventional mixed-tank	Ti/Ni-Sb-SnO ₂	[38] 2018
PEM cell	PbO ₂	[47] 2018
Divided cell	Ti/ SnO ₂ -Sb	[48] 2018
Conventional mixed-tank	Pt/Ti	[49] 2019
Chamber electrolysis cell	Ti/ATO	[50] 2019
PEM cell	BDD	[51] 2019
Divided cell (H-cell)	β-PbO ₂ /Ta ₂ O ₅	[27] 2020
PEM cell	BDD	[52] 2020

Electrochemical Cells. Most of the works in which it is faced the electrochemical production of ozone are carried out in conventional mixed-tank or in single-pass flow cells, in which the liquid passing throughout the cell act as the electrolyte. Use of membrane is not necessary

and, frequently, the gases evolved on the anode and cathode are allowed to mix and a single formulation of the electrolyte is suitable for the production of ozone. However, in many other works, divided cells are evaluated, using separators such as porous ceramic or polymer exchange membranes. These cells favor that anode and cathode gases are vented separately, the use of different and more tailored formulations for the anolyte and catholyte and they also help to prevent the loss of efficiency associated to the cathodic reduction of the ozone generated (either by direct or mediated reduction processes). More recently, polymer exchange membrane (PEM) electrolyzers have been proposed as a very interesting alternative. In this case, the membrane is not used as a separator of compartments of the cell but as a component of a membrane electrode assembly (MEA), which allows to directly connect the anode and the cathode, behaving as the electrolyte of the cell. In this type of cells, the formulation of the liquid in which the ozone is produced can be more exigent, because the ionic circuit of the cell is not closed with this liquid but with the membrane which is in direct contact with both electrodes. This allows to obtain ozone with a very high quality. In addition, they can operate successfully with liquids of very low conductivity and, because they approach the concept of zero-gap cell [43], ohmic losses are minimized operating at rather low voltages [51,53–55]. In these cells, the choice of the electrodic materials is even more important because they may allow the optimization of the production of ozone and prevent damages to the membrane [47,56]. Thus, the principal challenge of PEM electrolyzers is associated to the degradation of the membrane electrode assembly (MEA) by the $\bullet\text{OH}$ generated by the decomposition of ozone in the membrane, which may cause a deterioration of the performance and affect the service lifetime of the electro-ozonizer [47,57]. In addition, during the direct treatment of wastewater with electro-ozonizers technology, the membranes can be blocked with Ca^{2+} and Mg^{2+} or they may be damaged by Na^+ ions, which can replace the protons as mobile species in the polymer membrane, affecting negatively to the performance of the electro-ozonizers, because they move more slowly and increase the ohmic resistance of the cell. This problem is expected to be overcome in the near future with the development of new types of membranes with enhanced properties such as the rejection of multi-charged cation.

Electrode materials. For the generation of ozone different electrode materials have been evaluated in the last decades showing important differences in terms of the promotion of the production of ozone and stability. The most interesting are Pt, metal oxides such as PbO_2 or

SnO₂ and conductive diamond coatings, which historically have been proposed sequentially as a technological improvement.

Thus, as for many other electrochemical applications, platinum has traditionally been the focus of many studies about ozone production, either as pure material or as coating on different substrates. It has two relevant properties for ozone generation: an outstanding stability and a very high oxygen evolution overvoltage [58]. However, because of the necessity of applying high current densities, the heat generated on the electrode can become a weak point as it may affect to the decomposition of ozone [59]. Because of that, two types of studies are worth to mention: the electrolysis at extremely high current densities and the electrolysis of eutectic solutions at the lowest temperature possible [33]. Regarding the first, Fischer and Massenez electrolyzed H₂SO₄ at current densities of up to 100 A/cm² with small Pt anodes. They found a dependence of yield on anode geometry, believing that varying heat transfer rates and differing stabilities of the mode of electrolytic gas evolution were the critical factors to explain this geometrical dependence. A different steady-state value of anode surface temperature would thus be obtained, and as this is the single most important parameter to ozone synthesis. Regarding the second strategy, worth to highlight the work of Briner, Haefeli and Paillard focused on the electrolysis of the H₂SO₄ recognized that ozone concentration increases with the temperature decreases. They concluded that the effect could be fully exploited by electrolyzing the 5M eutectic, which remains liquid to -70°C. They obtained a maximum yield of 8.5% current efficiency at -67°C. Consequently, the ozone generation by platinum electrode is achievable but it requires extreme conditions to develop at suitable rates which, in turn, also lead to high costs and low efficiencies. For this reason, the application was limited, and research with other electrode materials was initiated.

