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A critical review over the electrochemical disinfection of bacteria in synthetic and real wastewaters using a boron-doped diamond anode

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ABSTRACT

Inadequate access to clean water and sanitation are the most relevant problems afflicting developing and industrialized nations. Global water scarcity is expected to grow worse in the coming decades and this has motivated the scientific community to identify new, safe, and robust water disinfection technologies at lower cost and with less energy, diminishing the use of chemicals and impact on the environment. Usually, conventional methods of water treatment can solve this problem satisfactorily, such as chlorination, but, sometimes, they can be chemically, energetically, and operationally intensive. Therefore, the science and technology has encouraged the development of other alternative disinfection technologies. In this frame, electrochemical disinfection or electrodisinfection is currently experiencing a renaissance due to the tremendous contributions of novel electrocatalytic materials as well as the use of electric current as an inexpensive and suitable reagent to drive the inactivation of waterborne pathogens, avoiding conventional chemical oxidizers or reducing agents. Electrodisinfection has a significant technical impact, because it can be easily scaled up or design small–portable devices, benefiting from advantages such as versatility, environmental compatibility, automation, inherent safety, and potential cost effectiveness among others. Diamond films emerge as a novel and sustainable solution to electrogenerate powerful oxidants for effectively controlling waterborne pathogens in drinking water. The overarching goal of this critical review is to evidence the importance of diamond electrochemical methods as alternative for the eradication of waterborne infectious agents from public and drinking waters. The mechanisms of bacteria inactivation, and the fundamentals and applications of electrochemical oxidation with diamond to disinfect synthetic and real waters and wastewaters are exhaustively discussed. The use of hybrid and sequential processes involving electrochemical oxidation with other techniques, as well as endodontic and food control applications, are also analyzed. A section remarking the future challenges of electrodisinfection with diamond is finally presented.

1. Introduction

Around 20% of the world's population (estimated in 6.5 billion of people) lack access to clean and safe water. According with the United Nations predictions, this estimate will rise close to a 40% by 2050. This situation is very worrying especially considering the extreme pressure that will be placed on our valuable freshwater resources. Also, it should be emphasized that the problems related to water supply are not only based on quantity water, but also with its quality [1]. A growing number of contaminants, such as heavy metals, persistent organic, and micro-pollutants, as well as bacteria, protozoa, virus, and other microorganisms, are entering water supplies, making disinfection and/or purification even more challenging. For this reason, public health and environmental concerns drive efforts to pollute waters formerly considered clean. More effective, lower-cost, and robust technologies to disinfect and decontaminate waters from source to point-of-use are needed, without further stressing the environment or endangering human health by the treatment itself [2].

In the case of disinfection, an important challenge is to provide safe water at reasonable cost, with lower energy requirements and an effective control, avoiding more problems due to the disinfection approach itself. The main disinfectant worldwide used because of its potency and low cost is free chlorine. It is very effective for eradicating (inactivating) or diminishing several infectious agents, mainly viruses

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Nomenclature

Symbols and acronyms

AFM	atomic force microscopy
ATP	adenosine triphosphate
BDD	boron-doped diamond
BDDP	boron-doped diamond powder
CF	carbon felt
CFU	colony-forming unity
Ch a	chlorophyll *a*
COD	chemical oxygen demand (mg O_2 L^{-1})
DDE	double diamond electrode
DNA	deoxyribonucleic acid
DSA	dimensionally stable anode
EAOP	electrochemical advanced oxidation process
EC	electrocoagulation
E_{cell}	cell voltage (V)
EC_V	energy consumption per volume unit (kWh m^{-3})
ECWP	flow-through cell with BDD perforated electrodes
EF	electro-Fenton
EO	electrochemical oxidation
GAC	granular activated carbon
HRT	hydraulic residence time
I	current (mA or A)
j	current density (mA cm^{-2} or A m^{-2})
MPN	most probable number
NOM	natural organic matter
$^{\bullet}OH$	hydroxyl radical
PE	photoelectrolysis
PEF	photoelectro-Fenton
PFU	plaque-forming unit
Q	electric consumed charge (Ah L^{-1})
Re	Reynolds number
rGO	reduced graphene oxide
ROS	reactive oxygen species
SE	sonoelectrolysis
SEM	scanning electron microscopy
SLR	surface loading rate
SPE	solid polymer electrolyte
$SO_4^{\bullet -}$	sulfate radical anion
SS	stainless steel
TEM	transmission electron microscopy
TOC	total organic carbon (mg C L^{-1})
UNCD	boron-doped ultrananocrystalline diamond
UV	ultraviolet light
UVA	ultraviolet-A light ($\lambda = 320$–400 nm, $\lambda_{max} = 360$ nm)
UVC	ultraviolet-C light ($\lambda = 190$–285 nm, $\lambda_{max} = 254$ nm)
WWTP	wastewater treatment plant

and bacteria. However, new microorganisms continue to emerge and consequently, it is or could be ineffective and, other disinfectants are required.

It is noticeable that toxic disinfection by-products can be produced by using chlorination or other disinfection agents, such as trihalomethanes, chloroform, and haloacetic acids [3,4]. Such problems point to the critical need to discard chlorine disinfection and implement alternative technologies. For effective control of waterborne pathogens in drinking water, chemical systems such as ozone, silver, copper, ferrate, iodine, bromine, hydrogen peroxide, and potassium permanganate, as well as physicochemical systems such as TiO_2 photocatalysis and photodynamic disinfection, have been proposed as alternatives to chlorination. New disinfection strategies including ultrasonication, pulsed electric fields, irradiation, magnetic enhanced disinfection, microwave systems, coagulation, flocculation, sedimentation, and media or membrane filtration, provide reliable physicochemical removal along with effective inactivation [5]. The use of light from visible to ultraviolet (UV) to photochemically inactivate pathogens is also an interesting alternative and the electrochemical technologies have been recently attained a resurgence in interest by the scientific and industrial communities.

The use of UV or sunlight irradiation for water disinfection in plastic bottles to kill pathogens (viruses, bacteria, and protozoa) was proposed [6,7], although a health risk by chemicals released from the bottle material was raised due to the plastic quality. The water matrices composition, toxic disinfection by-products in the presence of high concentrations of organic matter associated with inadequate sanitation, and the inefficient inactivation of emerging pathogenic germs, have motivated the scientific community to develop more water disinfection/purification alternatives. In this context, significant advances are required to understand the inactivation mechanisms for the control of waterborne infectious agents to create new, safe, and robust disinfection methods, matching or improving positive aspects of chlorine and UV disinfection while avoiding their negative effects [1]. Recent developments in materials science offer hope for new approaches, based on homogenous or heterogeneous catalysis, to the challenges of water disinfection and decontamination to attend the increasing demands for clean water [8].

One of the growing applications for the inactivation of different types of pathogens is the electrochemical disinfection or electrodisinfection. It has emerged as one of the more interesting alternatives to chlorination, considering important factors for its total application. Reactive oxygen species (ROS) generated in these systems avoid the formation of products potentially toxics from chlorine and decreases the health risks, during the elimination of waterborne infectious agents (helminths, protozoa, fungi, bacteria, rickettsia, viruses, and so on) from public and drinking water [5]. Many researchers have focused on developing new electrocatalytic materials, innovative reactors and investigating fundamental behaviors at the aqueous interface to obtain advanced electrochemical technologies for water purification.

Similar to chlorination and irradiation disinfection, the efficacy of the electrochemical disinfection is mainly based on the efficient generation of disinfectants and on their oxidation power in the electrode surface-layer or in the bulk of electrolytes. In free chloride waters, physisorbed hydroxyl radicals $M(^{\bullet}OH)$ are formed by the oxidation of water on the surface of anode (M) by Eq. (1):

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \qquad (1)$$

$^{\bullet}OH$ reacts non-selectively with a wide range of recalcitrant organics or waterborne pathogenic agents, at a limited release rate. However, the role of direct oxidation by $M(^{\bullet}OH)$ is often lower than expected due to the short radical lifetime, reaction competition, and the adsorption of a relatively low number of microorganisms at the electrode, as well as by the fact that the amount of $M(^{\bullet}OH)$ electrochemically generated is dependent on the nature of the electrocatalytic material used [5,8]. Therefore, the electrochemical production of other disinfectants (chlorine/$HClO$/ClO^-, also called active chlorine), chlorine dioxide, ozone, hydrogen peroxide, peroxodisulfate, peroxodicarbonate, peroxodiphosphate, chloramines, bromine, and ferrates, in anodic, and rarer in cathodic reactions, is needed.

Various electrodes have been used in electrochemical disinfection, like metals, metal oxides, carbonaceous materials, and dimensionally stable anodes (DSA). Nevertheless, diamond electrodes such as boron-doped diamond (BDD) are considered the most effective electrocatalytic materials for the degradation of refractory/priority pollutants and waterborne agents. This results from the in situ production of common chlorine-based disinfection agents from Eqs. (2)–(4), along with the high generation of ROS via Eqs. (1) and (5)–(8). Other oxidizing agents, namely peroxodisulfate, peroxodicarbonate and peroxodiphosphate, can also be competitively formed with ROS from the oxidation of sulfate or bisulfate by Eq. (9), bicarbonate by Eq. (10) and phosphate by Eq. (11) at the BDD surface [5,8].

$$2Cl^- \rightarrow Cl_2(aq) + 2e^- \tag{2}$$

$$Cl_2(aq) + H_2O \leftrightarrow HClO + Cl^- + H^+ \tag{3}$$

$$Cl_2 + 4H_2O \rightarrow 2ClO_2 + 8H^+ + 8e^- \tag{4}$$

$$^{\bullet}OH \rightarrow {}^{\bullet}O + H^+ + e^- \tag{5}$$

$$2^{\bullet}O \rightarrow O_2 \tag{6}$$

$$2^{\bullet}OH \rightarrow H_2O_2 \tag{7}$$

$$O_2 + {}^{\bullet}O \rightarrow O_3 \tag{8}$$

$$2SO_4^{2-} \rightarrow 2SO_4^{-\bullet} \rightarrow S_2O_8^{2-} + 2e^- \tag{9}$$

$$2HCO_3^- \rightarrow C_2O_6^{2-} + 2H^+ + 2e^- \tag{10}$$

$$2PO_4^{3-} \rightarrow P_2O_8^{4-} + 2e^- \tag{11}$$

Although diamond films are a promising and effective material to produce various powerful disinfectants, few drawbacks limit their large-scale applicability. In this review, a critical discussion on the fundamentals and applications of emerging electrochemical methods with BDD anodes like electrochemical oxidation (EO) to the remediation of drinking water containing waterborne infectious agents is given, evidencing their advantages. This topic represents an important advance in the use of new technologies to improve the quality of drinking water and it is also a challenge for the scientific community because the strategies of electrochemical technologies include not only the treatment of drinking water by EO but also the development of new processes or combined methods with less harmful effects, often denoted as process-integrated environmental protection. This review also remarks the novel use of EO with a BDD anode for endodontic and food control applications.

2. Methods

2.1. Data sources and search strategy

The Scopus and SciFinder database were chosen for exhaustively searching the peer-reviewed literature focusing the reviews and scientific articles related to the electrodisinfection of waters and wastewaters using a BDD anode. In each database, four literature searches were made with the following keywords: electrochemical advanced oxidation processes AND disinfection, electrochemical oxidation AND disinfection, anodic oxidation AND disinfection, and diamond anode AND disinfection. Publications (reviews and scientific articles) written in English were first selected covering a period from 2006 to 2020. They started in 2006 because, up to our knowledge, at this year Jeong et al. [9] published the first article covering an excellent electrochemical disinfection of *Escherichia coli* in a synthetic free-chloride wastewater with a BDD anode. For each retrieved paper, the title, authors, reference data, and abstract were included in a list for its individual analysis. Letters to the editors, book chapters, conferences, and communications in congresses were excluded. The analysis of the full text of all the selected reviews allowed deciding its inclusion in the present review from the following criteria:

(i) A correct application of single and coupled electrochemical methods,
(ii) the electrodisinfection of synthetic and real waters and wastewaters,
(iii) an adequate description of the experimental methodology utilized, with information over the electrochemical system, the kind of cell and electrodes employed, appropriated experimental conditions, and the equipment for analysis and measurement of microorganisms, and
(iv) a detailed discussion of the results obtained, mainly regarding the pathogen inactivation with electrolysis time and operating variables, the effect of free-chloride or chloride media, the evaluation of the oxidizing agents and inorganic by-products originated to explain the inactivation mechanism, the influence of organic pollutants and/or natural organic matter (NOM), and the presentation of images to show the morphological changes of the inactivated bacteria. The decay of total organic carbon (TOC) and/or chemical oxygen demand (COD) of real wastewaters was also considered. The review presents figures and tables aiming to remark these parameters for each treatment.

From the above analysis, the development of 3 main kinds of methods involving the electrodisinfection of microorganisms in waters and wastewaters with a BDD anode was identified: EO and combined (hybrid and sequential) processes. Additionally, a little number of scientific papers were selected related to the novel dental treatment by EO, which was substantially different from a wastewater treatment, as well as some works related to food control. On the other hand, a high number of papers dealing with the assessment of the behavior of the media checked in the absence of pathogens were selected to better understand the oxidizing agents and by-products formed during the EO process.

The present review describes the characteristics of each one of the above processes, followed by a critical analysis of its application to the electrodisinfection of microorganisms. In each treatment, the electrochemical system and cell employed, as well as the role of the oxidizing agents and by-products generated as a function of the operating parameters, are emphasized.

2.2. Bibliometric analysis

Following the above criteria, 7 key review articles were identified. Two of these reviews presented a general information over the electrodisinfection in waters and wastewaters up to 2008 [5] and recent years [10], whereas another review reported the use of nanomaterials in water disinfection [11,12], analyzing the potentially of the electrolyzed water as disinfectant agent. Finally, other three reviews were focused on the electrochemical technologies used for wastewater treatment, but with a little description over electrodisinfection [13–15].

The bibliometric analysis was completed by the identification of 88 scientific articles related to the electrodisinfection with a BDD anode. Fig. 1a depicts the annual distribution of such articles, where the higher number of papers can be observed over the last three years. This makes in evidence the current great interest of the electrochemical technologies with a BDD anode for water disinfection.

Fig. 1b shows that the EO is the most utilized single electrochemical advanced oxidation process (EAOP) for the bacterial electrodisinfection of waters and wastewaters. This method is applied in 63.6% papers, which can be extended up to 69.3% if the dental treatments (5.7%) using EO with a BDD anode are taken into account as well. Combined processes, including hybrid (9.1%) and sequential (7.9%) ones, have been explored to lesser extent. Apart from the above 88 articles, a 13.6% of the overall scientific papers has been focused the evaluation of the oxidizing agents formed in the electrodisinfection process without microorganisms, both in free-chloride and chloride matrices. A reduced number of scientific articles, only 22 over 88 (25.0%), have considered different synthetic free-chloride solutions, whereas the major part of contributions has utilized chloride matrices, sometimes synthetic ones and primordially, real wastewaters (groundwater, secondary effluents of wastewaters treatment plants (WWTPs), urine, etc.). This discloses the importance of the studies developed for achieving bacterial inactivation

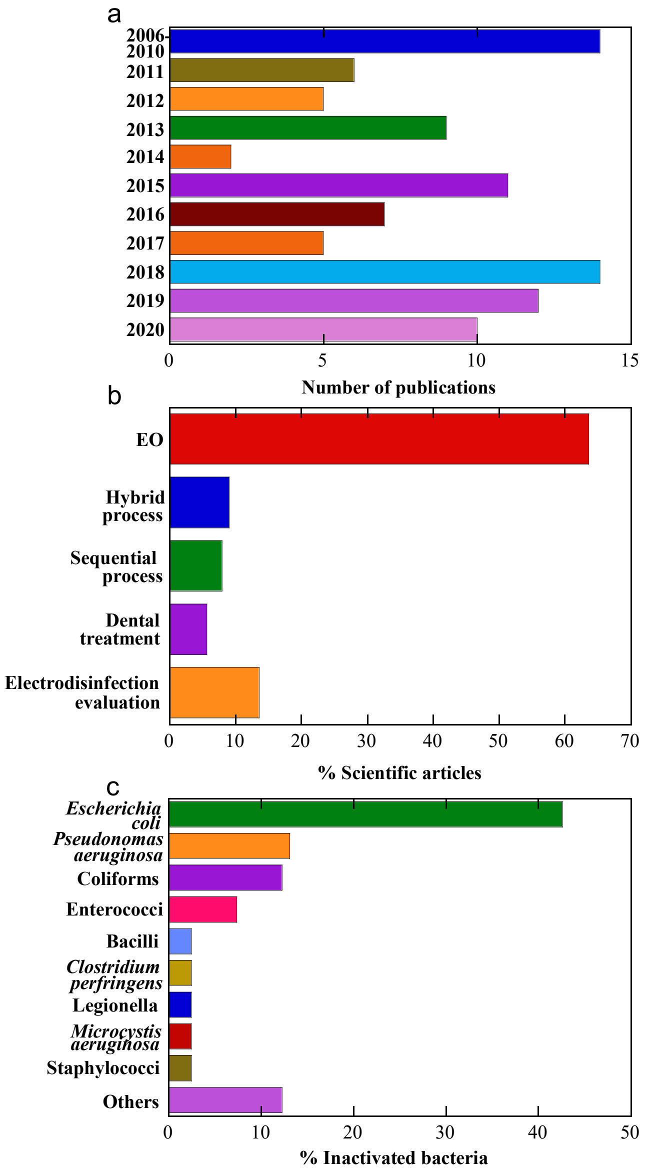

Fig. 1. Bibliometric analysis of the literature identified. (a) Number of publications per year, (b) percentage of scientific papers, and (c) percentage of inactivated bacteria.

upon environmental conditions by means of electrodisinfection using a BDD anode.

Regarding the bacteria inactivated, a total of 122 were identified in the 88 scientific articles selected. Fig. 1c highlights that *Escherichia coli* (42.5%) was the preferential bacterium chosen, followed by *Pseudonomas aeruginosa* (13.1%) and total coliforms (12.2%). The inactivation of other bacteria was studied to smaller extent, including enterococci (7.5%), Bacilli (2.4%), *Clostridium perfringens* (2.4%), *legionella* (2.4%), *Microcystis aeruginosa* (2.4%), and staphylococci (2.4%). Finally, the treatments involved a 12.9% of other bacteria.

3. Mechanisms of bacteria inactivation by electrodisinfection with a BDD anode

The mechanisms of bacteria inactivation are difficult to establish in view of the large variety of existing microorganisms and their cell complexity. The electrodisinfection process causes their death that becomes evident by their morphological changes, in some cases even involving the cellular wall breaking, as disclosed by several authors. Jeong et al. [9] treated a suspension of 10^8 CFU mL^{-1} *E. coli* in 0.2 M KH_2PO_4 (neutral pH) by EO using an undivided stirred tank reactor with a BDD anode and a Pt cathode. After 5 min of electrolysis at 100 mA cm^{-2}, 1 log unit of cells was inactivated due to the oxidative action of BDD($^{\bullet}$OH) and peroxodiphosphate ion, which are originated by the oxidation of water and hydrogenphosphate at the BDD surface, as will be explained in Section 4.1.1. Fig. 2a and b show the images obtained by transmission electron microscopy (TEM) and Fig. 2c and d those found by atomic force microscopy (AFM) of the untreated and treated cells, respectively. Drastic changes in the walls and contents of the cells can be observed. Comparison of Fig. 2a and b informs of a loss of wall uniformity in the treated cells, most of which appeared empty, whereas Fig. 2c and d make in evidence that the smooth and flat surface of the untreated cells became rough and sunken upon treatment, suggesting the escape of their inner contents.

The same behavior has been described by Bruguera-Casamada et al. [16] when electrolyzed suspensions of 10^6 CFU mL^{-1} of Gram-negative (*E. coli* and *P. aeruginosa*) and Gram-positive (*Bacillus atrophaeus*, *Staphylococcus aureus* and *Enterococcus hirae*) bacteria in 7 mM Na_2SO_4 with an undivided stirred BDD/stainless steel (SS) tank reactor. Under these conditions, BDD($^{\bullet}$OH) and peroxodisulfate ion formed from anodic sulfate oxidation are considered as the main oxidizing agents, as will be discussed in Section 4.1.1. Fig. 3a–e depicts the scanning electron microscopy (SEM) images of the above bacteria before and after 45 min of EO treatment at 33.3 mA cm^{-2}. Again, the morphology of all cells was largely altered after electrolysis since their surface became much rougher, whereas a great deal of cellular debris can be seen due to the release of material from the inactivated cells, especially in the Gram-negative bacteria.

Similarly, Bakheet et al. [17] described the gradual loss of the integrity of 1.8×10^6 CFU mL^{-1} of the cyanobacterium *Cylindrospermopsis raciborskii* in 0.050 M Na_2SO_4 during the EO process with an undivided stirred BDD/BDD tank reactor at 10 mA cm^{-2}. The SEM images of the starting and destroyed cells after 180 min of electrolysis are presented in Fig. 4a and 4b, respectively. It can be seen a damage of the wall of the treated cells, which became more fragile by the attack of the electrogenerated oxidants, BDD($^{\bullet}$OH) and peroxodisulfate, as pointed out above.

The destruction of cell walls during electrodisinfection is considered as a key factor to justify the cell inactivation. However, less is known about the overall inactivation mechanism for which a deep analysis of the structural components of cells is required. In this way, Zhou et al. [18] studied the evolution of the organic components (protein-like and fulvic/humic-like substances) by 3D fluorescence excitation-emission matrix of the algae *Microcystis aeruginosa* in sulfate medium during EO using an undivided stirred BDD/Pt tank reactor. From these results, these authors proposed the simple mechanism shown in Fig. 5. It consists of 3 consecutive steps before to obtain the treated water: (i) inactivation of the cells weakening their walls, (ii) releasing of their organic components to the medium, and (iii) degradation of such organics. Fig. 5 also highlights that each step is produced by the attack of oxidants generated at the BDD anode, namely BDD($^{\bullet}$OH), peroxodisulfate, and its derivative sulfate radical anion ($SO_4^{\bullet-}$), among others.

A more detailed study on the inactivation mechanism has been reported by Qi et al. [19], who treated a suspension of 10^7 CFU mL^{-1} *E. coli* in 0.050 M Na_2SO_4 using an undivided stirred BDD/SS tank reactor in the presence and absence of solid reduced graphene oxide (rGO). The latter hybrid process was more efficient as result of the additional destruction of cells over the rGO surface. The TEM images of Fig. 6a show that the round initial bacteria (image A) became distorted in the presence of rGO due to the extraction of phospholipids from the membrane by the graphene nanosheets (image B). In contrast, the image C highlights that long thin and sticky cells were found after electrolysis in the BDD/SS system, proving the intercellular damage of the membrane, whereas the image D makes in evidence a more vulnerable damage upon electrolysis with suspended rGO. These findings corroborate the existence of different

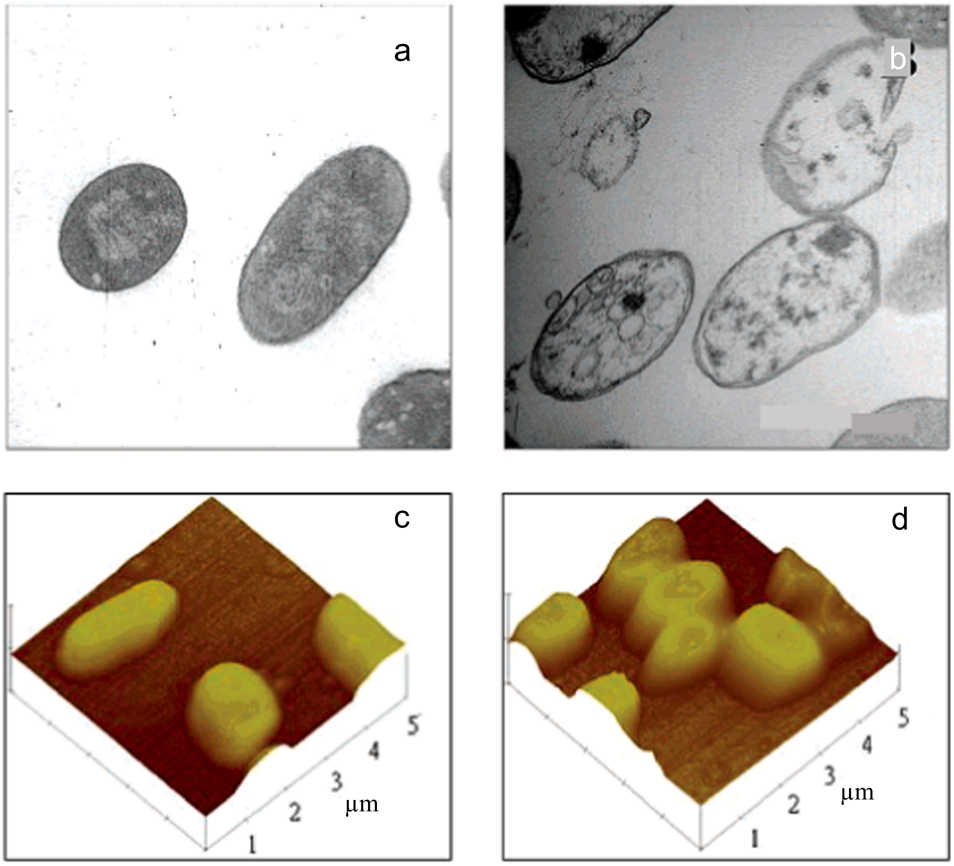

Fig. 2. (a, b) TEM and (c, d) AFM images of *E. coli* in a suspension of 10^8 CFU mL^{-1} in 0.2 M KH_2PO_4 (pH 7.1) at 25 °C under EO with an undivided BDD/Pt cell at j = 100 mA cm^{-2}. (a, c) Untreated bacteria, and (b,d) after 5 min of electrolysis. Adapted from [9].

mechanisms depending on the experimental conditions used. Based on several membrane tests, including cell permeability, enzyme assays, and K^+ leakage, the mechanism of Fig. 6b concerning the hybrid electrolytic system was proposed. It shows that the electrical field between the electrodes promoted the adsorption of the bacteria at the solid rGO surface while the oxidizing agents, mainly $^{\bullet}OH$, were anodically electrogenerated. The cell inactivation then proceeds via three parallel processes involving: (A) charge transfer between the cell wall and rGO, (B) disruption of the cell wall by sharp edges of graphene nanosheets, and (C) oxidation by the electrogenerated oxidants.

Finally, the inactivation mechanism for *E. coli* has been more widely clarified by Long et al. [20,21] when a suspension of 2 × 10^8 CFU mL^{-1} bacteria in 40–45 mM Na_2SO_4, KH_2PO_4 and NaCl was electrolyzed in an undivided stirred BDD/SS tank reactor at 20 mA cm^{-2}. The morphological changes observed for *E. coli* under different operating conditions for each electrolyte are presented in Fig. 7. The subcellular mechanism was analyzed from the change of a high number of parameters, namely total protein, K^+ leakage, membrane potential, permeability and protein, lipid peroxidation, intracellular enzyme, cellular ATP level, and DNA. From these findings, the authors concluded that the bacteria inactivation takes place as follows:

(i) In sulfate medium, it was mainly induced by the damage of the cell wall with oxidation of proteins related to the K^+ transport system that hinders both, the subcellular localization of cell division protein and the synthesis of ATP. It was observed a considerable lipid peroxidation as well.
(ii) In phosphate medium, it underwent total destruction as a whole cell since the disinfection progress involved the major mineralization of the intracellular enzymes, and total and membrane proteins.
(iii) In chloride medium, it was primordially associated to the degradation of intracellular enzymatic systems, due to the attack of BDD($^{\bullet}OH$) and active chlorine originated from the anodic Cl^- oxidation, as will be described in Section 4.1.2.

Much more information is needed to extensively know the inactivation mechanisms not only of *E. coli* but also of a high number of bacteria. The subcellular processes should be largely analyzed to characterize the molecules that are oxidized and caused cell inactivation, as a function of the electrolytic conditions and the kind and amounts of electrogenerated oxidizing agents.

4. Electrochemical disinfection of wastewaters using a BDD anode

As can be seen in Fig. 1a, over the last thirteen years the electrochemical disinfection is considered an important alternative to chlorination providing both primary and residual disinfection [5], and it has been preferentially performed by using EO. Therefore, this section is devoted to exhaustively summarize and discuss the applicability of EO for inactivating different waterborne infectious agents in free-chloride or chloride media, by direct or combined approaches. First, the most representative electrochemical systems will be described to understand the extent and the effectiveness of the EO disinfection approaches as potential commercial alternatives (Section 4.1). Second, the EO fundamentals are also described according to the oxygen- and chlorine- based disinfection agents' production to understand the mechanisms and their oxidation power, as well as their inactivation efficacy as a function of water matrix or solution composition (Section 4.2.1). Finally, the application of electrodisinfection with BDD anodes for the inactivation of different pathogen agents is summarized and discussed in Sections

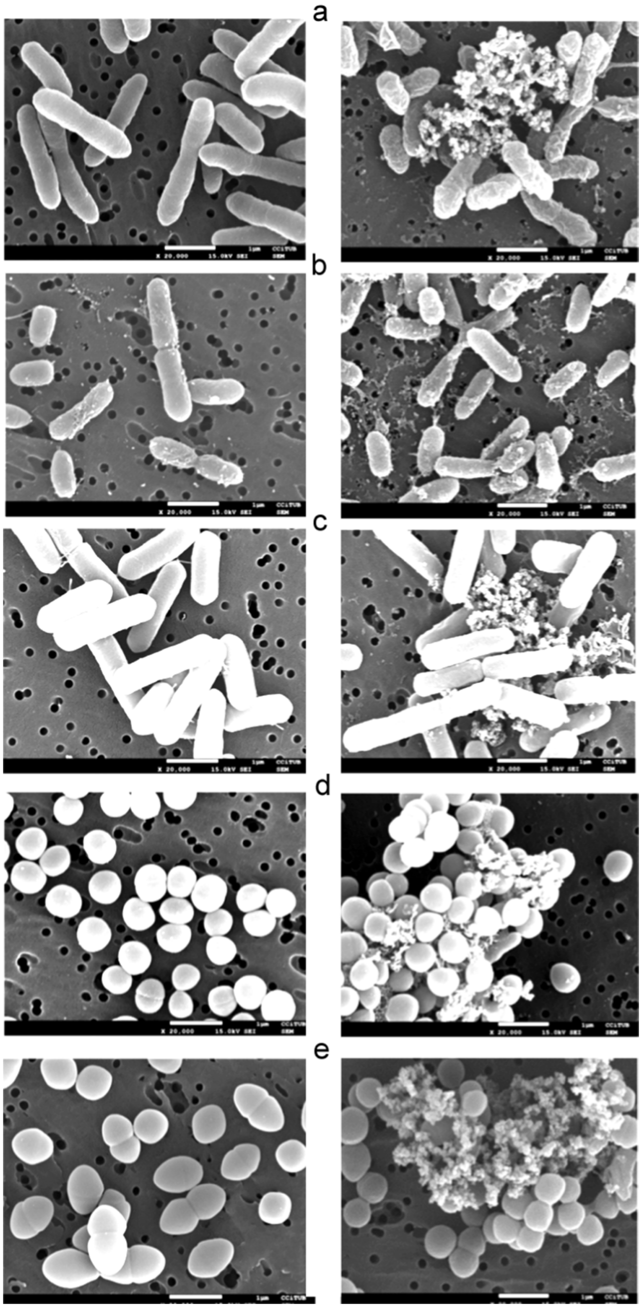

Fig. 3. SEM images for suspensions of: (a) *E. coli*. (b), *P. aeruginosa*, (c) *B. atrophaeus*, (d) *S. aureus*, and (e) *E. hirae* supported on polycarbonate membrane filters. Samples obtained in 7 mM Na_2SO_4 at pH 7.0, before (left) and after (right) 45 min of EO treatment with an undivided BDD/SS cell at $j = 33.3$ mA cm^{-2} and 25 °C. Adapted from [16].

4.2.2 and 4.2.3, evidencing the main achievements attained based on their water matrices and electrochemical technology used.

4.1. Electrochemical disinfection systems

To scale-up the process and promote the adaptation of the technology for commercial applications, the translation from laboratory achievements is needed considering the electrochemical systems used. Tables 1-5 summarizes a great variety of disinfection achievements obtained by employing different electrochemical reactors, evidencing, in several cases, the type of electrochemical system used and their operating conditions. Figs. 8–12 illustrate the most important EO arrangements that have been used to inactivate different pathogen agents.

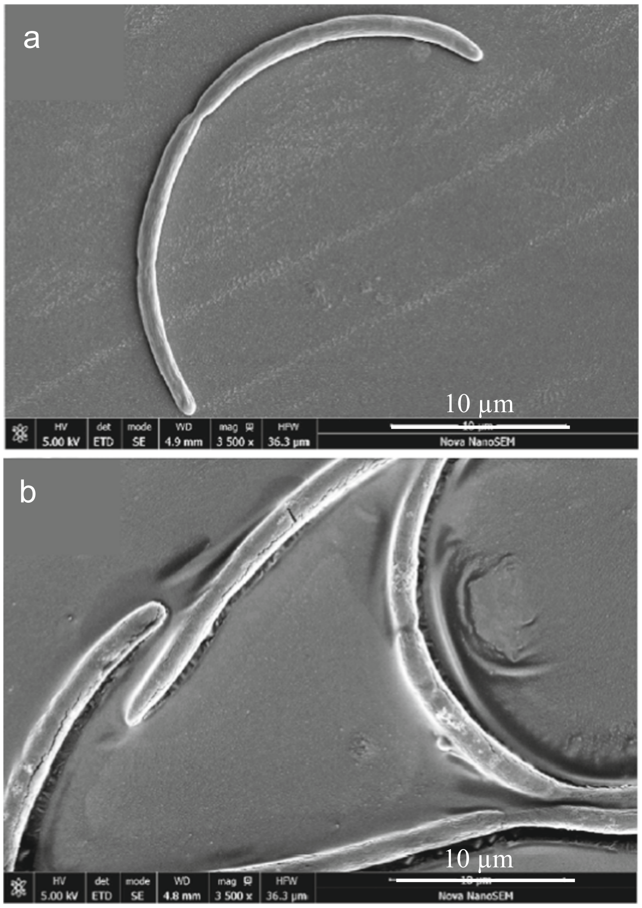

Fig. 4. SEM images of *C. raciborskii* in a suspension of 1.8×10^6 CFU mL^{-1} in 0.050 M Na_2SO_4 by EO with an undivided BDD/BDD cell at $j = 10$ mA cm^{-2}. (a) Untreated bacteria and (b) after 180 min of electrolysis. Adapted from [17].

Agitated beakers or stirred tanks, and flow reactors in divided or undivided setup have been adopted in many laboratory studies. However, undivided electrochemical systems are preferentially employed [22–24]. These arrangements avoid the use of a membrane or separator that provokes an increase on the potential cell, and consequently, affecting the electric cost of the disinfection process, as well as the efficient oxidants production [22,23].

Fig. 8a depicts an example of an undivided stirred tank reactor where an Nb|BDD anode and a SS cathode were used for the inactivation of *E. coli* in synthetic free-chloride medium [25]. This cell option is very common in the laboratories and allows having specific benefits [24] such as: (i) dry and safe electrical connections, (ii) easy sample withdrawal and simplicity of the electrolyte additions, (iii) non difficulty on the insertion and removal of the electrodes without draining the container, (iv) convenient mixing and stirring solution (for promoting the homogenization of the treated solution and for enhancing the mass transport by diffusion/convection of the waterborne agents toward the electrodes and of the by-products from them [22,26] plus heating using a magnetic stirrer/hot plate), and (v) in some cases, the capability to measure the cell or electrode potential and their distribution. Note that to provide a correct kinetic analysis of electrodisinfection related to the inactivation of waterborne pathogen agents, the temperature regulation and pH adjustment are also necessary control requirements. However, the use of undivided agitated beaker or undivided stirred tank reactors could offer apparent experimental conditions that are irreproducible and undefined (not completely fixed) and consequently, the reaction disinfection environment is difficult to be scaled.

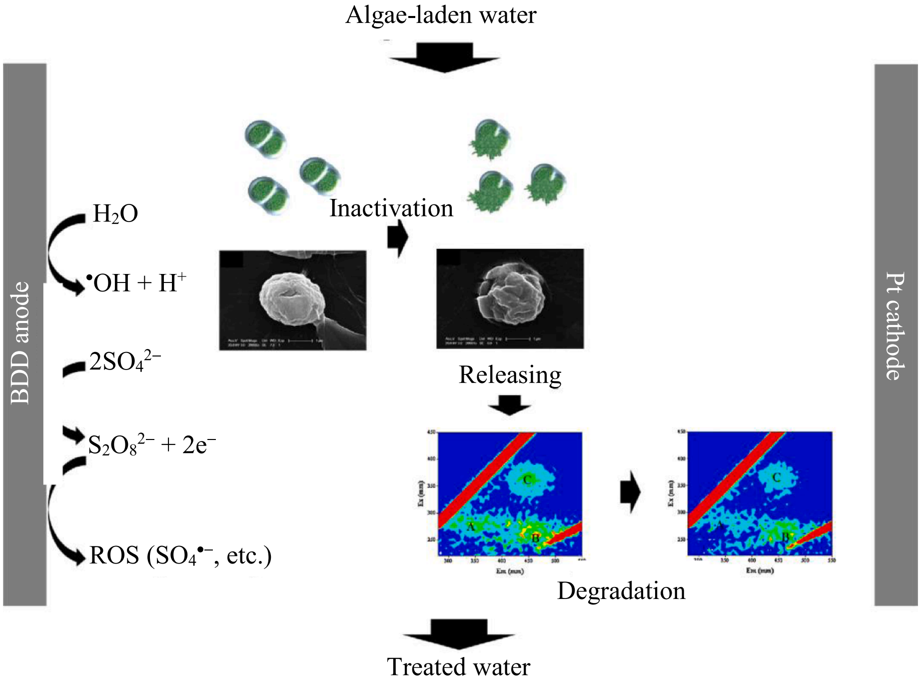

Fig. 5. Proposed schematic diagram for the inactivation of *Microcystis aeruginosa* in sulfate medium by EO with an undivided BDD/Pt cell. Adapted from [18].

The channel flow electrochemical cell design is the most appropriate strategy for different operating modes (discontinuous or continuous with single pass or batch flow) and conditions, allowing the scaling-up of the process [5,24]. An effective electrochemical disinfection scale-up in size, amount or production including contaminated water supply, total microorganism inactivation, product removal, efficient oxidants electrogeneration, and so on, implies a controlled electrolyte flow at a practical pressure drop to a number of larger electrodes [27]. Conversely to stirred batch/tank cells, flow cells have several benefits [24], such as: (i) the reaction environment can be accurately and quantitatively described (mathematical descriptions, computational model, prototype evaluation and simulations [23,24,27]), (ii) higher mass transfer coefficient (controlled by the electrolyte flow rate (laminar, transitional or turbulent) and by turbulence promoters inside to the channel flow in the cells) and higher surface area/volume ratio to promote a faster inactivation lysis and degradation by-products, (iii) electrode size can be increased or stacks of multiple cells can be constructed, (iv) batch recirculation or cascade mode operations can be used to increase significantly the disinfection rates, (v) a great variety of electrode materials and electrode structures can be used, (vi) their components are suitable to be produced in large amounts, (vii) the potential and current distribution can be uniformly maintained by selecting accurate electrode geometry, and (viii) large surface area and porous electrodes can be employed, as well as parallel plate electrodes, 3D-flow-by, filter-press and flow-through electrodes, and rod and tubular electrodes in monopolar, bipolar or mixed arrangement.

Undivided electrochemical flow channel cells are shown in Fig. 8b and 8c and Figs. 9-12, illustrating flow reactors, the electrode material and structure, membrane type, operating mode (continuous and discontinuous), and the approach used to assemble the internal cell compartment. Fig. 8b and 8c show examples for typical undivided cells, batch flow-by-filter-press, and continuous flow-by-filter-press reactors [28,29], respectively, which have been used in the laboratory with centrifugal pumps connected to an individual bacterial suspension-reservoir magnetically stirred. Generally, this type of undivided flow cells for EO disinfection contains a BDD plate as anode (supported on Nb, Si, Ta or Ti) and a material (SS or Pt as well as BDD, DSA, Ti, Zr, W, CF, Fe or Al) plate as cathode, with a separation gap ranging from 0.5 to 1.5 cm. These electrodes are contained in a cell capacity that varies between 45 and 130 mL (several examples are reported in Tables 1–4). The disinfection cell compartment is frequently placed in vertical position to allow that the anolyte circulates, driven by peristaltic pumps, from down to superior solution-outlet favoring well-defined hydrodynamics and rates of mass transfer to/from electrodes, together with ease microorganism supply and gas elimination (see Fig. 8b and c) [28,29], but in some cases, horizontal position is well-employed. The power supply serves to provide a constant current (I) or current density ($j = I/$electrode area) to the two-electrodes cell by operating under galvanostatic mode, determining the cell voltage or potential difference between the electrodes (E_{cell}) that serves to estimate the electrical requirements of each disinfection assay and consequently, the energy consumption per volume unit (EC_V) and economic cost.

Several variants are possible in the undivided electrochemical flow reactors depending on the scale and disinfection requirements (see Figs. 9–12), e.g., systems connected to an individual reservoir, gravity flow from constant head tanks, use of peristaltic pumps, non-recirculating flow (from holding tank to receiving tank, batch and single pass mode, etc.), vertical or horizontal electrodes arrangements, multi-BDD plates systems, and zero-gap reactors separated by ion permeable membranes or microporous materials [23,24,27].