In order to overcome the limitations of platinum anodes, application of electrodes consisting of lead or tin dioxide coatings was a significant progress for the electrochemical ozone production technology. These coatings can undergo high current densities without considerable wear and reaching higher current efficiencies than Pt. Thus, the first feasible studies about ozone generation by PbO₂ anodes were carried out at low temperatures (as low as -12°C) and using highly concentrated acid as electrolyte (concentration could reach up to 70%) achieving better results than those obtained by Pt [34,60]. Mechanistically, it was found [61] that the ozone formation proceeds via the reaction of the oxygen intermediates with

dissolved oxygen, which is always present at the anode surface. This reaction is very fast and limited only by diffusion in acid solution. However, the competition between oxygen and ozone generation was found to be a problem and, to overcome it, fluoroanions additions were found to enhance the ozone formation, although this improvement was not found to be totally viable because these species are generally toxic to human beings and harmful to the environment [60]. In addition, the leakage of toxic lead ion to the aqueous phase during the use of lead dioxide coatings was also found to be a significant problem and many efforts were made trying to avoid using different manufacturing procedures and formulations of the coatings [32,39,41,44,62–64]. In addition, the doping of a PbO_2 -based electrode with certain ions such as, Bi^{3+} , Fe^{3+} , Co^{2+} , and F^- was found to considerably increases its electrocatalytic activity in the formation of hydroxyl radicals, which are the precursors of either O_3 synthesis or enhanced the oxidation of substances contaminants. In this context, the introduction of a large amount of the dopant ultimately led to formation of oxide composites whereas small amounts of dopants increased the electrocatalytic activity without changing the corrosion properties of PbO_2 [56]. Tin dioxide coatings have demonstrated a very similar behavior with respect to lead dioxide showing the same drawbacks related to stability. Worth to highlight the good performance of the antimony nickel doped SnO_2 electrode which shows a current efficiency of more than 30% under mild experimental conditions.

At the turn of the century conductive diamond coatings emerged as new electrode materials with many applications in electroanalytical chemistry and in environmental electrochemical technology. Among them, the boron-doped diamond electrodes have demonstrated to be the most interesting with several technologically important characteristics for the ozone electro-generation, including their inert surface with a low adsorption capacity, corrosion stability even in acidic media, and a wide potential window (approximately 3.5 V) [65–68]. These electrodes present a very high overpotential for oxygen evolution in acidic conditions showing the same advantages that lead dioxide coatings and avoiding the environmental problems highlighted for them [66,69]. Studies with this electrode has demonstrated that the rate of O_3 generation is highly dependent on the applied current density and the low solubility of oxygen in water is one of the main limitations found. The methods that are being investigated to improve the production of ozone aim to suppress the oxygen evolution reaction via adsorbed anion (a process which is rate determining at high current densities)

and the use of a solid electrolyte, which probably forms incomplete adsorption layers and leads to a considerably higher current efficiency.

4. Operation conditions for the electrochemical production of ozone

Table 5 shows operation conditions and electrolyte formulations used in different recently published works focused on the production of ozone with electrochemical technology.

Table 5. Electrolyte formulation and operation conditions used for the electro-ozonation process

Electrolyte formulation	Temperature	Current density / Voltage	Reference/years
0.3 mol L ⁻¹ HNO ₃	25-30°C	1.5 A cm ⁻²	[44] 2006
10 mM HClO ₄	25°C	74 mA cm ⁻²	[45] 2009
0.5 M H ₂ SO ₄	25°C	1.8V	[30] 2010
0.1 mol L ⁻¹ H ₂ SO ₄	25°C	100 mA cm ⁻²	[46] 2015
0.5 M H ₂ SO ₄	24°C	1.25 A cm ⁻²	[39] 2016
1M HClO ₄	25°C	3.9 mA cm ⁻²	[38] 2018
0.5 M H ₂ SO ₄	25°C	40 mA cm ⁻²	[47] 2018
0.05 M Na ₂ SO ₄	25°C	30 mA cm ⁻²	[48] 2018
0.5 M H ₂ SO ₄	25°C	5 V	[49] 2019
Real water	25°C	833.3 A m ⁻²	[51] 2019
0.5 M H ₂ SO ₄	25°C	40 mA cm ⁻²	[27] 2020
Synthetic wastewater with 3000 ppm of Na ₂ SO ₄	25°C	0.0416 and 0.88 A cm ⁻²	[52] 2020

As stated before for the non-electrochemical production of ozone, the operation at low temperature is important to reach high efficiencies in the production of ozone because of the thermal stability of this molecule [7,8]. This was demonstrated in works made in the seventies and eighties of the last century. However, currently, most works are carried out at room temperature trying to develop less exigent processes from the energy point of view. Also, it is important the application of very high current densities because they favor ozone versus the easier oxygen production [33,59]. Both parameters are antagonistically related to each other, because the higher is the current density applied, the higher is also the heat losses associated to the process and, hence, the raise in the temperature in the liquid in which ozone is collected. Because of that, temperature regulation becomes an extremely important action if high productions of ozone are looked for.