As shown in Fig. 9, undivided electrochemical flow reactors can be also assembled by integrating numerous cell units (e. g.: Diacell® 1001 (see Fig. 9b) can be accommodated with one, two, three, four or more Diacell® 101 modules (see Fig. 9a)), with their electrodes typically connected in bipolar configuration to increase the electrode surface area and consequently, improving the inactivation efficiency [30]. Recent undivided 3D flow reactor with diamond particles (see Fig. 9c) [29], filter-press flow cells with perforated bipolar Al electrodes (see Fig. 9f) [31], and undivided flow cell with multi-anodic BDD plates with cylindrical cathodes (see Fig. 9e) [32] have also been reported. The improvements on the performance of above flow cells include different electrode configuration inside the cells (3D, multi-plates, and perforated) that promote high turbulence, and hence, a more efficient mass transport inside the disinfection compartment cell is attained,

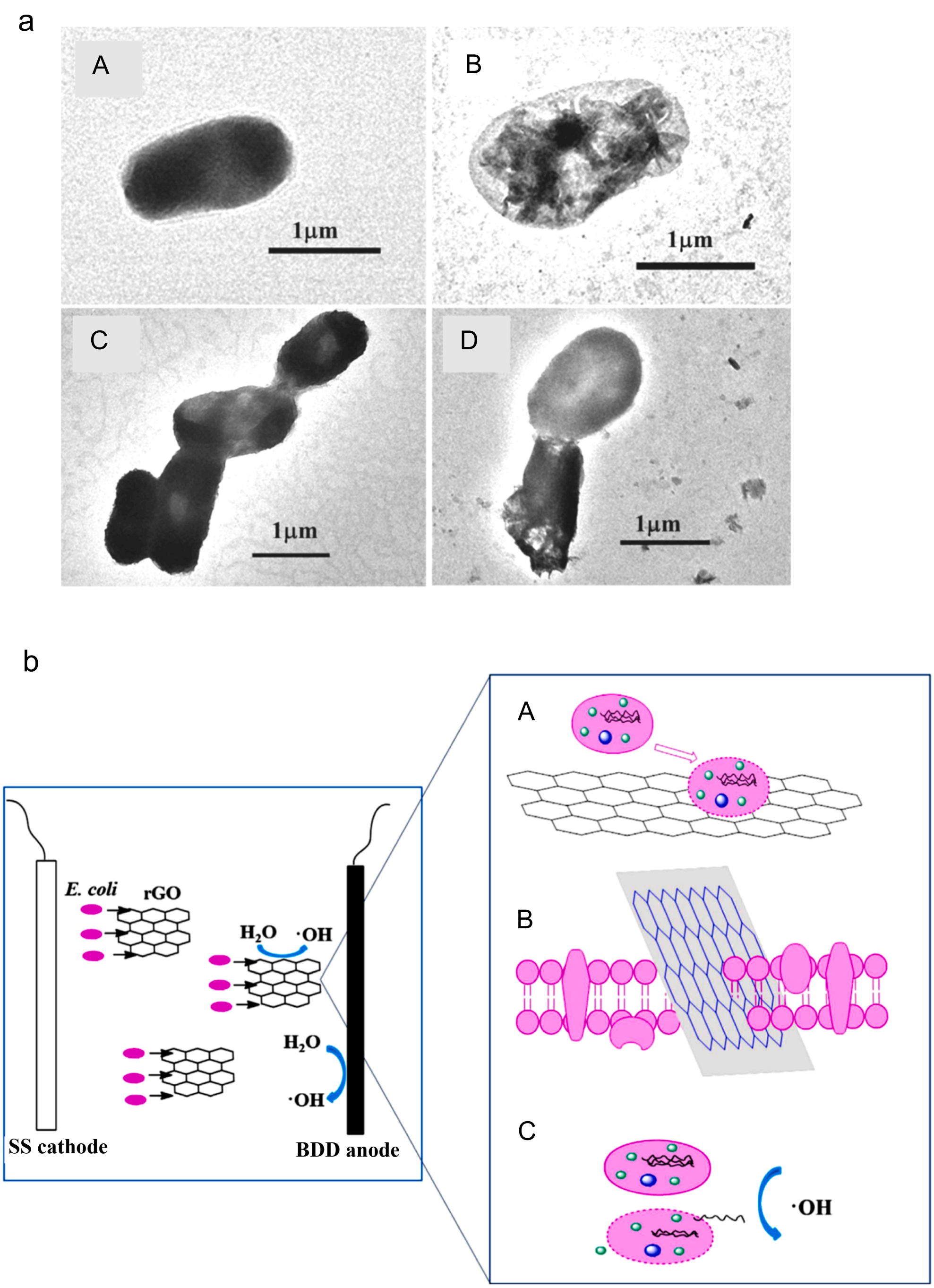

Fig. 6. (a) TEM images of 10^7 CFU mL^{-1} *E. coli* in 0.050 M Na_2SO_4. (A) Untreated bacteria, (B) bacteria after 150 min with 1.0 μg mL^{-1} rGO, (C) bacteria after 60 min of electrolysis using a Nb|BDD/SS cell (4 cm^2 area) at j = 15 mA cm^{-2}, and (D) bacteria after 30 min of electrolysis with a 3D Nb|BDD/SS cell with suspended 1.0 μg mL^{-1} rGO at j = 15 mA cm^{-2}. (b) Schematic graphs for the proposed disinfection mechanism by the hybrid process. Left graph: promoted migration of *E. coli* to the surface of rGO. Right graph: three death mechanisms: (A) Charge transfer between negative charged cell membrane and electronic acceptor rGO, (B) disruption of cell membrane by sharp edges of rGO nanosheets, and (C) oxidation by·$^{\bullet}$OH. Adapted from [19].

inactivating several log cell units of different waterborne pathogen agents at low electric current charges passed. Examples of laboratory flow cells extensively used, such as the typical filter-press electrolyzers, are illustrated in Fig. 9d and f [31,33]. Innovative examples of flow-through cells with a solid polymer electrolyte (SPE) and a polymer exchange membrane-electrolyte–electrode assembly, CabECO® and MIKROZON® cells, are also illustrated in Fig. 10 [34,35].

Generally speaking, the water to be disinfected acts as the electrolyte in the cell, and consequently, its conductivity determines the cell voltage [5]. Therefore, in great number of electrodisinfection studies, a supporting electrolyte is added to the synthetic or real water matrices [5,10,12]. In contrast, the CabECO® cell is completely different (see Fig. 10a and b) because uses a SPE as electrolyte that connects directly the anodic and cathodic materials of the cell (zero-gap technology), thus allowing its efficient use to electrochemically disinfect water matrices with low conductivity with high O_3 production [34]. In this way, ohmic resistance related to the ion transport is reduced, no water conductivity dependence is attained, and the gas formation and bubbles gases interferences are avoided. In the MIKROZON® cell [35], a structured silicon substrate and a double sided BDD coating (5 μm) are used (see Fig. 10c) in ten slots that allow the total contact area of membrane, BDD coating and water, which is crucial for O_3 production to achieve several log pathogen units removals in both continuous and discontinuous operating modes (see Fig. 10d and e). This approach allows preventing the formation of chlorates as a consequence of the very low contact time of the electrode and water. Then, the expected advantages by using flow-through cells with membrane technology are that the hydraulic residence time and the reduced electrode-gap favored a more efficient interaction between the electrochemically produced oxidants (ozone, chlorine, and persulfate among many others at the anode, as well as

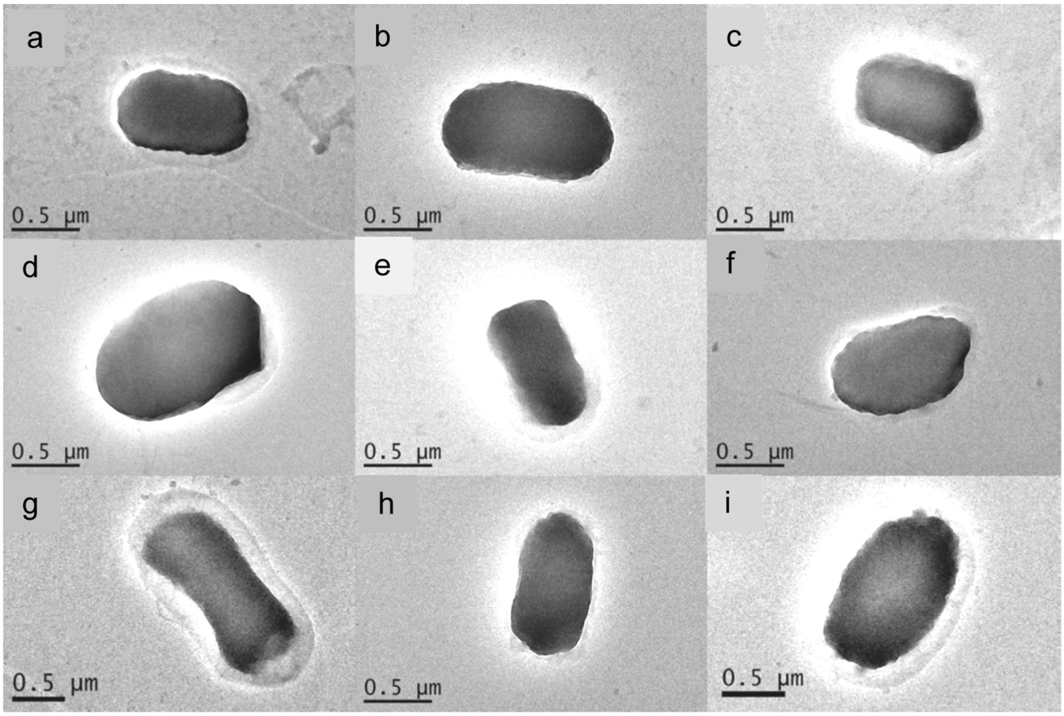

Fig. 7. TEM images of *E. coli* with 2×10^8 CFU mL^{-1} in different media upon EO with an undivided BDD/SS cell at $j = 20$ mA cm^{-2}. In chloride medium: (a) initial, (b) 67% inactivation, and (c) 99% inactivation. In sulfate medium: (d) initial, (e) 69% inactivation, and (f) 99% inactivation. In phosphate medium: (g) initial, (h) 75% inactivation, and (i) 99% inactivation. Adapted from [20].

H_2O_2 by reduction of oxygen at the cathode) and the pathogen agents in the water. Another electrochemical flow type are the multi-cylindrical cells design with mesh-like BDD electrodes structures operating in discontinues and continuous mode for bacteria disinfection [36], as illustrated in Fig. 11. An example of an undivided horizontal electrochemical system with two parallel BDD electrodes, along with SEM images of their surfaces, are shown in Fig. 12 [37].

The classical plane parallel electrode geometry has been extensively incorporated to flow reactors due to many practical advantages (see Figs. 8 and 9). The reaction environment in these cells has been both experimentally and theoretically described, especially in relation to fluid flow, fluid dispersion, mass transfer, potential distribution, and concentration change. An appropriate selection of plane parallel cell design, filter press cell configuration, and electrode material is an important aspect to be considered [23,24,27].

Regarding the diamond materials, a wide range of electrode sizes (from a few cm^2 in the laboratory up to m^2 in pre-pilot electrolysis plants) and connections (monopolar or bipolar) are found, and the operating currents range from the mA to the A scale. Typically, divided and undivided stirred tank reactors or flow cells have been tested by using diamond materials in different forms ranging from coated plates to more complex structures such as diamond coated metal meshes or foams, powders, composites, perforated supports, conductive wires, and nanostructures [5,27]. Additionally, surface area, roughness, support conductivity, and activity towards redox reactions are considered important features on the synthetic diamond films to improve their chemical stability, large overpotential for oxygen and hydrogen evolution, wettability, high electrocatalytic activity, selectivity, and their mechanical properties that become essentials in the large cell stacks [27]. In fact, cost, availability, service life, and maintenance requirements are important practical aspects that are directly and intrinsically linked to the features described above, and these have limited its applicability for the wastewater treatment at large scale, but these restrictions cannot be significant in specialized small-scale disinfection devices, allowing the commercialization of the diamond electrodisinfection devices [5,27]. Another important factor is that other catalysts can be applied on the diamond film surface by electrodeposition, electroless coating, 3D printing, dipping coating, or standard varnishing techniques, as well as by physical or chemical vapor deposition, to enhance its electrocatalytic activity and selectivity. The development of micro- and nanostructured diamond materials to provide new substrates and catalysts is also an exciting trend [27].

While many electrochemical disinfection studies using undivided agitated beakers or undivided stirred tanks have been reported in the existing literature (see Tables 1–4), no concrete information concerning efficiency and energy consumption can be obtained from these data to envisage the commercialization of this approach. Thus, an accurate methodology has to use electrochemical flow systems for analyzing the disinfection results to assess in single or comparative approach the cell design, the kinetics and mechanisms, and the effect of operating conditions over the inactivation of pathogen agents, the removal of organic load, and the detection of disinfection by-products, along with an efficient oxidizing species production to perform a gradual technological scale-up.

4.2. *Electrochemical oxidation*

The preference showed by the scientific community to apply EO as disinfection approach is due to its simplicity and popularity among the EAOPs, in terms of electrolytic technology and production of oxidants [5]. In fact, this simplest approach has already demonstrated its efficacy to mineralize different organic compounds in wastewaters. However, the effectiveness of this procedure depends on the nature of the anode material because it determines the nature of the electrogenerated oxidants and their oxidation power [22,26,38]. This section is devoted describing the fundamentals of EO, followed by its application to electrodisinfection in free-chloride and chloride matrices using a BDD anode.

Table 1

Selected results obtained for the inactivation of bacteria in synthetic free-chloride media by electrochemical oxidation (EO) using an undivided stirred tank reactor with a BDD anode. ⊥ Only one work was performed with a divided stirred reactor.

Anode/cathode	Effluent	Electrolysis conditions	Main results	Ref.
Escherichia coli				
Nb|BDD plate/Pt sheet, 6 cm^2 area	80 mL of 0.2 M phosphate buffer (pH 7.2), with cell suspension of 10^6 CFU mL^{-1}, 25 °C	j[a] = 33–100 mA cm^{-2} for 30 min	4.5 log cell reduction: 20 min (50 mA cm^{-2}) 5 min (100 mA cm^{-2}) TEM and AFM images of cells	[9]
Si|BDD plate/SS[b] plate, 3 cm^2 area	100 mL of 7 mM Na_2SO_4, with cell suspension of 10^6 CFU mL^{-1}, pH 3.0 and 7.0, 25 °C	j = 33.3 mA cm^{-2} for 45 min	6 log cell reduction at both pH values. Low TOC removal. Inactivation kinetics using a logistic model. SEM images of cells	[16]
Ni|BDD plate/SS plate, 4 cm^2 area	250 mL of 40–45 mM sulfate or phosphate, with cell suspension of 2 × 10^8 CFU mL^{-1}	I[c] = 80 mA up to 600 min	2 log cell reduction at 72 min (sulfate) or 600 min (phosphate). Inactivation mechanism from changes of TOC, total protein, K^+ leakage, membrane potential, cell permeability, etc. TEM images of cells	[20]
Nb|BDD plate/SS plate, 4 cm^2 area	200 mL with 10^5 CFU mL^{-1} cells in 0.2 M Na_2SO_4 at pH 7. Inactivation was evaluated in the absence and presence of organics (DMP[d], DEP[e], phenol, resorcinol and THB[f].	j = 20 mA cm^{-2}, 60 min	5.78 log inactivation in 40 min in absence of organics. However, 4 log units in 60 min when DMP was added. When resorcinol concentration increased from 0 to 0.03 mM, inactivation decreased from 5.40 to 3.24. Complete degradation was established in 40 min at pH 10 and 47 min at pH 7.	[25]
Si|BDD plate/SS plate, 30 cm^2 area	250 mL of 1 mM Na_2SO_4, three microorganism solutions of 6.4 × 10^2 CFU mL^{-1}.	j = 5–10 mA cm^{-2}, 300 s.	Reduction of microorganism populations to the detection limit is achieved in 60, 100 and 300 s for *E. coli*, coliforms and *E. faecalis*, respectively.	[48]
Nb|BDD plate/SS plate, 4 cm^2 area	200 mL of 0.005, 0.05, 0.1 or 0.2 M Na_2SO_4 plus 4 mL of phosphate buffer solution (pH 7.1, c = 0.1 M). Microorganism solutions of 10^7 CFU mL^{-1}. Comparison with NaH_2PO_4 and $NaNO_3$	j = 5–40 mA cm^{-2}, 40 min	*E. coli* in 0.2 M Na_2SO_4 without electrolysis after 2 h was not inactivated. Inactivation rate increased with j, being optimal at 20 mA cm^{-2}. Higher oxygen production reduces the inactivation at 40 mA cm^{-2}. Inactivation increased when Na_2SO_4 concentration grew due to the role of $S_2O_8^{2-}$. Lower inactivation by using NaH_2PO_4 and $NaNO_3$ as electrolytes.	[49]
Five different electrode materials, including Nb|BDD/SS, 6 cm^2 area. ⊥Divided cell with a Nafion® 117 cation exchange membrane.	100 mL of effluent with 10^5–10^6 CFU mL^{-1} cells, pH 7.1 and 25 °C in 0.2 M KH_2PO_4, adding or not 0.05 M *t*-BuOH.	j = 100 mA cm^{-2}, 3 min	2.4 log cell inactivation at BDD after 3 min without *t*-BuOH. Inactivation was inhibited by the addition of 0.05 M *t*-BuOH. 1.3 log inactivation was achieved at Pt for 3 min without *t*-BuOH. No inactivation was achieved with Ti|RuO_2, Ti|Pt–IrO_2 and Ti|IrO_2 anodes.	[50]
Other bacteria				
Si|BDD plate/SS plate, 3 cm^2 area	100 mL of 7 mM Na_2SO_4, with suspension of 10^6 CFU mL^{-1} of *Bacillus atrophaeus*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Enterococcus hirae*, pH 3.0 and 7.0, 25 °C	j = 33.3 mA cm^{-2} for 45 min	6 log cell reduction at pH 3.0 for *B. atrophaeus, S. aureus* and *P. aeruginosa*. 5 log cell reduction at both pH values for *E. hirae*. SEM images of cells	[16]
Si|BDD plate/ SS plate, both electrodes with 12.5 cm^2 area	4 L of 50 mM Na_2SO_4 (conductivity 9.35 μS cm^{-1}) with 1.8 × 10^6 CFU mL^{-1} of *Cylindrospermopsis raciborskii*. Chl a[g] ≈ 110 μg L^{-1}, Carotenoids ≈ 43.79 μg L^{-1}, Fv/Fm ≈ 0.44. Na_2SO_4: 100, 25 and 2 mM (15.35, 4.57 and 0.512 μS cm^{-1}, respectively) and *Cyanotoxin cylindrospermopsin*.	j = 0–12.5 mA cm^{-2} for 180 min	70% (2.5 mA cm^{-2}), 76% (7.5 mA cm^{-2}), or 95% (10 and 12.5 mA cm^{-2}) cell removal at 180 min and about 72, 74, 85 and 90% of Chl a, respectively. Complete inactivation in 45 min. *Cylindrospermopsin* concentration reduced from 1.83 to <0.05 μg L^{-1} in 30 min by the action of $^{\bullet}OH$, $SO_4^{\bullet-}$ and subsequently $S_2O_8^{2-}$.	[17]
Nb|BDD, Ti/IrO_2-Ta_2O_5 or Pt anode/ SS plate, all electrodes with 10 cm^2 area	200 mL of 30 mM electrolyte (Na_2SO_4, $NaNO_3$, Na_2HPO_4) with 1.0 ~ 4.0 × 10^6 CFU mL^{-1} *Microcystis aeruginosa* cells	j = 50–200 mA cm^{-2} for 60 min	10%–20% cells inactivated when Ti/IrO_2-Ta_2O_5 and Pt anodes were used at 200 mA cm^{-2} with Na_2SO_4, $NaNO_3$, Na_2HPO_4. 54.4%, 62.3%, and 99.1% of cells inactivated with BDD in $NaNO_3$, Na_2HPO_4 and Na_2SO_4, respectively.	[18]
Four Si|BDD plates/SS plate (central cathode), 30 cm^2 area	250 mL of 1 mM Na_2SO_4 containing 4.4 × 10^3 CFU mL^{-1} of *Enterococcus faecalis.*	j = 5–10 mA cm^{-2}, 120 s in batch	Cell reductions from initial concentration to 50% and to the detection limit in 120 and 300 s at 10 mA cm^{-2} and Re = 1 × 10^4.	[48]
Ti|BDD rectangular/Ti|BDD rectangular, 7.5 cm^2 area	80 mL of free-chloride surface water (pH 6.6, 18 mg L^{-1} TOC, 0.870 and 0.183 mg L^{-1} of NO_3^- and NO_2^-), with suspension of 6750 CFU mL^{-1} of total coliforms and 5600 CFU mL^{-1} of fecal coliforms	j = 2, 11 and 20 mA cm^{-2} up to 12 min	92%, 96% and 100% disinfection for 2, 11 and 20 mA cm^{-2}, respectively. 25% TOC removal, 79% NO_2^- decay and 65% of NO_3^- increase at 10 mA cm^{-2} for 20 min	[52]

[a] j: current density.
[b] SS: stainless steel.
[c] I: current.
[d] DMP: dimethylphthalate.
[e] DEP: diethyl phthalate.
[f] THB: *m*-trihydroxybenzene. Fv/Fm: physiological test.
[g] Chl a: Chlorophyll *a* concentrations can be used as indirect biomass measurements for cell integrity.

4.2.1. Fundamentals

In EO, the oxidation of organic matter in wastewaters occurs in the electrolytic cell by:

(i) Direct oxidation by a direct electron transfer to the anode, and
(ii) mediated oxidation by the electrogeneration of oxidizing species from water discharge or supporting electrolyte oxidation at the anode at high *I*.

In the former case, a poor wastewater depollution is achieved, while a partial or total decontamination is attained in the latter.

A great variety of heterogeneous oxidizing species can be formed from water discharge and other oxidant precursors, favoring a selective (electrochemical conversion) or complete (electrochemical combustion or electrochemical incineration) oxidation of the organics in wastewaters [39]. As already stated in the existing literature, the oxidation power of the above oxidants is relied to the electrocatalytic material used, and consequently, affecting the efficiency of the EO process. A comprehensive model explains this behavior when only water discharge occurs, classifying the anodes in two general cases [40]: active and non-active. It is assumed that, in both kinds of anodes (denoted as M), the formation of physisorbed hydroxyl radicals ($M(^{\bullet}OH)$) is attained by the oxidation of water from Eq. (1). Depending on the electrode material, these heterogeneous $M(^{\bullet}OH)$ interact strongly or weakly with the anode surface. For active anodes, higher oxides or superoxides (MO) are formed from Eq. (12), while only $M(^{\bullet}OH)$ is produced from Eq. (1) at non-active anodes.

$$M(^{\bullet}OH) \rightarrow MO + H^+ + e^- \qquad (12)$$

It is important to indicate that MO is formed as chemisorbed “active oxygen” when higher oxidation states are available on M surface, above the standard potential for oxygen evolution ($E^{\circ} = 1.23$ V vs. SHE), and after that, it participates as mediator via Eq. (13) in the selective oxidation of organics (so called electrochemical conversion), which occurs generally at metal oxide anodes.

$$MO + R \rightarrow M + RO \qquad (13)$$

The direct reaction of free $M(^{\bullet}OH)$) or physisorbed $M(^{\bullet}OH)$ with organics leads to CO_2 and water (commonly named as electrochemical incineration) by Eq. (14):

$$a\, M(^{\bullet}OH) + R \rightarrow M + m\, CO_2 + n\, H_2O + x\, H^+ + y\, e^- \qquad (14)$$

where R is an organic compound with *m* carbon atoms and without any heteroatom, which needs $a = (2\,m + n)$ oxygen atoms to be totally mineralized to CO_2.

Both oxidative reactions via Eq. (13) and (14) compete with the side reaction of O_2 evolution given by Eq. (15) and (16), affecting the efficiency of the EO process.

$$MO \rightarrow M + \tfrac{1}{2}\, O_2 \qquad (15)$$

$$M(^{\bullet}OH) \rightarrow M + \tfrac{1}{2}\, O_2 + H^+ + e^- \qquad (16)$$

In the case of $M(^{\bullet}OH)$, an indirect consumption through dimerization to hydrogen peroxide is also attained close to the anode surface by Eq. (17) or in the reaction cage by Eq. (7), as well as its reaction with the latter species to form the weaker oxidant hydroperoxyl radical ($M(HO_2^{\bullet})$) by Eq. (18). Ozone, another weaker oxidant, can also be generated from water discharge at the anode ($E^{\circ} = 1.51$ V vs. SHE) by Eq. (19). Nevertheless, heterogeneous $M(^{\bullet}OH)$ is the strongest ROS that mainly attacks the organics in front of H_2O_2, $M(HO_2^{\bullet})$, and O_3, although these oxidants also become relevant for the inactivation of bacteria in free-chloride media by EO [41].

$$2\, M(^{\bullet}OH) \rightarrow 2\, M + H_2O_2 \qquad (17)$$

$$2\, M(^{\bullet}OH) + H_2O_2 \rightarrow M(HO_2^{\bullet}) + H_2O \qquad (18)$$

$$3\, H_2O \rightarrow O_3 + 6H^+ + 6\, e^- \qquad (19)$$

Typical examples of active and non-active anodes are Pt, IrO_2, and RuO_2 for the former and PbO_2, SnO_2, and BDD for the latter. In both cases, simultaneous oxidation of water and pollutants is attained by applying high cell voltages to the electrochemical cell, thus maintaining the anode activity. Although O_2 evolution can be largely avoided by applying low cell voltages, the anode activity could be lost because of the adsorption on its surface of some by-products formed from direct anodic oxidation. This effect is not achieved at non-active anodes because no catalytic active sites are provided to favor direct anodic reactions or adsorption of by-products on their surfaces. In this context, BDD films are considered the best non-active anodes in EO due to their great effectiveness to mineralize different organics in wastewater treatment by $M(^{\bullet}OH)$, since produce more quantities of [42] or other oxidants at their surfaces. Thus, its application in disinfection is a promising alternative. When BDD films are used, other weaker oxidizing species like peroxodisulfate, peroxodicarbonate, and peroxodiphosphate can also be competitively formed with ROS from the corresponding anodic oxidation of sulfate (or bisulfate) by Eq. (9), bicarbonate by Eq. (10) and phosphate by Eq. (11) present in the water matrices. It is important to indicate that $S_2O_8^{2-}$ is a weaker oxidant that is formed by dimerization of the sulfate radical anion ($SO_4^{\bullet-}$), which is a strong oxidant. The formation and concentration of $SO_4^{\bullet-}$ depends on pH and the participation of heterogeneous $^{\bullet}OH$ formed at the diamond surface [41], as follows:

$$2\, HSO_4^- \rightarrow S_2O_8^{2-} + 2H^+ + 2e^- \qquad (20)$$

$$HSO_4^- + {}^{\bullet}OH \rightarrow SO_4^{\bullet-} + H_2O \qquad (21)$$

$$SO_4^{2-} + {}^{\bullet}OH \rightarrow SO_4^{\bullet-} + OH^- + e^- \qquad (22)$$

In section 4.2.2., several examples will be given to remark the comparative bacteria inactivation by electrochemical disinfection by using BDD anodes in free-chloride medium.

A very different behavior is found when different water matrices or solutions containing chloride are treated by EO [22,43,44]. This process becomes more relevant than mediated oxidation by ROS, preferentially by heterogeneous $M(^{\bullet}OH)$, because it competes with the electrogenerated active chlorine species (mainly $Cl_2(aq)$, HClO and/or ClO^-) formed from Cl^- oxidation at the anode. The anodic oxidation of Cl^- to $Cl_2(aq)$ via Eq. (2) is the first step. After that, the hydrolytic disproportion of $Cl_2(aq)$ to HClO is attained by Eq. (3), which is in equilibrium with ClO^- ($pK_a = 7.54$) by Eq. (23):

$$HClO \leftrightarrow ClO^- + H^+ \qquad (23)$$

As stated in the Introduction, electrochemical disinfection in chloride medium emerges as one of the more interesting alternatives to chlorination because this option allows to produce in situ active chlorine species that is a great advantage to inactivate or decrease the concentration of several infectious agents in water. The predominance of these active chlorine species to guarantee an effective disinfection strategy depends on the pH conditions of solutions, wastewaters, or water matrices: $Cl_2(aq)$ ($E^{\circ} = 1.36$ V vs. SHE) up to pH 3.0, HClO ($E^{\circ} = 1.49$ V vs. SHE) in the pH interval 3.0–8.0 and ClO^- ($E^{\circ} = 0.89$ V vs. SHE) at pH > 8.0 [22,43,44]. Considering that HClO is the strongest agent, the disinfection action of active chlorine becomes more potent in acidic medium. Nevertheless, it is important to remark that the effectiveness of electrochemical chlorine disinfection is limited by the production of chlorite (ClO_2^-), chlorate (ClO_3^-) and perchlorate (ClO_4^-) ions, as exemplified by Eq. (24)-(26) [22,43,44]:

$$ClO^- + H_2O \rightarrow ClO_2^- + 2H^+ + 2\, e^- \qquad (24)$$

$$ClO_2^- + H_2O \rightarrow ClO_3^- + 2H^+ + 2\, e^- \qquad (25)$$

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2\, e^- \qquad (26)$$

Table 2
Relevant data obtained for the inactivation of *Escherichia coli* in chloride media by EO with a BDD anode.

Electrochemical cell	Anode/cathode	Effluent	Electrolysis conditions	Main results	Ref.
Potable water					
Undivided stirred tank reactor	Si|BDD rectangular/Ti mesh, 10 cm^2 area	400 mL of stormwater, with *E.coli* and 3 pathogens suspension between 238 and 9001 CFU (100 mL)$^{-1}$, pH 6.7–7.6	$j = 4.2$ mA cm^{-2} for 30 min	Total disinfection or >95.7% cell reduction. Disinfection by-products detected	[53]
Undivided stirred tank reactor	Si|BDD rectangular or DSA [a]-Ti|Ir$_{0.2}$Ru$_{0.4}$Ti$_{0.6}$O$_2$ rectangular/Ti mesh, 10 cm^2 area	400 mL of synthetic stormwater, with *E. coli* suspension of 12,,000 CFU (100 mL)$^{-1}$	$j = 1.75$ and 4.2 mA cm^{-2} for 30 min	Total disinfection: 15 and 2 min (DSA), 15 and 6 min (Si|BDD) for 1.75 and 4.2 mA cm^{-2}, respectively. Inactivation inhibition with *t*-butanol using Si|BDD, no for DSA	[54]
Undivided stirred tank reactor with horizontal electrodes	Nb|BDD squared mesh/Nb|BDD squared mesh, 100 cm^2 area	800 mL of tap water, with cell suspension of 10^4 CFU mL^{-1} of *E. coli*, *P. fluorescens*, *P. aeruginosa*, and *B. subtilis* spores	$j = 0.6$–2.0 mA cm^{-2}	Time for total disinfection, Q [b] and EC$_V$ [c]: 143 min, 0.15 Ah L^{-1}, 0.696 kWh m^{-3} (0.6 mA cm^{-2}), or 5.5 min, 0.017 Ah L^{-1}, 0.104 kWh m^{-3} (2.0 mA cm^{-2}).	[37]
Diachem® W cell	Nb|BDD plate (2 μm thickness)/Ti-Pt plate, 77.4 cm^2 area	2 L of artificially contaminated river water with 10^7–10^8 CFU mL^{-1}of *E.coli*, *P. aeruginosa* and *L. pneumophila.* Other microorganisms 1 × 10^5 CFU mL^{-1}. Flow rate of 100, 250 and 500 mL min^{-1}. NaCl content of 0.1, 0.45 and 0.85%. *L. pneumophila* ≈ 10 × 10^7 CFU mL^{-1}	E_{cell} [d] = 3–5 V for 150 min	By electrolyzing a 0.1% NaCl solution at 3 V and 250 mL min^{-1}, total inactivation of *E. coli* (96 min) and *P. aeruginosa* (>150 min). Application of 4 V, 250 mL min^{-1} and 64 min to eliminate *L. pneumophila*	[28]
CONDIAPURE® glass system with an undivided Diachem® cell	Si|BDD rectangular/Si|BDD rectangular, 12 cm^2 area	3 L of drinking water, with cell suspension of 10^8 CFU mL^{-1} of *E. coli*, *Enterococcus faecium* and *P. aeruginosa*	$j = 42$, 208 and 333 mA cm^{-2} (O$_3$ production) in batch	Time for total disinfection, Q and EC$_V$: 30 min, 0.096 Ah L^{-1}, 0.0157 kWh m^{-3} (42 mA cm^{-2}), 10 min, 0.143 Ah L^{-1}, 0.0048 kWh m^{-3} (208 mA cm^{-2})	[55]
Undivided Diacell® 101 (1 compart.) and Diacell® 401 (4 parallel compart.)	Si|BDD circular/Si|BDD circular, 67 cm^2 area	5 L of tap water without and with 1 g L^{-1} NaCl and 60–800 mg L^{-1} COD (from lettuce), with *E. coli* suspension of 10^5 CFU mL^{-1}, pH 6.5, 5 °C, flow rate 800 L h^{-1}	$j = 2.4$ or 21.6 mA cm^{-2} up to 120 min in batch	Total disinfection: 0.9 min (no NaCl, 60 mg L^{-1} COD, $Q = 0.02$ Ah L^{-1}), 0.2 min (with NaCl, 60 mg L^{-1} COD, $Q = 0.003$ Ah L^{-1}). Disinfection kinetic models. Free, combined and total chlorine analysis	[55]
Undivided flow-through cylindrical cell	2 Nb|BDD circular mesh/2 carbon felt, 15 cm diameter, 12 cm height	100 L of swimming pool water, with suspension of 10^2 CFU (100 mL)$^{-1}$ *E. coli* and *P. aeruginosa*, pH 7.5, flow rate 2 L min^{-1}	$I = 1.5$ A for 30 min in batch	Total disinfection. A time of 60 min was needed using a Ti|Pt anode at 3.0 A. Evolution of ClO$^-$ and ClO$_4^-$	[56]
Urban wastewater					
Undivided stirred tank reactor	Si|BDD rectangular (19 cm^2 area)/Zr rectangular	115 mL of secondary WWTP [e] effluent, 27 mg L^{-1} COD, with *E. coli* suspension of 1250 CFU mL^{-1} and 100 μg L^{-1} 17α-ethynylestradiol (EE2)	$j = 0.9$–2.6 mA cm^{-2} up to 30 min	Total disinfection and overall EE2 removal in 5 min at 2.1 mA cm^{-2}. 85% COD decay at 30 min	[58]
Undivided flow-through filter-press cell	Nb|BDD plate/Nb|BDD plate, 48 cm^2 area	1 L of secondary WWTP (conductivity 970–1218 μS cm^{-1}, pH 7.9–8.1, TOC: 8.9–10.5 mg L^{-1}, Cl$^-$: 119–161 mg L^{-1}, HCO$_3^-$ 140–150 mg L^{-1}) an model waters with *E. coli* suspension of 10^6 CFU mL^{-1}.	$j = 2.5$ – 120 mA cm^{-2}	WWTP water: 1.4 min for 4 log cell reduction at 120 mA cm^{-2} and 60 min for 3 log cell reduction at 2.5 mA cm^{-2}. For model water: 1.4 min for 4 log cell reduction at 7.5 mA cm^{-2} (Cl$^-$ 0 mg L^{-1}, HCO$_3^-$ 0 mg L^{-1}) and 20 min for 4 log cell reduction at 7.5 mA cm^{-2} (Cl$^-$ 0 mg L^{-1}, HCO$_3^-$ 145 mg L^{-1}), consuming 0.045 and 0.66 kWh m^{-3}, respectively. 3 log cell reduction in 13 min at 35 °C and 21 min at 9 °C. Laminar flow is better than turbulent	[59]
Undivided flow-through electrochemical cell	Four latticed Nb|BDD (54 cm^2) as anodes and cathodes	5 L of wastewater from a municipal sewage treatment plant with *E. coli* suspension of 10^5 CFU (100 mL)$^{-1}$, 173 mg L^{-1} NaCl at pH 7.3. Temperature 6–30 °C and flow rate 25–125 L h^{-1}	$j = 15$ – 105 mA cm^{-2} for 20 min	Production rate of free chlorine at range of 25–125 L h^{-1} varied from 24 to 30 mg (Ah)$^{-1}$. Disinfection improves by increasing the temperature. *E. coli* at $T > 6$ °C, pH < 8.5, TOC < 22 mg L^{-1} proceedingeffectively with $Q =$ 0.10–0.15 Ah L^{-1} related to EC$_V$ = 2.0–2.6 kWh m^{-3}.	[60]
Mini Diacell® 101 PP	Si|BDD circular /Si|BDD, 12.5 cm^2 area	20 L of WWTP taken during a period of eight months (Oct. 2007–Dec. 2009) with NaCl ranging from 60 to 1050 mg L^{-1}, and initial *E. coli* concentration ranging from 1.3 × 10^4 to 5.2 × 10^5 CFU mL^{-1}, pH 7.4, 18.1 °C, flow rate 500 L h^{-1}	$I = 0.5$, 1 and 1.5 A (40, 80, 120 mA cm^{-2}) for 40 min	Cell reduction up to 234 (40 min), 0 (20 min) and 0 (10 min) CFU mL^{-1} for 40, 80, and 120 mA cm^{-2} with Cl$^-$ ranging from 39.8 to 77.3 mg L^{-1}. > 99.5% cell deactivation when Cl$^-$ varied from 60 to 1050 mg L^{-1}, after 1 h. In several cases, the Spanish legislation limit was achieved after 15	[61]

(*continued on next page*)

Table 2 (*continued*)

Electrochemical cell	Anode/cathode	Effluent	Electrolysis conditions	Main results	Ref.
				min. Trihalomethanes formed <100 mg L^{-1}	
Undivided flow-through filter-press cell	Si|BDD circular/Si|BDD circular, 78 cm^2 area	600 mL of secondary WWTP effluent, with *E. coli* suspension of 2800 CFU $(100\ mL)^{-1}$, flow rate 25 L min^{-1}	$j = 0.13$, 1.3 and 13.0 mA cm^{-2} up to 120 min in batch	Total disinfection at 120 min for 0.13 mA cm^{-2}, but in <5 min at higher *j*. Oxidants: ClO^- and chloramines. ClO_3^- and ClO_4^- not formed at 0.13 mA cm^{-2}	[62]
Undivided flow-through filter-press cell	Si|BDD circular/SS circular, 78 cm^2 area	600 mL of three secondary WWTP effluents, with *E. coli* suspension of 16,000 CFU $(100\ mL)^{-1}$, flow rate 25 L min^{-1}	$j = 0.13$–1.3 mA cm^{-2} up to 180 min in batch	Inactivation: 1.6 log cells at 180 min (0.13 mA cm^{-2}) and 4.2 log cells at 40 min (1.3 mA cm^{-2}). $EC_V < 0.2$ kWh m^{-3}. Evolution of ClO^-, ClO_3^-, ClO_4^-, $CHCl_3$ and chloramines	[63]
Undivided flow-through filter-press cell	DSA rectangular (80 cm^2 area) or Si|BDD circular (68 cm^2 area)/ carbon felt rectangular (350 cm^2 area)	3 L of O_2-saturated secondary WWTP effluent for H_2O_2 production, with *E. coli* suspension of 5400–24,000 CFU (100 mL^{-1}), pH 8.2–8.5	$j = 0.125$–2.5 mA cm^{-2} in batch	Total disinfection: DSA (2.5 mA cm^{-2}, $Q = 0.03$ Ah L^{-1}). Si|BDD (all $j > 0.439$ mA cm^{-2}, *Q* from 0.01 to 0.02 Ah L^{-1}, $EC_V < 0.2$ kWh m^{-3}). Evolution of H_2O_2, ClO^- and chloramines	[64]
Undivided flow-through filter-press cell	Si|BDD circular/SS circular, 78 cm^2 area	Synthetic secondary WWTP effluent with suspension of 10^7 CFU mL^{-1} of *E. coli*, *K. pneumoniae* and *E. faecalis*	$j = 1.0$ mA cm^{-2} in batch	7 log cell reduction, $Q = 0.03$ Ah L^{-1}. Evolution of ClO^-, $ClO_3^{-\cdot}$ and chloramines	[65]
Diacell® type 401 or Diacell® 1001 cell	Diacell® type 401 with 1–4 compartments: bipolar Si|BDD/ SS, 70 cm^2 area. Diacell® 1001 with 1–10 compartments: monopolar Si| BDD/5 SS, 70 cm^2 area	4 L of WWTP, with *E. coli* suspension of: 5400–9100 CFU $(100\ mL)^{-1}$, $Cl^{-:}$ 165 mg L^{-1}, $SO_4^{2-:}$ 261.85 mg L^{-1}, TOC: 14.95 mg L^{-1}, COD: 25 mg O_2 L^{-1}, pH 7.85–8.25, flow rate 50 L h^{-1}	$j = 0.014$–1 mA cm^{-2}	4 log cell inactivation at 0.05 A with the Diacell® 1001 equipped with 3 modules after $Q = 0.0035$ Ah L^{-1}, producing NH_2Cl, $NHCl_2$, NCl_3; hypochlorite; ClO_3^-; and ClO_4^-. 4 log cell inactivation at 0.01 A with the Diacell® type 401 equipped with bipolar electrodes after $Q = 0.002$ Ah L^{-1}. Higher formation of chloramines	[66]
Single compartment electrochemical cell Diacell® type 101 , Diacell® 1001 and commercial pilot plant with five parallel Diacell® 1001	Diacell® type 101: Si|BDD plate/ SS plate, 78 cm^2 area. Diacell® 1001: Five cells with 10Si|BDD electrodes/5 SS plates, 700 cm^2 area. Commercial pilot plant with five parallel Diacell® 1001: 50Si| BDD electrodes/25 SS plates, 3500 cm^2 area	4 L or 300 L of urban wastewater intensified with 100 mg L^{-1} of caffeine, Flow rate 21.4 or 50 L h^{-1}, Cl^-:110–180 mg L^{-1}, SO_4^{2-}: 120–400 mg L^{-1}, TOC: 12–14 mg L^{-1}, COD: 35–42 mg O_2 L^{-1}, pH 7.8–8.5. *E. coli:* 9100 MPN $(100\ mL)^{-1}$ for Diacell® type 101 and 1001, and 5400 MPN $(100\ mL)^{-1}$ for commercial pilot plant	$j = 1.20$ mA cm^{-2}	Complete cell reduction was achieved with Diacells® 101 (4 L) and 1001 (4 L), as well as the commercial pilot plant (300 L) at *Q* of 0.002, 0.01 and 0.013 Ah L^{-1}, respectively. Higher concentration of oxychlorinated species and chloramines in the bench-scale plant. No production of chlorate in the pilot	[30]
CabECO® cell	4 Nb|BDD mesh/electrodes in contact with a cation exchange membrane, 24 cm^2 of total area	100 L of WWTP effluent with total coliforms: 399,978 CFU (100 mL^{-1}, *E. coli*: 18,733 CFU $(100\ mL)^{-1}$, *P. aeruginosa:* 15 CFU $(100\ mL)^{-1}$, Cl^-: 75.0 mg L^{-1}, $SO_4^{2-:}$ 14.8 mg SL^{-1}. pH 7.8. Flow rate 90 – 300 L h^{-1}	$j = 41.67$–166.67 mA cm^{-2}, 60 min	Total disinfection achieved at 90 L h^{-1} and 166.67 mA cm^{-2}. <0.05 Ah L^{-1} required to remove around 3 and 4 log units. Sterilization is less efficient and only 2-log units are attained after 0.05 Ah L^{-1}	[67]
ConDiacell® type ECWP [f] and CabECO® cells	ConDiacell® type ECWP: undivided cell with 5 flow-through Nb|BDD (420 mm^2 each)/ SS. CabECO® cell: BDD mesh/BDD mesh, 24 cm^2 active area, in contact with a perfluorinated ion-exchange membrane	5–300 L of WWTP effluents modified by the addition of strains of *E. coli* (10^4 CFU mL^{-1}) and *P. aeruginosa* (10^5 CFU mL^{-1}). Continuous or discontinuous mode used	$j = 0$ – 19.04 mA cm^{-2}	Cell design influences on the performance of electrodisinfection. Both commercial cells attained good disinfection levels up to 3 or 5 log pathogen removal until $Q = 0.04$ Ah L^{-1}. Continuous is more efficient than discontinuous operation mode. Pathogen removals are at least one log higher in continuous mode. No ClO_3^- and ClO_4^-, <2 μg L^{-1}, in continuous mode with ConDiacell® type ECWP	[68]
CabECO® cell	BDD mesh/BDD mesh, 24 cm^2 active area, in contact with a perfluorinated ion-exchange membrane	5 L of groundwater with a mixture of ~ 200 MPN $(100\ mL)^{-1}$ of *E, coli* (and coliforms), *E. fecalis*, *P. aeruginosa* and *L. pneumophila*	$I = 0.31$–2.30 A for 120 min in batch	Complete inactivation of *E. coli*, coliforms and *E. fecalis* in 30, 10 and 15 min for 0.93, 1.24 and 2.30 A, respectively. No COD reduction. Evolution of O_3, active chlorine and total chorine, ClO_3^- and ClO_4^-	[69]
Synthetic urine					
Diamonox 40 cell	Nb|UNCD [g] plate (2 μm thickness)/W plate, 42 cm^2 area	2 L of synthetic urine (+0, 1 and 5% (w/v) fecal matter), with *E. coli* suspension of 10^9 CFU $(100\ mL)^{-1}$	$E_{cell} = 4$–12 V up to 50 min	Cell reduction below 10^3 CFU (100 mL^{-1}) in 5, 8, 16, 25 and 34 min at 12, 10, 8, 6 and 4 V, respectively. Production of significant total chlorine concentration of 2.2, 2.3, 2.3 and 0.7 mg L^{-1} for 12, 10, 8 and 6 V. Good disinfection level in 20 min at 6 V with	[70]