In addition to operation conditions, the formulation of the electrolyte (or supporting liquid which is going to collect the ozone generated on the electrodes) is extremely important. One of the key parameters is the pH, because of ozone decomposition into hydroxyl radicals (shown in Eq. 2) is promoted at pHs over 6, as it also happens during the production of ozone by non-electrochemical technologies. At this point, it is worth to highlight the importance of the species contained in the electrolyte because anions and cations contained in its formulation should not promote decomposition reactions of ozone [27,49]. This is particularly important when these anions directly consume ozone (such as the chlorine or the hypochlorite formed by its disproportionation), act as precursors of hydrogen peroxide giving way to the formation of peroxone [48,70,71] (such as peroxosulfates) or simply compete in the electric charge transfer during the production of ozone if they are directly oxidized on the surface of the anode of the electro-ozonizer. As well, the occurrence of other species that consume ozone (such as organics) will also affect negatively to the accumulation of the target oxidant in the liquid media [52]. In addition, presence of species which has a positive impact on the solubility of ozone can help to achieve higher concentrations of ozone in the liquid preventing its transport to the gas phase. In this context, different studies support an increase in the ozone concentration when the electrolyte concentration increase. However, is important find the optimal concentration, because there is a conductivity from which the ozone concentration decreases due to increased anionic adsorption educe the ozone yield [34,43,72].

5. Applications of electro-ozonation

Table 6 summarizes several of the recent applications in which electro-ozonizers have been applied. As seen, electro-ozonizers technology can be successfully applied not only for the removal of anthropogenic pollutants but also for the disinfection of water and wastewater and it has been tested not only with synthetic solutions but also with real samples.

Table 6. Applications of electro-ozonizers

Application	Treatment conditions	Efficiency	Ref. /year
	Synthetic water: deionized water in chloride medium, 10^7 - 10^8 Pseudomonas Aeruginosa. Ozone electrogeneration by CONDIAPURE® (BDD alectrodes with Nafion separation membrane) Continuous reactor	4-8 Log unit removal in 120 min	[73] 2015

Removal Pseudomonas Aeruginosa			
Landfill leachate	Leachate of Shanghai Treatment Plant, Shanghai, China. 3.5 L Ozone electrogeneration by Ti/RuO ₂ -IrO ₂ anode Batch reactor	64.8% COD removal in 97 min	[74] 2017
Degradation of carbamazepine	Solution of 10 mg L ⁻¹ of carbamazepine Ozone electrogeneration by Ti/ SnO ₂ -Sb anode Batch reactor	63.5% carbamazepine removal in 15 min	[48] 2018
Removal of Total coliforms and Pseudomonas aeruginosa	Solution of Highly-faecal polluted surface, (10 ⁵ total coliforms and Pseudomonas aeruginosa) Ozone electrogeneration by CabECO® cell (4 DIACHEM® electrodes with two Nafion separation membranes) Continuous reactor	3 Log unit removal (total coliforms) and 1 Log unit removal (Pseudomonas aeruginosa) in 60 min	[75] 2018
Removal of Total coliforms, pseudomonas aeruginosa and total aerobic microorganisms	Solution of Highly-faecal polluted surface, (10 ³ Total coliforms, pseudomonas aeruginosa and total aerobic microorganisms) Ozone electrogeneration by CabECO® cell (4 DIACHEM® electrodes with two Nafion separation membranes) Continuous reactor	Total inactivation in 120 min	[76] 2018
Fecal-polluted water	Solution 95/5 (surface water/treated wastewater) 100L Ozone electrogeneration by CabECO® cell (4 DIACHEM® electrodes with two Nafion separation membranes) Continuous reactor	99% Pseudomona s Aeruginosa and Total Coliforms removal for 0.02 Ah L ⁻¹	[51] 2019
Leachate concentrate	Solution of local landfill site in Beijing Ozone electrogeneration by Ti/ATO anode Continuous reactor	60% Removal efficiency in 240 min	[50] 2019
Clopyralid degradation	Solution of 100 mgL ⁻¹ of Clopyralid, Ozone electrogeneration by μZON® cell (diamond electrodes and Nafion membrane), 1A Discontinuous reactor	99% clopyralid removal in 180 min	[52] 2020

The main conclusions of these studies about the applicability of ozone produced electrochemically include a very good performance of the technology with results that are not only associated to the effect of ozone but to the synergistic combination of the action of ozone with direct electrochemical processes and also with the action of other mediators such as peroxosulfates, hydrogen peroxide, etc. It is also clearly seemed all the technology progress described in this review, with a tendency to use PEM electrolyzers and diamond coatings as anodes in processes operating at low temperature and very high current densities.

6. Conclusions

From this work the following conclusions can be drawn:

- Electro-ozonizers are a very interesting alternative to conventional ozonizers, showing important advantages such as the operation at much lower voltages and the direct production of ozone into the liquid where it is going to be used.
- Both operation conditions and equipment selection are important to reach high efficiencies with the electrochemical technology of production of ozone
- The antagonistic effects of temperature and current density becomes one of the technological challenges to be overcome in the electro-ozonizer technology
- Electrolyzers based on the use of membrane electrode assemblies are extremely promising, reaching very high efficiencies and allowing the use of more suitable formulations for the generation of ozone
- Important progress in the anode technology which have end up with the use of conductive-diamond coatings as anodes.

Acknowledgements

Financial support from the Spanish Agencia Estatal de Investigación throughout project PID2019-107271RB-I00 is gratefully acknowledged. Mayra Rodríguez-Peña also acknowledges CONACYT 722138

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