(continued on next page)

Table 2 (*continued*)

Electrochemical cell	Anode/cathode	Effluent	Electrolysis conditions	Main results	Ref.
				1% (w/v) fecal matter. EC_V depends on liquid volume and voltage used	
Diamonox 40 cell	Nb|BDD plate/W plate, 42 cm^2 area	2 L of synthetic urine (+fecal matter), with *E. coli* suspension of 10^9 CFU $(100 mL)^{-1}$, flow rate 2 L min^{-1}	$E_{cell} = 6–12$ V up to 30 min	7 log cell reduction in 30 min at 6 V ($EC_V = 5$ kWh m^{-3}) and in 6 min at 12 V ($EC_V = 10$ kWh m^{-3}). Little effect of fecal matter. Evolution of total chorine	[33]
Diamonox 40 cell	Nb|BDD plate/W plate, 42 cm^2 area	2 L of synthetic urine, 2.34 g L^{-1} Na_2SO_4,, 3.88 g L^{-1} KCl and 9.93 g L^{-1} NaCl, with *E. coli* suspension of 10^{10} CFU $(100 mL)^{-1}$.	Different modes (pulse or continuous) by applying 6 V	6 log cell reduction in single cycle mode after 100 min, and by 10% and 50% duty cycle pulsed mode in 35 and 40 min, respectively.	[71]
Undivided flow- through filter-press cell	Si|BDD circular/Si|BDD circular, 78 cm^2 area	1 L of synthetic urine, 700 mg L^{-1} TOC, with suspension of 5×10^4 CFU mL^{-1} of *E. coli* and *P. aeruginosa*	$j = 1.0–10$ mA cm^{-2} up to 60 min	5 log cell reduction in 20 min at 10 mA cm^{-2}, $Q = 0.8$ Ah L^{-1}. 90% TOC decay at $Q = 30$ Ah L^{-1}. Evolution of NO_3^-, NH_4^+, ClO^- and ClO_3^-. No chloramines found	[72]
Undivided flow-through filter-press cell	Si|BDD circular/SS circular, 78 cm^2 area	Synthetic hospital urine, with TOC from 2.3 to 6.7 mg L^{-1}, suspension of 10^7 CFU mL^{-1} of *E. coli, K. pneumoniae* and *E. faecalis*	$j = 1.0$ mA cm^{-2}	7 log cell reduction, $Q = 1.25$ Ah L^{-1}.	[65]
Undivided flow-through filter-press cell	Si|BDD, Ti|RuO_2, Ti|IrO_2, Pt/SS, all circular of 78 cm^2 area	600 mL of synthetic urine, 90 mg L^{-1} TOC, 80 mg O_2 L^{-1} COD, with *E. coli* suspension of 9000 MPN, pH 8.0, 25 °C	$j = 15$ mA cm^{-2}	Total inactivation for $Q < 10$ Ah L^{-1} as Si|BDD < Ti|RuO_2 ~ Ti|IrO_2 < Pt. Total TOC and COD removal for Si|BDD at Q of 9 and 5 Ah L^{-1}, respectively. Evolution of PO_4^{3-}, SO_4^{2-}. NO_3^-, NO_2^-, NH_4^+, ClO^-, ClO_4^- and chloramines	[73]
Other synthetic and real wastewaters					
Undivided stirred tank reactor	Ni|BDD plate/SS plate, 4 cm^2 area	250 mL of 40–45 mM chloride, with *E. coli* suspension of 2×10^8 CFU mL^{-1}	$I = 80$ mA up to 600 min	2 log cell reduction at 48 min. Inactivation mechanism from changes of TOC, total protein, K^+ leakage, membrane potential, cell permeability, etc. TEM images of cells	[20]
Single compartment cell (EC Electro MP-Cell)	Si|BDD plate/SS plate, 80 cm^2 area	850 mL of solution containing 10^4 CFU mL^{-1} *E. coli* in 200 mg L^{-1} SO_4^{2-} plus 100 mg L^{-1} of Cl^- in continuous and recirculation modes, flow rates = 0.05–0.42 L min^{-1} (Re = 15–105) at 25 °C	$j = 2.5–5.0$ mA cm^{-2} for 100 min in recirculation (batch) mode	A fraction of 0.075 and 0.150 for cell inactivation in continuous mode at Re = 84 (0.28 L min^{-1}) and Re = 102 (0.36 L min^{-1}), respectively, while the cell was not detected in recirculation mode at 0.40 L min^{-1} (Re = 360). Optimum operative conditions limited ClO_3^- formation	[74]
Diacell® 100 (1 compart.)	Si|BDD circular/SS circular, 78 cm^2 area	30 L in continuous (1 pass) or 10 L in batch of synthetic ballast water (3.0 or 30 g L^{-1} NaCl), with *E. coli* suspension of 10^6 CFU mL^{-1}, flow rate 20 L min^{-1}	j up to 127.3 mA cm^{-2} (I up to 10 A) for 30 min in batch	6 log cell reduction for both operation modes, in <3 min in batch for $j < 25.5$ mA cm^{-2}. Lower $EC_V = 0.005$ kWh m^{-3} in continuous with 30 g L^{-1} NaCl at 12.7 mA cm^{-2}	[75]
Diacell® 101 cell	Si|BDD plate (2 μm thickness)/Si|BDD plate, 67 cm^2 area	5 L of wash water inoculated with *E. coli O157:H7* cocktail at 10^5 CFU mL^{-1}, 8–10 °C, 115 mg L^{-1} NaCl and pH 6.5 adjusted with 80 mg L^{-1} of citric acid.	$j = 30–180$ mA cm^{-2}, 120 min	Complete microbial inactivation and COD removal in 40 min at 180 mA cm^{-2}, liquid flow rate of 750 L h^{-1} and high B doping level (8000 μmol mol^{-1}).	[76]

[a] DSA: dimensionally stable anode.
[b] Q: electric consumed charge.
[c] EC_V: energy consumption per volume unit.
[d] E_{cell}: cell voltage.
[e] WWTP: wastewater treatment plant.
[f] ECWP: flow-through cell with BDD perforated electrodes.
[g] UNCD: boron doped ultrananocrystalline diamond.

In the specific case of electrogeneration of active chlorine species, DSA electrodes are preferentially used because these can produce large quantities of active chlorine species, even superior to that produced by diamond films. This converts the Cl-mediated EO process with DSA electrodes as a potential electrodisifection approach. However, the production of highly recalcitrant chloroderivatives by Eq. (25) and (26), along with trihalomethanes, chloroform, and haloacetic acids limits its applicability. The occurrence of perchlorates during EO in chloride medium is of a great importance because these are associated to several serious health [5,27]. These products are also formed with BDD, although their productions are closely relied to the electrochemical system used and operating conditions [32,45–47]. It is important to remark that the diamond technology could represent a key in electrodisinfection strategies because establishing correctly the experimental conditions and other factors, the disinfection action takes advantages of both heterogeneous $M(^{\bullet}OH)$ and active chlorine disinfectants, minimizing the quantity of chloroderivatives formed and the rate of parasitic reactions like Eq. (25) and (26) [22]. For ClO_2^-, even when its formation is considered as parasitic reaction; it can be used as disinfectant when it is purposefully produced onsite using undivided electrochemical or divided cells by anodic oxidation of hypochlorite by Eq. (24) or cathodic reduction of chlorate [27]. The good performances for BDD electrodisinfection systems can be observed in the selected results collected in Tables 2 and 3 concerning the inactivation of several bacteria in chloride

Table 3
Selected results obtained for the inactivation of several bacteria in different aqueous matrices by EO with a BDD anode.

Electrochemical cell	Anode/cathode	Effluent	Electrolysis conditions	Main results	Ref.
Pseudonomas aeruginosa					
Bench-scale unit with an oxidation cell	A bed of bipolar diamonds (0.4 mL) with titanium-iridium-oxide as contact electrodes	1 L of *P. aeruginosa* ≈ 10^6 CFU mL^{-1}, NaCl ≈ 8 mg L^{-1}. Flow rate of 1–2 L h^{-1}.	j = 140–210 mA cm^{-2} for 30 min	DC reduces between 0.9 and 4.0 log cells, AC between 0.4 and2.9 log cells. Depending on the contact time of the oxidants, inactivation was in the range 1.6–3.6 log at the higher flow rate and 2.4–4.4 log at the lower rate by using DC.	[29]
CabECO® cell, designed to produce O_3 in low conductivity medium	Si|BDD/Si|BDD, in contact with a cation exchange membrane, 24 cm^2 of total area	5 L water collected at the inlet of municipal WWTP merged with the effluent of secondary clarifier (ratio 95/5 v/v). Cell content of 45 CFU (100 mL^{-1})	j = 0.083 – 83.3 mA cm^{-2}	45% and 90% of cell reduction at 8.33 and 83.3 mA cm^{-2}, respectively. Lower than 50% of TOC removal at all j applied. Evolution of ClO_3^- and ClO_4^- as well as of F^-, NO_3^-, Br^- and SO_4^{2-}.	[34]
Undivided flow-through cell	Si|BDD circular/Ti circular, 78 cm^2 area	500 mL in solutions with 900–4500 mg L^{-1} NaCl, and cell suspension of 6.6 × 10^8 CFU mL^{-1}, pH 7.2, 25 °C, flow rate 250–1250 mL min^{-1}	j = 50 mA cm^{-2} for 120 min in batch	Total disinfection in 120, 60 and 45 min for 900, 2300 and 4500 mg L^{-1}, respectively, flow rate 250 mL min^{-1} Evolution of oxidants, ClO^- and ClO_3^-	[77]
Undivided flow-through filter-press cell	Si|BDD circular/Si|BDD circular, 78 cm^2 area	1 L of synthetic urine, 700 mg L^{-1} TOC, with cell suspension of 10^4 CFU mL^{-1}	j = 0.5–10 mA cm^{-2} up to 60 min in batch	Total disinfection in 120 min at 0.5 mA cm^{-2} (Q = 0.25 Ah L^{-1}) and in 60 min at 5 mA cm^{-2} (Q = 1 Ah L^{-1})	[72]
Undivided stirred tank reactor	Si|BDD plate, Ti|RuO_2 plate, or Ti|IrO_2 plate/SS plate, 3 cm^2 area	100 mL of 7 mM Na_2SO_4 or 7 mM Na_2SO_4 + (1–7) mM NaCl, with cell suspension of 10^6 CFU mL^{-1}, pH 5.8, 25 °C	j = 33.3 mA cm^{-2} for 60 min	Total disinfection in 30 min in 7 mM Na_2SO_4 and in < 5 min with 1–7 mM NaCl with Ti|IrO_2. Faster than with Ti|RuO_2 and Si|BDD.	[80]
CONDIAPURE® cell	Two Nb|BDD/two Nb|BDD, in contact with a cation exchange membrane), 24 cm^2 of total area	10 L of particular water matrix with ≈10^7 – 10^9 CFU mL^{-1}, flow rate 10 L min^{-1}	j = 42 and 167 mA cm^{-2}	Inactivation levels of 4 log units (60 min) and 8 log units (15 min) after Q = 105 mAh L^{-1} for 42 mA cm^{-2} (0.07 mg L^{-1} O_3) and 167 mA cm^{-2} (0.46 mg L^{-1} O_3), respectively. After 10 min (250 mg L^{-1} NaCl), 7, 6 and 5 log cell inactivation at 167 mA cm^{-2}, while ≈ 6 and 3 log cell inactivation after 60 min (20 mg L^{-1} NaCl) at 42 mA cm^{-2}. ClO_3^- and ClO_4^- determinations.	[81]
MIKROZON® cell, designed to produce O_3 in low conductivity media	Si|BDD/Si|BDD, in contact with a cation exchange membrane, 113 mm^2 area	Secondary WWTP effluent, with cell suspension of 2.7 × 10^8 CFU (100 mL^{-1}), flow rate 66 L h^{-1}	I = 0.3–1.0 A in batch	6 log cell reduction at 0.3 A. 3.5 log cell reduction at 0.6 A. 5 log cell at 1.0 A. Evolution of ClO^- and ClO_3^-	[82]
Total coliforms					
CabECO® cell, designed to produce O_3 in low conductivity	BDD/BDD, in contact with a cation exchange membrane, 24 cm^2 of total area	5 L water collected at the inlet of municipal WWTP merged with the effluent of secondary clarifier (ratio 95/5 v/v). 4,935 CFU (100 mL^{-1})	j = 0.083 – 83.3 mA cm^{-2}	90% of disinfection at 83.3 mA cm^{-2}. <50% of TOC removal at all j applied. Evolution of ClO_3^- and ClO_4^- as well as of F^-, NO_3^-, Br^- and SO_4^{2-}.	[34]
MIKROZON® cell, designed to produce O_3 in low conductivity media	Si|BDD/Si|BDD, in contact with a cation exchange membrane, 113 mm^2 area	Secondary WWTP effluent, with suspension of 3.2 × 10^8 CFU (100 $mL)^{-1}$ of total coliform, flow rate 66 L h^{-1}	I = 0.3, 0.6 and 1 A in batch for Q = 0.3, 0.6 and 1.0 Ah L^{-1}, respectively	6.5 log cell reduction at 0.3 A. 4.2 log cell reduction at 0.6 A. 6 log cell at 1.0 A	[35]
Undivided Diacell 100 (1 compart.)	Si|BDD circular/Si|BDD circular, 70 cm^2 area	10 L of WWTP effluent, with suspension of 2.2 × 10^4-5 × 10^5 CFU (100 $mL)^{-1}$ of total coliforms and 10^4-1.3 × 10^5 CFU (100 $mL)^{-1}$ of fecal coliforms, flow rate 10 L min^{-1}	I = 1 and 2 A up to 10 min in batch	> 95% disinfection in 9 min at 1 A and in 4 min at 2 A. EC_V = 0.40 and 0.65 kWh m^{-3}, respectively	[83]
Undivided stirred tank reactor	Ti|Sb-SnO_2|PbO_2 plate/SS plate, 12 cm^2 area	250 mL of influent of sequence batch reactor and effluent of constructed wetland, with suspension of 2.9 × 10^5 and 3.2 × 10^4 CFU mL^{-1} of total coliforms and fecal coliforms, respectively	j = 30 mA cm^{-2} up to 60 min	Total disinfection in 15 min for sequence batch reactor and in 3 min for constructed wetland.Evolution of COD, NO_3^-, NH_4^+ and active chlorine. Study of anode stability.SEM images of cells	[84]
Marine bacteria					
Diaclean cell	Si|BDD circular/Si|BDD circular, 70 cm^2 area	Real ballast water (pH 7.94, 2.13 mg L^{-1} TOC and 16.26 g $L^{-1}Cl^-$) in continuous at flow rate of 200–1000 L h^{-1},՝ with 10^6 CFU mL^{-1} of marine heterotrophic bacteria	I = 0.7–7.3 A	4.5 log cell reduction after Q = 0.22 A h L^{-1}. EC_V from 0.009 to 0.264 kWh m^{-3}. Evolution of total residual oxidant. No ClO_4^- formed at flow rate > 200 L h^{-1}	[85]
Divided stirred tank reactor	BDD plate/air-diffusion, 5 cm^2 area, separated with a cation exchange membrane	200 mL of synthetic ballast water (pH 8.0–8.2, conductivity 45 mS), with suspension of 16500 CFU mL^{-1} of marine bacteria of *Alexandrium minutum*, 12000 CFU mL^{-1} of *A. taylori* and 4.7 × 10^8 CFU mL^{-1} of *P. aeruginosa*, 25 °C	j = 5–15 mA cm^{-2} in the anolyte up to 60 min, sometimes previous cathodic treatment for 30 min	Total inactivation of *A. minutum* and *A. taylori* in 15 min at 5 mA cm^{-2}. Total inactivation of *P. Aeruginosa* in 60 min at 10 mA cm^{-2}. 88% cell inactivation in cathodic pre-treatment.Evolution of H_2O_2 and active chlorine	[86]
Commercial flow-through filter-press l reactor (Electro MP-Cell)	Si|BDD/SS cathode, 80 cm^2 area	300 mL of solution containing KNO_3 (3.0 g L^{-1}), KH_2PO_4 (0.74 g L^{-1}), Na_2HPO_4 (0.26 g L^{-1}), $MgSO_4$ (0.2 g L^{-1}); NaCl (30 mg L^{-1}) and 1 × 10^9 CFU mL^{-1} of *Chlorella vulgaris* in recirculating batch	j = 25–100 A cm^{-2}, resulting in E_{cell} from 4 to 6 V	Algae inactivation at batch mode after 8 Ah L^{-1}: 45% at 25 A cm^{-2} (Re = 20), 93% at 25 A cm^{-2} (Re = 100), 79% at 100 A cm^{-2} (Re = 20) and 80% at 100 A cm^{-2} (Re = 100). 0.97% of algae inactivation at batch mode after 7 Ah L^{-1} in 100 mg L^{-1}	[87]

(*continued on next page*)

Table 3 (*continued*)

Electrochemical cell	Anode/cathode	Effluent	Electrolysis conditions	Main results	Ref.
		mode or continuous mode (from 190 to 670 mL min^{-1}) at 25 °C.		of Cl^- at Re = 100 and 7.5 mA cm^{-2}. Algae inactivation at continuous mode: 30% at 25 A cm^{-2} (Re = 20) and 80% at 75 A cm^{-2} (Re = 20) and 60% at 25 A cm^{-2} (Re = 20) and 90% at 75 A cm^{-2} (Re = 20) with 30 and 100 mg L^{-1} of Cl^-, respectively	
Other bacteria					
Undivided flow reactor	Nb-grids|BDD/Ti|Pt plate, both electrodes with 0.01 m^2 area	300 mL of 1 × 10^6 CFU mL^{-1} of *Microcystis aeruginosa* recirculated with flow rates from 25 to 100 mL min^{-1}, Cl^- content from 100 to 1000 g m^{-3}	j = 1.0 and 6.0 mA cm^{-2}, E_{cell} from 8 to 20 V.	80% cell removal in all cases at different times. At Re = 10, 6.0 mA cm^{-2} and 1000 g $m^{-3}Cl^-$, maximum removal after 6 ks, and 20 ks under the weakest condition. From 1.0 to 4.0 mA cm^{-2}, k_{app} increased 50%. k_{app} increased 10% from Re = 10 to 4.0 at 6.0 mA cm^{-2}.	[36]
Undivided stirred tank reactor	Si|BDD rectangular/Ti mesh, 10 cm^2 area	400 mL of 4 stormwater samples, with suspension of 5140–8090, 3950–37170 and 43–267 MPN (100 $mL)^{-1}$ of enterococci, *Campylobacter* and *Clostridium perfringens*, pH 6.7–7.6	j = 4.2 mA cm^{-2} for 8–30 min depending on the stormwater	Total disinfection of all bacteria	[53]
Undivided flow-through cell	Si|BDD circular/Ti circular, 78 cm^2 area	500 mL of solutions with 2250 mg L^{-1} NaCl, and suspension of 4.4 × 10^7 CFU mL^{-1} of *Legionella pneumophila*, pH 7.2, 25 °C, flow rate 250 mL min^{-1}.	j = 20–100 mA cm^{-2} for 120 min in batch	7 log cell inactivation in 120 min for 20 mA cm^{-2}. 7.5 log cell inactivation in 120 min for 50 mA cm^{-2}. 7.5 log cell inactivation in 60 min for 100 mA cm^{-2}.	[77]
Undivided stirred tank reactor	Si|BDD plates (10 units)/graphite rod cathode, 16 cm^2 area	300 mL of hospital effluent wastewater containing 29 pharmaceuticals, illegal drugs and their metabolites and resistant types of microorganisms (total coliforms: 5.5 to 7 log CFU mL^{-1} and *S. aureus*: 2.7–3.8 log CFU mL^{-1})	j = 45 mA cm^{-2}, 30 min in batch	>60% of efficiency to eliminate pharmaceuticals, drugs and bacteria in 30 min. Total removal of ampicillin, penicillin, and gentamicin-resistant coliforms, especially *E. coli*, and *S. aureus*.	[88]
Undivided Plug-flow micro-reactor	Si|BDD plate/SS plate, 7.5 cm^2 area	250 mL (1 mL min^{-1}) of liquid hog manure with *Lactobacillus*, *Escherichia*, *Bacillus*, *Streptococcus*, *Eubacterium*, *Clostridium* and *Propionibacterium* at 2.2 × 10^6 CFU mL^{-1}	I = 600 mA up to 250 min	Total bacterial count for anaerobic and aerobic bacteria was reduced up to 5.7 × 10^3 CFU mL^{-1}	[89]
Undivided flow-through filter-press cell	BDD plate/SS plate	Fertigation solutions in continuous without and with 20 mg L^{-1} KCl, with suspension of 3.5 × 10^4 CFU mL^{-1} of *rhizoctonia solani*, flow rate 127–720 mL min^{-1}	j = 1.14–9.09 mA cm^{-2}	1 log cell inactivation in 6 min for all j values without KCl.Total disinfection in 1–2 min from 2.37 to 9.09 mA cm^{-2} with KCl.Evolution of active and total chlorine, NH_4^+, NO_3^- and SO_4^{2-}. Low ClO_4^- formed	[90]

media, which is superior to those given in Table 1 for the EO approach with the same kind of anodes using free-chloride solutions.

4.2.2. Free-chloride medium

Electrochemical disinfection with diamond electrodes, for bacteria inactivation in free-chloride synthetic solutions, has no comprehensive investigated. Although it is the friendliest disinfection approach (no toxic disinfection by-products can be produced), possibly the different concentrations of chloride in real water matrices strongly have incentive to the electrochemistry community for better understanding the inactivation mechanisms and the disinfectant agents electrogenerated in these kinds of waters than in free-chloride synthetic solutions. This selection has also allowed to comprehend how a selective electrogeneration of disinfectant agents can be performed, avoiding toxic by-products formation.

A selected number of works for the inactivation of bacteria in free-chloride synthetic solutions by EO disinfection approach has been summarized in Table 1, specifying the electrochemical system and the best experimental conditions obtained. An inspection of this table indicates that the main inactivated bacteria have been *E. coli*, coliforms and *E. faecalis*, but other microorganisms have also been considered as model pathogen agents (*S. aureus, Enterococcus hirae, Bacillus atrophaeus, Staphylococcus aureus, P. aeruginosa, M. aeruginosa, Cyanotoxin cylindrospermopsin*, and *Cylindrospermopsis raciborskii)* to test the disinfection efficiency of diamond technologies. Conventional undivided batch and stirred beaker cells (see Fig. 8a) and undivided flow cells (see Fig. 8b) have been widely utilized to disinfect pathogen suspensions in free-chloride synthetic solutions. BDD films in plate shape, supported on Nb, Si and Ti, have been largely used as anodic materials (with sizes ranging from 2 to 30 cm^2) in these electrochemical systems, with counterpart of Pt sheet, SS plate, Ti/BDD plate and graphite rod as cathodes. Other anodes have also been tested to compare the diamond films inactivation efficiency, such as, DSA and Pt electrodes.

These laboratory-scale experiments have been carried out with solution volumes that vary between 80 and 250 mL by applying j ranging from 2 to 200 mA cm^{-2}. Generally, sulfate has been used as supporting electrolyte to promote the electrogeneration of ROS as disinfectants; however, phosphate and nitrate were also added to the solutions to comprehend the oxidants conversions. All results reported in Table 1 evidence the great disinfection level attained, reaching higher log cell units inactivation in short treatment times (ranging from 10 s to 120 min) via the participation of different ROS, mainly heterogeneous BDD($^•$OH).

As already mentioned in Sections 2.1 and 3, Jeong et al. [9] demonstrated, for first time, the applicability of EO disinfection using Nb|BDD electrodes in an electrochemical free-chlorine system with 10^8 CFU mL^{-1} of *E. coli* in 0.2 M phosphate buffer. No inactivation was confirmed without applied j, demonstrating that the contact of cells with the synthetic diamond film did not prove any changes due to the non-active nature of this anode. Conversely, a faster inactivation (4.5 log cell reduction in 5 min) was corroborated by morphological analysis with TEM (see Fig. 2a and b) and AFM (see Fig. 2c and d) microscopies when j was increased from 50 to 100 mA cm^{-2} (see Table 1), although the inactivation was not reached linearly. The drastic changes in the cells evidenced the efficient attack of ROS (mainly attributed to the disinfectant action of O_3 and H_2O_2 as well as heterogeneous BDD($^•$OH) at higher concentrations) by cell membrane fragmentation, which can lead to the lyses phase at 4 °C and pH 5.6, as already explained in section 3.

Table 4

Relevant data for the inactivation of several bacteria in chloride media by combined processes with EO with a BDD anode.

Electrochemical cell	Anode/cathode	Effluent	Electrolysis conditions	Main results	Ref.
Hybrid process					
Undivided stirred tank reactor	Nb|BDD plate/SS plate	250 mL of 20–100 mM Na_2SO_4, 0.5–2.0 μg mL^{-1} rGO[a], with cell suspension of 10^7 CFU mL^{-1}	$j = 10–20$ mA cm^{-2} for 30 min	For 50 mM Na_2SO_4 at 15 mA cm^{-2}: 4 log cell reduction (no rGO), 7 log cell reduction with 1.0 μg mL^{-1} rGO. Tests of membrane, cell permeability, enzyme assays, K^+ leakage. TEM images of cells	[19]
Undivided flow-through filter-press electrochemical reactor	Si|BDD mesh type/SS, 64 cm^2 area with a 3D reactor and a packed bed of GAC [b] between anode and cathode for EO/adsorption	2 L of greywater in batch mode during 7 h at 35 L h^{-1}, 0.67 g L^{-1} Na_2SO_4, containing *E. coli* (10^5 CFU (100 $mL)^{-1}$), spores of *Clostridium perfringens* (SCP (10^4 CFU (100 $mL)^{-1}$)) and *somatic coliphages* (SOMCPH (10^4 CFU (100 $mL)^{-1}$).	$j = 15$ A m^{-2}	Proportion of dead *E. coli* cells was increased from 40% to 88% after 5 h of electrolysis in 3D reactor. Removals of *E. coli* (4.6–5.1 log), SCP (0.1–0.6 log) and SOMCPH (3.2–3.3 log) were achieved. Simultaneous (electro)sorption and electrooxidation at the surface of GAC with BDD anode improve the disinfection	[91]
UV/electrolysis hybrid module. An UVC lamp (20 W) flow reactor, coupted to a undivided flow-by filter-press cell	Nb|BDD/Nb|BDD, 54 cm^2 area	5 L of biologically treated wastewater with $1–3 \times 10^5$ *E. coli* in 100 mL. Flow rate range: 100 L h^{-1}. Effects on 10 and 30 °C as well as at pH values ranging from 5.7 to 8.1	$j = 50$, 70 and 100 mA cm^{-2}	Lower reactivation in darkness of bacteria are by 2.7 log levels. At 4,200 Lux, 4.3 log reactivation was attained after 24 h.. The unwanted reactivation of reversibly UV damaged is considerably increased with rising light intensity and rising temperature, with a concentration of total oxidants of 0.5 mg L^{-1} (10–30 °C, pH = 5.7–8.1) consuming 0.17 kWh m^{-3}	[92]
Undivided flow-by filter-press cell with a quartz cover for irradiating with 4 W UVC light	Si|BDD circular/SS circular, 78 cm^2 area	4 L of secondary WWTP effluent, 25 °C, with suspension of 5400–16000 CFU (100 $mL)^{-1}$ of *E. coli*	$j = 0.13$ mA cm^{-2} for 120 min in batch	Inactivation: 1.2 log (EO), 2.1 log (photolysis) and 4 log (PE [c]). Evolution of ClO^-, ClO_3^-, ClO_4^- and chloramines	[93]
Undivided flow-by filter-press cell. External ultrasound generator of 200 W and 24 kHz	Si|BDD circular/SS circular, 78.5 cm^2 area	2 L of domestic wastewater, 25 °C, with cell suspension of 2400–24000 CFU (100 $mL)^{-1}$ of *E. coli*	$j = 0.127–0.637$ mA cm^{-2} in batch	92% inactivation by EO and total disinfection by SE [d] in 120 min at 0.127 mA cm^{-2} for 16000 CFU (100 $mL)^{-1}$.Evolution of ClO^-, ClO_3^-, ClO_4^- and chloramines	[94]
Divided flow electrochemical system	Ni|BDD/CF [e] or SS, both electrodes with 4 cm^2 area	Stock suspension with $(3–4) \times 10^6$ CFU mL^{-1} of *M. aeruginosa* in 20 mM Na_2SO_4 at 200 rpm (Re = 2083, pH 3–9, $FeSO_4$ (0.1–0.5 mM) for EF [f]	$I = 200$ mA for 60 min	Inactivation efficiencies at the best pH 3: BDD/CF, BDD/SS and BDD/SS +(0.2 mM Fe^{2+}): 1.2 log, and BDD/CF +(0.2 mM Fe^{2+}): 3.2 log. No significant effects were produced by air flow rate	[21]
UVC lamp irradiating 4.0 W directly to the quartz cover that substitutes one of the plates of the Diacell® 101.	Diacell® type 101: Si|BDD plate/SS plate, 78 cm^2 area	4 L of urban wastewater intensified with 100 mg L^{-1} of caffeine, Flow rate 21.4 or 50 L h^{-1}. *E. coli*: 9100 MPN (100 $mL)^{-1}$, Cl^-: 110–180 mg L^{-1}, SO_4^{2-}: 120–400 mg L^{-1}, TOC: 12–14 mg L^{-1}, COD: 35–42 mg O_2 L^{-1}, pH 7.8–8.5	$j = 0.13$ mA cm^{-2}	Complete cell reduction was achieved by PE at $Q = 0.006$ A h L^{-1}. PE disinfection produces lower concentration of chlorine species. Soft operating conditions produce hypochlorite and chloramines, but not chlorates and perchlorates	[30]
Commercial pilot plant with five parallel Diacell® 1001 with an UVC lamp (26 W) irradiating directly an auxiliary tank	Five Diacell® type 101: 50Si|BDD plate/25 SS plate, 3500 cm^2 area	300 L of urban wastewater intensified with 100 mg L^{-1} of caffeine, Flow rate 21.4 or 50 L h^{-1}. *E. coli*: 5400 MPN (100 $mL)^{-1}$, Cl^-:110–180 mg L^{-1}, SO_4^{2-}: 120–400 mg L^{-1}, TOC: 12–14 mg L^{-1}, COD: 35–42 mg O_2 L^{-1}, pH 7.8–8.5	$j = 1.20$ mA cm^{-2}	Complete inactivation cell was achieved by PE at $Q = 0.007$ Ah L^{-1}. No chlorate or perchlorate produced	[30]
Undivided flow-through filter-press cell	Si|BDD/SS, 78.5 cm^2 with a perforated Al plate between anode and cathode for EO/EC [g] in situ	4 L of a domestic wastewater with 24000 CFU (100 $mL)^{-1}$ of *E.coli*, pH 8.5, 25 °C, flow rare 50 L h^{-1}, 172.9 mg L^{-1} NaCl, 9.19 mg L^{-1} TOC	$j = 6.65$ A m^{-2}	Simultaneously *E. coli* and turbidity were removed. Disinfection by-products were formed: hypochlorite; chlorate; perchlorate and chloramines	[31]
Undivided flow-through filter-press cell.	Si|BDD circular/SS circular, 78.5 cm^2 area with a perforated Fe or Al plate (49 cm^2 and 2 mm of thickness) between anode and cathode for EO/EC in situ	4 L of urban effluent from WWTP, 25 °C, with cell suspension of 2,200–90,000 CFU (100 $mL)^{-1}$ of *E. coli.* TOC = 25 mg L^{-1}, COD = 30 mg L^{-1}, chloride = 204.850 mg L^{-1}, nitrate = 23.740 mg L^{-1}, sulfate = 334.595 mg L^{-1} and ammonium = 43.434 mg L^{-1}	$j = 0.190–0.938$ mA cm^{-2} in recirculation mode (50 L h^{-1})	Total disinfection by EO/EC in 0.01 and 0.05 Ah L^{-1} at 0.670 and 0.938 mA cm^{-2} for 22,000 and 31,000 CFU (100 $mL)^{-1}$, consuming 0.030 and 0.080 kWh m^{-3}, respectively. ClO^- and chloramines as the main compounds responsible for the disinfection. Detection of ClO_3^- at $j > 0.670$ mA	[97]

(*continued on next page*)

Table 4 (*continued*)

Electrochemical cell	Anode/cathode	Effluent	Electrolysis conditions	Main results	Ref.
				cm^{-2} and $Q > 0.020$ Ah L^{-1}. Bipolar electrode (Al or Fe) did not enhance the disinfection approach. Higher turbidity removal by using Fe. Al suffered passivation	
Undivided flow-through filter-press cells.	Si|BDD circular/SS circular, 78.5 cm^2 area with 5 perforated Fe plate (250 cm^2 and 2 mm of thickness) between anode and cathode for EO/EC in situ	4 L of urban treated wastewater, 25 °C, with cell suspension of 1100–2200 CFU (100 mL)$^{-1}$ of *E. coli*, pH 7.06–7.8, chloride = 82.19 mg L^{-1}, nitrate = 14.80 mg L^{-1}, sulfate = 152.10 mg L^{-1} and ammonium = 18.89 mg L^{-1}	$j = 7$ mA cm^{-2} in continuous mode at 50 L h^{-1}	Total disinfection and turbidity removal by EO/EC at $Q = 0.1$ kAh L^{-1} consuming 2.24 kWh m^{-3}. In-situ electrogenerated free and combined chlorine species are the main responsible for disinfection (80 mg L^{-1}), whereas iron coagulant species lead to an efficient turbidity removal	[98]
Sequential process					
Divided flow electrochemical system	Green wall for biofiltration. For subsequent EO: Nb|BDD-mesh/cation exchange membrane (SPE [h])/SS-mesh, both electrodes with 50 cm^2 area	4 L of greywater (pH 6.62, conductivity 173 µS cm^{-1}, 28 mg L^{-1}Cl$^-$, turbidity 54.9 NTU, color 449Pt/Co units, TOC 66.5 mg L^{-1}, TSS 90.7 mg L^{-1}, COD 322 mg L^{-1}, BOD$_5$ 140 mg L^{-1}, 29,100 MPN (100 mL)$^{-1}$ *E. coli* and 61,300 MPN (100 mL)$^{-1}$ total coliforms	$j = 25$ mA cm^{-2} at 50 mL min^{-1}	Biofiltration removed over 90% of turbidity, apparent color, COD, TOC, BOD$_5$ and 1 log of *E. coli* and total coliforms. Further BDD electrolysis inactivated over 3.5 log of both *E. coli* and total coliforms in 10–15 min. Recycled water obtained with <2 MPN (100 mL)$^{-1}$	[99]
CabECO® cell	GAC absorption bed, after a C-F [i] chamber (PREDICO system) for a subsequent EO: Nb|BDD mesh/Nb|BDD mesh, 24 cm^2 active area, in contact with a perfluorinated ion-exchange membrane	10 L of polluted surface water highly microbially loaded water (coliforms, pseudomonas and total aerobic microorganisms by adding *Pseudomonas aeruginosa* and *E. coli*). Flow rate 150 L h^{-1}	$I = 0.31$–2.30 A for 120 min	PREDICO system can remove >3 log units of total aerobic microorganisms (sterilization) and 4 log units of coliforms (disinfection). A reduction in microorganisms (sterilization) by >3 log units and a reduction in pathogens by >4 log units (disinfection), and the efficiency depended on the hydraulic retention time in the coagulation chamber	[100]
Undivided stirred tank reactor	4 steel rectangular plates for EC. BDD rectangular/Ti rectangular for sequential EO. All electrodes with 15 cm^2 area	200 mL of model surface waters or model groundwaters (pH 7.5–8.3, TOC < 8.9 mg L^{-1}), with suspension of 10^7 PFU[j] mL^{-1} of human virus surrogates of MS2 and ΦX174	$I = 50$ mA for 5 min in EC and in EO	1.2 and 4.2 log MS2 reduction or 2.0 and 4.8 log ΦX174 reduction as maximal for surface water and groundwater, respectively. Inhibition by NOM, Fe^{3+} and turbidity	[101]
Undivided stirred tank reactor	Fe plate/Fe plate, 10 cm^2 area, for EC. Si|BDD plate/air-diffusion, 3 cm^2 area, for EF	200 mL of secondary WWTP effluent (pH 7.54) in EC. 100 mL of the resulting wastewater (pH 3.0 and 7.0) for sequential EF. Addition of 0.25 mM Fe^{2+}, 25 °C. Initial suspension of heterotrophic bacteria, *E. coli*, enterococci, *C. perfringens* spores, somatic coliphages and eukaryotes, up to 10^7 CFU mL^{-1}	$j = 20$ mA cm^{-2} up to 90 min in EC. $j = 33.3$ mA cm^{-2} up to 30 min in EF	EC for 90 min: 5 log *E. coli* reduction, lower decay of heterotrophs, enterococci and *C. perfringens*, and total removal of the others. EF alone for 30 min (pH 3.0 and 7.0): total removal of all bacteria, except heterotrophs and *C. perfringens* EC (30 min) – EF (30 min, pH 7.0): Faster removal of all bacteria	[102]
Undivided stirred tank reactor	Fe plate/Fe plate, 10 cm^2 area, for EC. Si|BDD plate or Ti|RuO$_2$ plate/air-diffusion, 3 cm^2 area, for EF and PEF	175 mL of dairy wastewater (pH 5.7) in EC. 120–150 mL of resulting wastewater (pH 3.0 and 7.0) with 0.25 mM Fe^{2+} for sequential EF or PEF, 25 °C with 6 W UVA light. Initial suspension of heterotrophic and lactic acid bacteria, *E. coli* and enterococci, up to 5 × 10^6 CFU mL^{-1}	$j = 10$ mA cm^{-2} for 60 min in EC. $j = 33.3$ mA cm^{-2} up to 120 min in EF and PEF	<1 log reduction of all bacteria by EC. 5 log reduction of all bacteria by EC-EF (pH 3.0) with Si|BDD. Total disinfection by EC-PEF (pH 3.0) with Si|BDD or Ti|RuO$_2$. >6 log cell reduction by EF at pH 5.7, faster for Ti|RuO$_2$ than Si|BDD	[103]

[a] rGO: reduced graphene oxide.
[b] GAC: granular activated carbón.
[c] PE: photoelectrolysis.
[d] SE: sonoelectrolysis.
[e] CF: carbon felt.
[f] EF: Electro-Fenton.
[g] EC: electrocoagulation.
[h] SPE: solid polymer electrolyte.
[i] C-F: coagulation-flotation.
[j] PFU: plaque-forming unity.

Table 5
BDD disinfection for the inactivation of several bacteria in endodontic applications.

Electrochemical device	Bacteria	Endodontic part	Electrolysis conditions	Main results	Ref.
Flexible pinpoint electrolysis unit with BDD powder (particle diameter <500 nm)-based polymer composite (ion-exchange polymer dispersion (20 wt% Nafion®) as anode and a Pt ribbon as cathode	Biofilms of *Porphyromonas gingivalis* (bovine tooth experiments) and *Enterococcus faecalis* (human tooth tests)	Root canals of bovine and human teeth in phosphate medium (pH 7.1)	Direct current at 7.5 V	*P. gingivalis* removed in 120 s from bovine tooth, whereas 15 s were needed to eliminate *E. faecalis* from human tooth. The electrochemical unit showed almost the same sterilization ability as the conventional 1 wt% aqueous NaClO treatment	[104]
Diamond coating with boron doping of niobium wires (200 μm diameter, 99.9% Nb-containing)	*C. dubliniensis* and *E. faecalis*	Dental implants with a medium-rough surface	$I = 60$ mA for 5 h	The implants colonized by microorganisms were rinsed with phosphate-buffered saline (137 mM NaCl, 2.7 mM KCl, 10 mM Na_2HPO_4, and 2 mM KH2PO4, pH 7.4). Thin wires as electrodes requiring substantial treatment time for successful inactivation of microorganisms	[105]
Prototype 2: BDD coating (2 μm of thickness) on pure Nb wire (0.2 mm)	*Staphylococcus epidermidis* or *Bacillus subtilis*. Bacterial growth is indicated as number of contaminated imprints after overnight incubation.	Roots from carious-free extracted human teeth immersed in phosphate saline solution	$I = 5–22$ mA (6 V constant) for 25 min	*B. subtilis* completely eliminated within 25 min. *S. epidermidis* removed after 10 min	[106]
Both the anode and cathode consist of a BDD layer, which is deposited onto a non-conductive ceramic substrate (porcelain, $Al_4[(OH)_8\|Si_4O_{10}]$, (Ca, Na,K)(Al,Si)$_4$O$_8$, SiO_2) by Chemical Vapor Deposition	Natural Biofilm: *Streptococcus cristatus, Streptococcus gordonii, Streptococcus mitis, Streptococcus oralis, Streptococccus parasanguinis, Streptococcus peroris, Streptococcus salivarius, Streptococcus sanguinis,* and *Streptococcus vestibularis*	Dental implant surfaces	$I = 105$ mA (9 V) for 5 min	Electrochemical disinfection was charge- and time-dependent. Complete disinfection in all instances was not reached. Implant threads had no negative effect on DDE[a] treatment. Bacteria exhibit varying resistance to electrochemical disinfection with *Bacillus subtilis, Neisseria* sp., *Rothiamucilaginosa, Staphylococcus haemolyticus*, and *Streptococcus mitis* surviving 5 min of DDE application at 6 V	[107]
Diamond coating with boron doping of thin Nb wires (200 μm in diameter)	*Candida albicans, Candida dubliniensis, Enterococcus faecalis, Roseomonas mucosa, Staphylococcus epidermidis* and *Streptococcus sanguinis.*	Implant surfaces in phosphate saline medium	$I = 5–22$ mA (6 V) for 20 min	Complete disinfection with a maximum treatment time of 20 min for several bacteria. However, in the case of spore-forming *B. pumilus* and *B. subtilis,* no complete disinfection reached	[108]

[a] DDE: double diamond electrode.

The key role of heterogeneous BDD($^{\bullet}$OH) or free-($^{\bullet}$OH) formed from Eq. (1) (being M the BDD anode) as the main disinfection agent was confirmed when an excess of *t*-BuOH (0.03 M), as an $^{\bullet}$OH scavenger, was added in the phosphate solution, because the inactivation of *E. coli* was completely stopped. The formation of H_2O_2 depended mainly on the concentration of the heterogeneous free-($^{\bullet}$OH) at BDD surface, and then, adding an excess of *t*-BuOH in the free-chloride medium, the H_2O_2 production from Eq. (17) was inhibited, limiting its contribution on the *E. coli* inactivation.

It is important to consider that other ROS can be electrogenerated at the BDD surface or via participation of heterogeneous free-($^{\bullet}$OH), such as H_2O_2, O_3 (see Eq. (8) or (19)), $O_2^{-\bullet}$ (see Eq. (18)), or $HO_2^{\bullet}$ from Eq. (27). Note that reaction of $^{\bullet}$OH with O_3 by Eq. (27) or H_2O_2 by Eq. (18) favors the generation of $HO_2^{\bullet}$ via Eq. (27), which is in equilibrium with $O_2^{-\bullet}$ from Eq. (28) [9].

$$^{\bullet}OH + O_3 \rightarrow HO_2^{\bullet} + O_2 \quad (27)$$

$$HO_2^{\bullet} \leftrightarrow O_2^{-\bullet} + H^+ \ (pKa = 4.8) \quad (28)$$

The participation of H_2O_2, O_3 and $O_2^{-\bullet}$ (or $HO_2^{\bullet}$) on *E. coli* removal was also investigated by Jeong et al. [9], but no inactivation of this bacteria was confirmed upon specific experimental conditions. Then, it was concluded that the heterogeneous free-($^{\bullet}$OH) acts as the main disinfectant agent in a region very close to the anode surface (Nernst layer), without any relevant effect of initial population of *E. coli.*, electrical current, temperature, and pH conditions. Consequently, this study became a reference to develop more electrochemical free-chlorine systems to promote inactivation of microorganisms due to the efficient participation of ROS, similarly to chlorine by electro-chlorination. However, the production and participation of $P_2O_8^{4-}$ in a phosphate disinfection medium were neglected, as well as the study of the subcellular mechanism and the identification of the by-products generated by cell fragmentations was unaccomplished.

The electrochemical disinfection of *E. coli* in free-chloride solutions was also investigated by Bruguera-Casamada et al. [16], Polcaro et al. [48], Long et al. [20], Li et al. [25,49], and Jeong et al [50]. Among these studies, some research groups investigated the inactivation of *E. coli* as a model microorganism, by performing different experimental trials to comprehend more about the inactivation mechanism or the action of the electrogenerated disinfectants [20,25,49]. Other studies evaluated the *E. coli* inactivation effectiveness by diamond technology compared to other anode materials [50] or respect to other waterborne agents [16,48]. In the first case, important advances were attained regarding the effect of different supporting electrolytes and the elucidation of the subcellular mechanism of bacterial inactivation [20,25,49].

Li et al. [49] evaluated the inactivation of 200 mL of microorganism solutions of 10^7 CFU mL^{-1} in different Na_2SO_4 concentrations (0.005, 0.05, 0.1 or 0.2 M) adjusting the pH at ≅ 7.1 with 4 mL of 0.1 M phosphate buffer solution in a stirred tank reactor like of Fig. 8a by applying a *j* from 5 to 40 mA cm^{-2}. When no *j* was not applied in 0.2 M Na_2SO_4, inactivation of *E. coli* suspension was not achieved after 2 h of experiment, confirming the behavior observed in [9]. Meanwhile, the inactivation rate of *E. coli* increased with *j*, being optimal at 20 mA cm^{-2} because at 40 mA cm^{-2}, the oxygen production from Eq. (16) was favored, reducing the inactivation efficiency (see Table 1). Under these experimental conditions (0.2 M Na_2SO_4, pH 7.1 and 10^7 CFU mL^{-1}), a 1.1 log removal of *E. coli* in free-chloride solution required approximately 0.40, 0.39, 0.04, and 0.45 kWh m^{-3} by applying 5, 10, 20 and 40 mA cm^{-2}, respectively, showing that lower energy requirements are

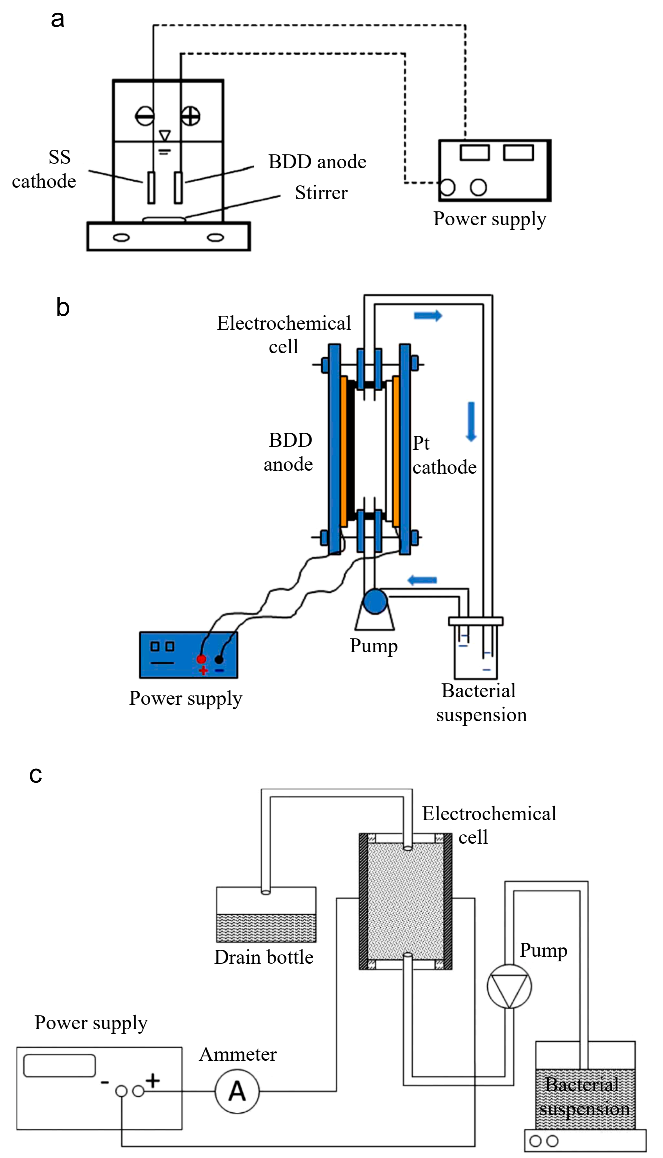

Fig. 8. Experimental setup of electrochemical systems with undivided cells with a BDD anode used for bacterial disinfection. Cell: (a) Stirred tank reactor. Adapted from [25]. (b) Batch flow-by filter-press reactor. Adapted from [28]. (c) Continuous flow-by filter-press reactor. Adapted from [29].

needed at 20 mA cm^{-2} to achieve an equivalent *E. coli* inactivation. As an important feature, the effect of Na_2SO_4 concentration was examined at 20 mA cm^{-2}, reaching 3.5 log inactivation of *E. coli* for 0.2 M Na_2SO_4, whereas 1.1, 0.9, and 0.1 log cell reductions were achieved for 0.1, 0.05, and 0.005 M Na_2SO_4, respectively, after 20 min of electrodisinfection. This behavior clearly indicated that heterogeneous free-($^{\bullet}OH$) at BDD surface might not be the only species responsible for the disinfection, as stated by Jeong, et al. [9], but no significant participation could be due to the participation of other ROS like H_2O_2, O_3 and $O_2^{\bullet -}$. Instead, the key role of peroxocompounds produced in the electrolysis of sulphate medium such as $S_2O_8^{2-}$ was confirmed for the *E. coli* inactivation. Perhaps, the operating conditions regarding *j* and precursor salt concentrations reported in [9] were not enough to promote the production of peroxocompounds. This effect was already observed by Furuta et al. [51] when solutions containing sulfate were electrolyzed with a DiaCell® where no *Legionella* inactivation was achieved due to the lower Na_2SO_4 concentration (440 mg L^{-1}) used as compared with 710 mg L^{-1} (0.005 M) for the most diluted solution employed in [49]. A comparison with NaH_2PO_4 and $NaNO_3$ (0.2 M) respect to Na_2SO_4 as electrolytes was also performed to inactive *E. coli* at 20 mA cm^{-2}, achieving 5.62 log cell reductions for Na_2SO_4, but only 0.25 and 0.88 log cell units reductions for NaH_2PO_4 and $NaNO_3$, respectively, thus showing the influence of $S_2O_8^{2-}$ in the former medium over the inactivation process.

Li et al. [25] also investigated the interactions between some organics (0.03 mM of dimethyl phthalate (DMP), diethyl phthalate (DEP), phenol, resorcinol and m-trihydroxybenzene (THB)) and 200 mL of 10^5 CFU mL^{-1} *E. coli* in 0.2 M Na_2SO_4 at pH 7 in the electrochemical disinfection using a Nb|BDD anode and a SS cathode in a stirred tank reactor like of Fig. 8a by applying 20 mA cm^{-2}. They confirmed a clear competition between organics degradation and cell inactivation during the different trials. For example, a complete *E. coli* inactivation (≅ 5.78 log cell reduction) was reached in 40 min in absence of organics in solution. Conversely, only 4 log units decreased for 60 min when DMP was added. Similarly, when the organic concentration was increased, disinfection was clearly prejudiced, for example, when resorcinol concentration increased up to 0.03 mM, *E. coli* inactivation decreased from 5.40 to 3.24 log units, along with a longer disinfection time. A pH influence was also established by these authors, since overall cell reduction was rapidly achieved at pH 10, whereas the *E. coli* inactivation rate was gradually reduced from pH 7 to pH 4.

Regarding the elucidation of the subcellular mechanism of bacterial inactivation, as already described in Section 3, Long et al. [20] electrochemically disinfected 250 mL of a *E. coli* suspension of 2×10^8 CFU mL^{-1} with 40–45 mM sulfate or phosphate in a stirring batch cell like of Fig. 8a with a Ni|BDD plate (4 cm^2 area) as anode and a SS plate as cathode by applying 80 mA up to 600 min. In sulfate solution, a noticeable cell membrane damage was mainly induced by the electrogenerated oxidants, attacking/eliminating membrane proteins with key functions (K^+ ion transport) and consequently, resulting in a gradual collapse of the cell membrane potential. Clearly, a collapse resulted in the anomalous localization of the cell division-related proteins, and thus, it inhibited the bacterial cell reproduction. On the other hand, the reduction of *E. coli* cells allows understanding that the organic components of the cells, including the membrane proteins, total proteins, and intracellular enzymes, were also mineralized while disinfection progressed [20]. This study provided significant insights into the bacterial inactivation mechanism on the subcellular level.

The nature of the anodic material (by means of its active or non-active character), as a crucial parameter, was also analyzed by Jeong et al. [50] to compare the *E. coli* inactivation effectiveness of diamond disinfection technology, as reported in Table 1. The effect of electrode material on the generation of oxidants and *E. coli* inactivation was evaluated using a divided cell consisting of a 100 mL with a cell population of 10^5 to 10^6 CFU mL^{-1} of cells in 0.2 M KH_2PO_4 at pH 7.1 and 25 °C, and a 50 mL cathodic compartment with a Nafion® 117 cation exchange membrane as a separator, by applying a *j* ranging from 17 to 167 mA cm^{-2}. Five different anode materials were used, including Nb|BDD, Ti|RuO_2, Ti|IrO_2, Ti|Pt–IrO_2, and Pt. A 2.4 log cell unit inactivation with Nb|BDD in 3 min was achieved without adding *t*-BuOH as heterogeneous free-($^{\bullet}OH$) scavenger. In fact, when 0.05 M *t*-BuOH was added to the solution, *E. coli* inactivation was largely inhibited. Instead, 1.3 log cell unit reduction was achieved with Pt for 3 min, whereas no inactivation was achieved with Ti|RuO_2, Ti|Pt–IrO_2 and Ti|IrO_2 anodes. As a result of the effectiveness of the electrodisinfection, the production of radical heterogeneous free-($^{\bullet}OH$) by BDD was about 10 times higher than that attained by Ti|RuO_2 and Pt. This result makes clearly in evidence that he inactivation efficacy depends on the nature of the electrode material toward radical BDD($^{\bullet}OH$) production from Eq. (1), also affecting the formation of higher amounts of other ROS. In fact, the production of heterogeneous free-($^{\bullet}OH$) at BDD was more substantial than at Ti|RuO_2 and Pt anodes, not being significant for Ti|IrO_2 and Ti|Pt–IrO_2. Simultaneously, BDD was more efficient on the generation of O_3 respect to the other electrodes, where heterogeneous free-($^{\bullet}OH$) played a key role in O_3 generation from Eqs. (8) or (19).

The evaluation of the *E. coli* inactivation effectiveness respect other

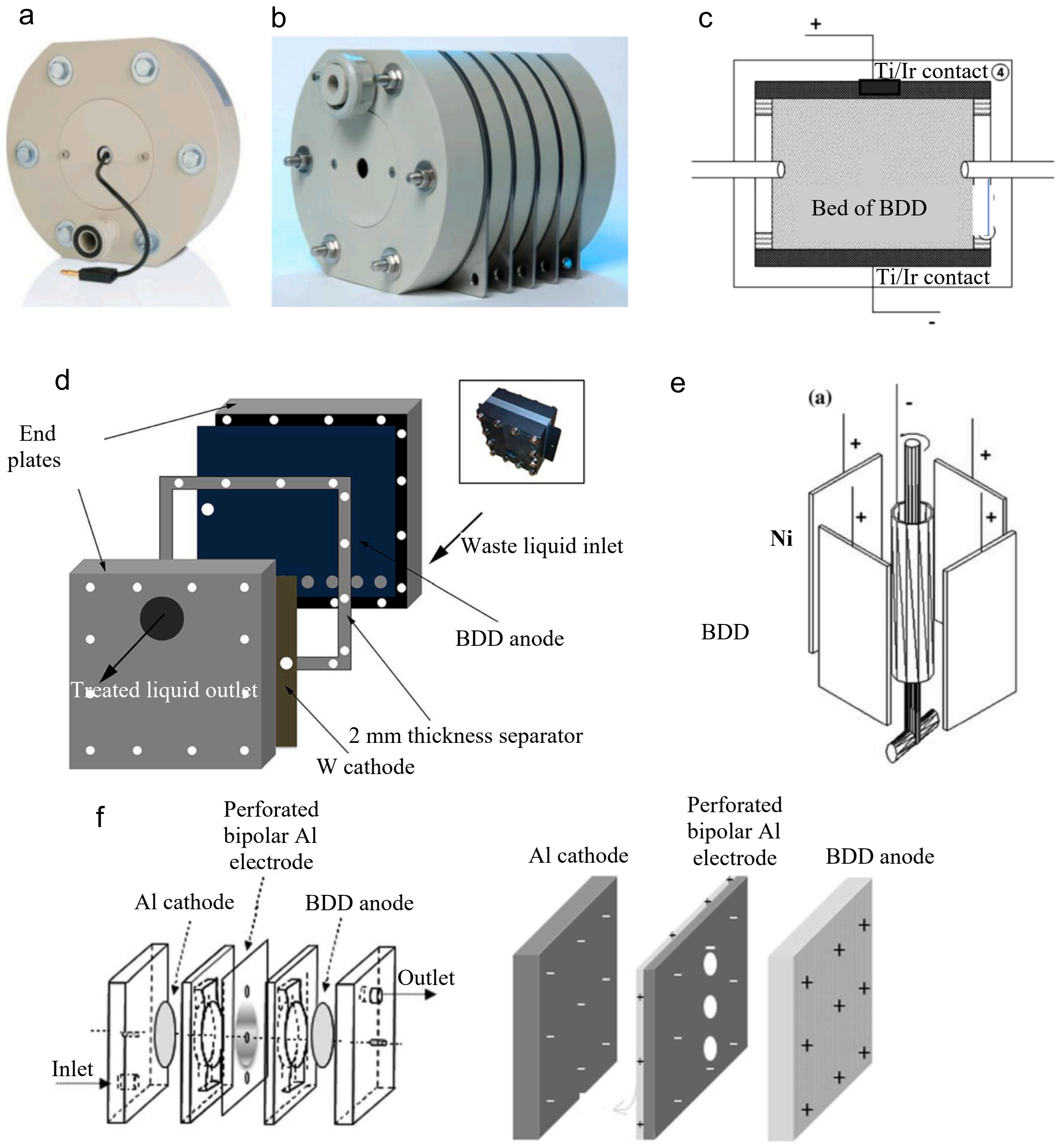

Fig. 9. Reactors with BDD anode used for electrochemical disinfection. Photograph of: (a) Diacell® 101, and (b) Diacell® 1001. Adapted from [30]. Sketch of: (c) Cross section of a bed of BDD (volume near 0.4 mL). Adapted from [29], (d) disassembled of a typical filter-press reactor with picture of the assembled cell in the inset panel. Adapted from [33], (e) filter–press cell with 4 BDD sheets as anode surrounding a cylindric Ni cathode. Adapted from [32], and (f) disassembled filter-press reactor with a perforated bipolar electrode. Adapted from [31].

waterborne agents was also assessed. For example, the inactivation of 250 mL of free-chloride bacterial suspensions containing 6.4×10^2 CFU mL^{-1} of *E. coli*, 4.4×10^3 CFU mL^{-1} of *Enterococcus faecalis*, and 2.3×10^3 CFU mL^{-1} of coliforms was investigated using an electrochemical cell with four sheets of Si/BDD (total anodic area = 30 cm^2) and a central cathode (cathodic area of 20 cm^2), as depicted in Fig. 9e [48]. According to the experimental conditions of j and stirring conditions (as Reynolds number (Re)), several disinfection trials were performed and the bacteria population was appreciably reduced with the length of exposure time (>300 s), but the disinfection efficacy depended on the type of microorganism, as shown in Fig. 13. The fast inactivation results for the EO disinfection achieved at $j = 10$ mA cm^{-2} in diluted Na_2SO_4 solutions under batch conditions indicated the essential role of the electrocatalytic material to produce efficiently heterogeneous free-($^{\bullet}$OH) at the BDD surface. The reduction of *E. coli*, coliforms, and enterococci cells to the detection limit was achieved in short electrodisinfection times of 60, 100, and 300 s, respectively, as can be seen in Table 1. An appreciable concentration of oxidants was also detected, including the peroxocompounds ($S_2O_8^{2-}$, $C_2O_6^{2-}$, and $P_2O_8^{4-}$) generated from the oxidation of ions present in the solution from Eqs. (9)–(11). These oxidizing species can be also useful to obtain a permanent disinfection, as in the case of *E. coli* (see Fig. 13). The electrochemical disinfection process was also tested with continuous mode experiments under the same operating conditions, completely inactivating *E. coli* and coliforms. An increase of j from 5 to 10 mA cm^{-2} favored an increase on the bacteria inactivation rate due to the enhancement of the oxidizing species in the liquid bulk, which can be considered as the most important impact to the global process.

It is noticeable that Polcaro et al. [48] demonstrated that the strong bactericidal action by using a BDD anode is due to the reactor design used (see Fig. 9e), the anode surface (where a high concentration of heterogeneous free-(($^{\bullet}$OH) is generated at the electrode/solution interface), and the local acidic pH values in the Nernst layer; whereas in the solution bulk, the electrogenerated oxidants contribute to the disinfection, leading to cell death. From the results reported in Table 1, it can be concluded that no shorter inactivation times were achieved in other

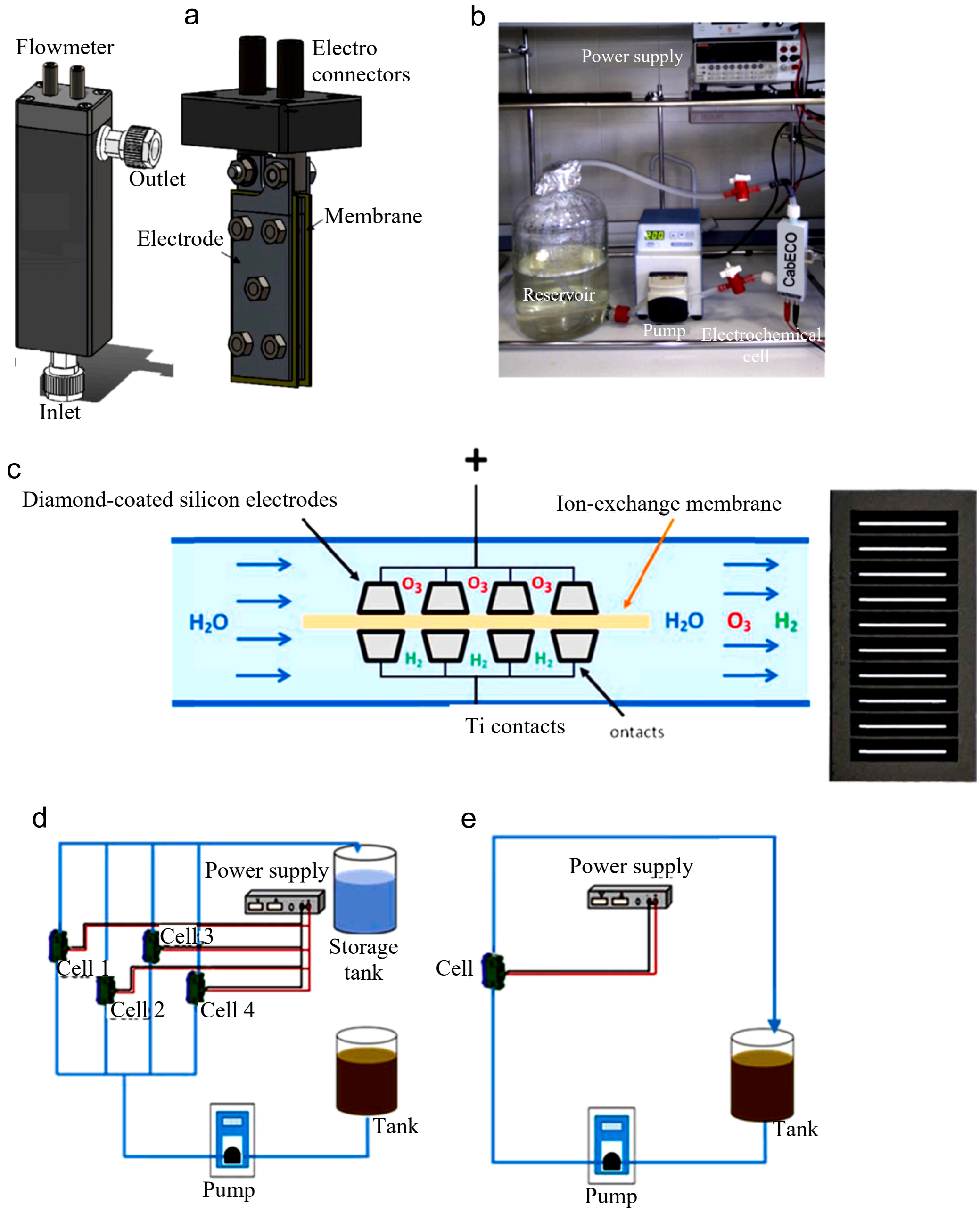

Fig. 10. Electrochemical systems with undivided zero-gap reactors with BDD anode for O_3 production. Photograph of (a) CabECO® cell, and (b) experimental setup. Adapted from [34]. (c) Left: Schematic depiction of the MIKROZON® membrane electrode assembly. Right: MIKROZON® electrode of structured silicon substrate with BDD coating on both sides. Schemes of (d) 4 MIKROZON® in continuous connected in parallel, and (e) 1 MIKROZON® in batch mode. Adapted from [35].

studies, even when other electrochemical cells or operating conditions were tested by using BDD or other anodes.

Bruguera-Casamada et al. [16] also compared the inactivation of different bacteria (*P. aeruginosa*, *Bacillus atrophaeus*, *Staphylococcus aureus* and *Enterococcus hirae*) with that of *E. coli* in 100 mL of synthetic water with 7 mM of Na_2SO_4 by using an undivided stirred BDD/SS tank reactor. A significant reduction of at least 5 log units was achieved within 60 min of EO with a BDD anode at $j = 33.3$ mA cm^{-2} with an initial solution pH of 3.0 or 7.0 (see Fig. 14). More than 95% of bacterial inactivation was mainly achieved in similar time intervals by the action of the heterogeneous free-(($^{\bullet}$OH) at the BDD surface from the anodic oxidation of water by Eq. (1), as well as the participation of other ROS such as $S_2O_8^{2-}$ and $SO_4^{-\bullet}$, formed via Eqs. (9) and (22), respectively. For example, *S. aureus* reached a 4 log reduction after 38 min of EO disinfection treatment, whereas *E. coli*, *P. aeruginosa*, *E. hirae* and *B. atrophaeus* required 30, 28, 23 and only 14 min, respectively. Fig. 14 evidenced that an overall inactivation of the two Gram-negative and the Gram-positive *bacilli* was reached, whereas Gram-positive cocci, *S. aureus* and *E. hirae* were more resistant, except in the case of *S. aureus* upon acidic conditions (pH ~ 3). These results highlighted that the most resistant bacteria were *S. aureus* and *E. hirae*, whereas the most fragile microorganism was the bacillus *B. atrophaeus*. As already explained in section 2, SEM micrographs showed that all bacteria presented changes in their morphology (see Fig. 3), identifying cellular debris due to their lysis as a consequence of a significant damage in the cell wall structure provoked by overall inactivation effect.

Other important features have been detailed when using free-chloride synthetic solutions with undivided stirred tank reactors to disinfect other bacteria by Bakheet et al. [17] and Zhou et al. [18]. In the former case, the effectiveness of EO inactivating the toxic

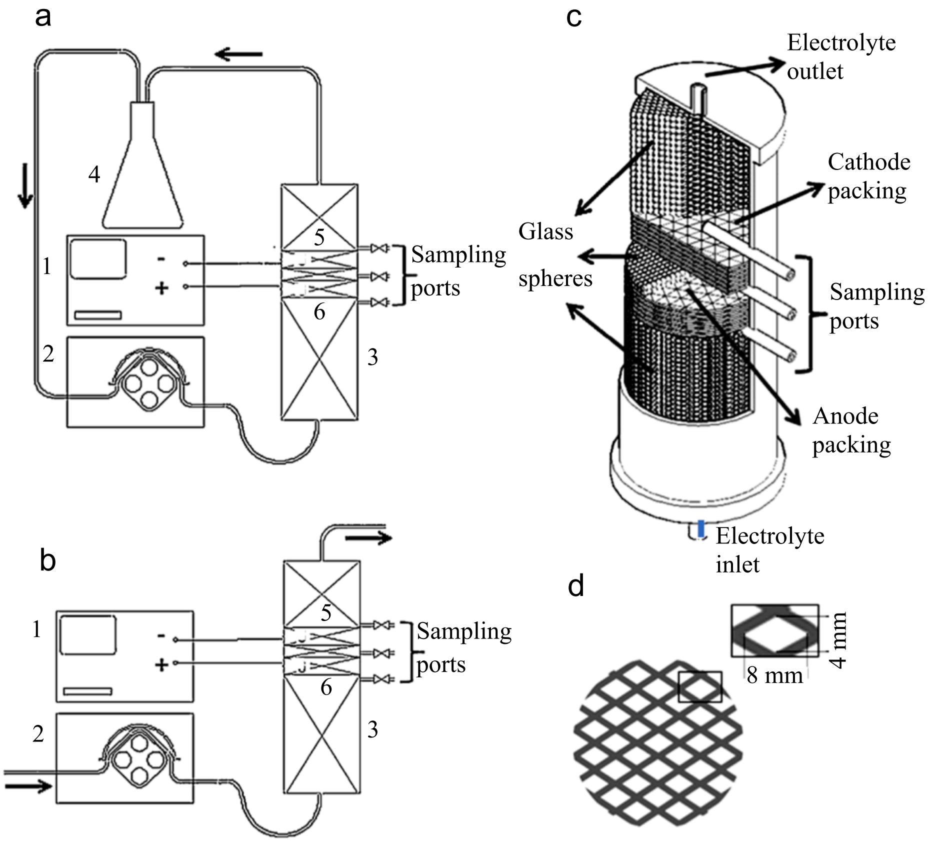

Fig. 11. Sketch of the setup of (a) batch and (b) continuous systems with a cylindrical reactor used for bacteria electrodisinfection. (1) Power supply, (2) pump, (3) electrochemical cell, (4) reservoir, (5) anode packing, and (6) cathode packing. (c) Axonometric sketch of the cell, showing the stacks of grids the BDD anode and Ti|Pt cathode packings, the inert filling (glass spheres), inlet, outlet, and sampling ports. (d) Detail of a grid. Adapted from [36].

filamentous cyanobacterium *Cylindrospermopsis raciborskii* (=1.8 × 10^6 CFU mL^{-1}) and removing the cyanotoxin *cylindrospermopsin* with BDD electrodes in 4 L of 0.050 M Na_2SO_4 (conductivity 9.35 μS cm^{-1}) solution was investigated at 20 °C by applying from 0 to 12.5 mA cm^{-2} with a typical two-electrodes reactor in monopolar connection under galvanostatic mode (see Fig. 8a). No *C. raciborskii* inactivation was attained after 180 min when no *j* was applied, confirming again the assertions by Jeong, et al. [9] and Li et al. [49] on the non-cell density removal via the contact with diamond surface. On the contrary, 45% and 70% of cell removals were achieved at j = 2.5 mA cm^{-2} for 60 and 180 min, respectively, whereas 76% and 95% decays were reached when *j* passed from 7.5 to 10 mA cm^{-2}, and then, the inactivation rate increased (see Table 1). Interestingly, similar cell reduction was assessed after 180 min of 10 and 12.5 mA cm^{-2}. In contrast, no significant changes were observed in the inactivation rate when an increase of the temperature from 22 to 25 °C was applied, and the E_{cell} value remained stable until 180 min of electrolysis. The authors also monitored Chlorophyll *a* (Chl a) and carotenoids concentrations because these can be used as indirect biomass measurements for cell integrity. 72%, 74%, 85%, and 90% of Chl a were removed by applying 2.5, 7.5, 10, and 12.5 mA cm^{-2}, respectively, indicating a gradual damage in the cell integrity, as expected by the higher oxidant generation. Moreover, a physiological test showed that cells were completely inactivated in 45 min and the initial *cylindrospermopsin* concentration of 1.83 μg L^{-1} was also removed to below the detection limit (<0.05 μg L^{-1}) in 30 min.

The impact of electrolysis at 10 mA cm^{-2}, as an opening/crack or fracture in the cell wall, on *C. raciborskii* viability was examined by SEM analyses. As can be seen in Fig. 4, the cell morphology of *C. raciborskii* changed before and after the treatment by the attack of the electrogenerated oxidants at BDD surface because Chl a and other cellular components were removed from the cell and released into the water. Then, *C. raciborskii* became more fragile and delicate, and thus, the cell damage became feasible. This behavior was clearly attributed to the major role in algae removal played by the heterogeneous free-($^{\bullet}OH$) at the anode surface, although Na_2SO_4 also contributed to the inactivation due to the production of $SO_4^{\bullet -}$ and $S_2O_8^{2-}$, especially in the initial stage. Considering complete cell inactivation and around 90% cell density removal, the energy consumption was estimated to be between 2.7 and 5.4 kWh m^{-3}. However, these electric requirements are not useful at commercial scale due to the small volume of treated solutions. An alternative is the development of small devices powered with free and renewable energies like solar photovoltaic cells.

Zhou et al. [18] studied the electrochemical inactivation of 200 mL solutions with 1.0–4.0 × 10^6 CFU mL^{-1} *Microcystis aeruginosa* in diverse supporting electrolytes (Na_2SO_4, $NaNO_3$, and Na_2HPO_4) at 30 mM concentration by using an undivided stirred BDD (also Ti|IrO_2-Ta_2O_5, or Pt)/SS tank reactor by applying different *j* values from 50 to 200 mA cm^{-2} for 60 min. The greater disinfection ability of BDD over other active anodes like Ti|IrO_2-Ta_2O_5, or Pt for *Microcystis aeruginosa* inactivation was well-proven at high *j* by EO in sulfate, nitrate, and phosphate media. While 54.4%, 62.3%, and 99.1% of cells were inactivated with BDD in $NaNO_3$, Na_2HPO_4, and Na_2SO_4, respectively, only 10%–20% cells were reduced when Ti|IrO_2-Ta_2O_5 and Pt anodes were used at 200 mA cm^{-2} with the same electrolytes. From these results, a simple inactivation mechanism (shown in Fig. 5) which is described in section 2 was proposed by these authors. Fig. 5 also highlights that heterogenous free-($^{\bullet}OH$), $S_2O_8^{2-}$, $SO_4^{\bullet -}$, and other ROS promoted the attack to the cells in each step, favoring the *M. aeruginosa* inactivation.

All the above findings demonstrated a large inactivation effectiveness by using diamond anodes in free-chloride solutions. This disinfection approach presents as major advantages:

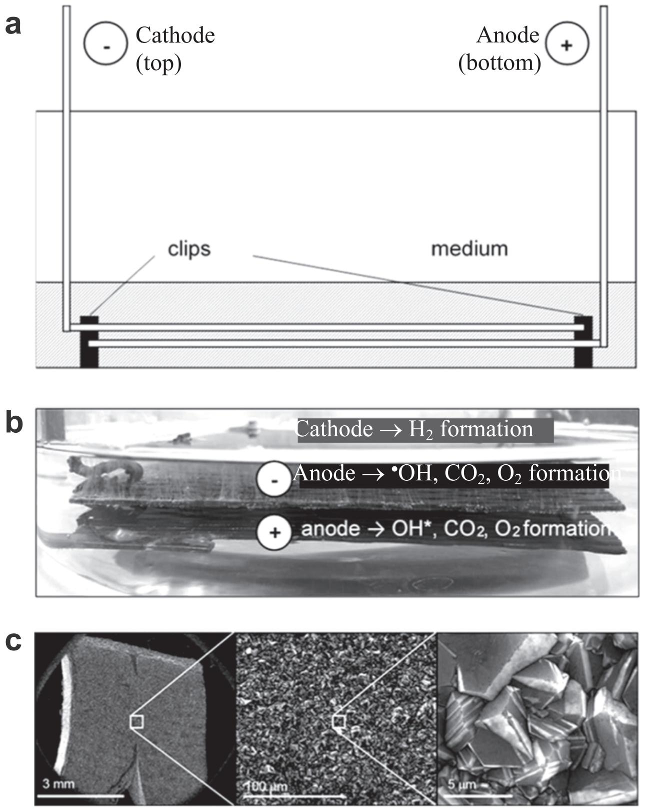

Fig. 12. Undivided horizontal electrochemical system for bacteria disinfection. (a) Scheme of the setup. (b) Image of the system with a BDD anode and cathode, along the main reactions involved. (c) SEM pictures of the cross link of the expanded metal with BDD coating. At the right, the diamond crystals with typically twinned grain structure. Adapted from [37].

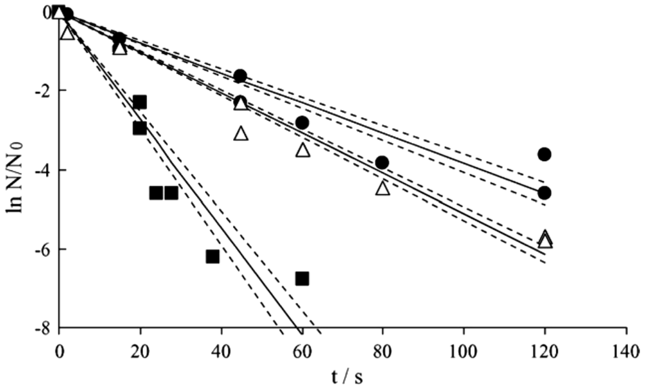

Fig. 13. Survival ratio as a function of the length of exposure time during the electrolysis for (■) *E. coli* (6.4 × 10^2 CFU mL^{-1}), and coliforms: (Δ) 2.3 × 10^3 CFU mL^{-1} and (●) 4.4 × 10^3 CFU mL^{-1} in batch experiments by applying 10 mA cm^{-2} and Reynolds number of the solution in the reactor = 1 × 10^4. Full lines represent the least squares regression lines for the data and dotted lines represent the standard error of the regression. Adapted from [48].

(i) Elucidation of inactivation mechanisms, in terms of cell integrity, damage cell walls, protein and genetic material degradation/liberation,
(ii) prevention of the toxic disinfection by-products,
(iii) in situ electrogeneration of disinfectant agents, mainly heterogenous free-(•OH) and other ROS,
(iv) comprehension of the key role of other oxidants, such as $S_2O_8^{2-}$, $SO_4^{•-}$, $C_2O_6^{2-}$ and $P_2O_8^{4-}$, during the cell inactivation,

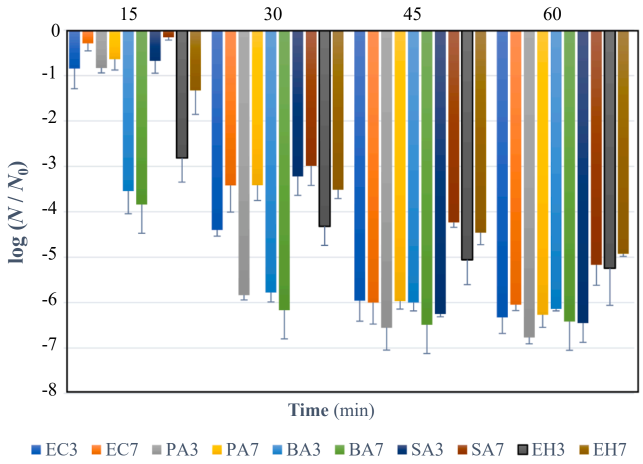

Fig. 14. Logarithmic reduction of bacterium content in suspension with electrolysis time for the EO treatment of 100 mL of 7 mM Na_2SO_4 and $N_0 = 10^6$ CFU mL^{-1} of each microorganism using an undivided stirred Si|BDD/SS (3 cm^2 area) tank reactor at j = 33.3 mA cm^{-2} and 25 °C. Bacterium: *E. coli* (EC), *P. aeruginosa* (PA), *B. atrophaeus* (BA), *S. aureus* (SA), and *E. hirae* (EH). The number 3 or 7 in each acronym means the initial solution pH, i.e., 3.0 or 7.0, respectively. Adapted from [16].

(v) inactivation effectiveness of *E. coli* or other bacteria as compared with conventional chlorination treatment, and
(vi) shorter inactivation times with BDD respect to other anodic materials because of the larger effective production of heterogenous free-(•OH), which can promote the formation of other ROS that contribute in a fast microorganism's reduction.

However, the following important drawbacks could be emphasized:

(i) Limitations due to the use of stirred tank reactors with a typical two-electrode arrangement,
(ii) poor apparent electric requirement estimations and costs due to the small-treated volumes of free-chloride solution. A correct strategy to a full-scale application can be the use of flow systems, and techno-economic studies are required to show the viability of the EO with BDD respect to other disinfection technologies.
(iii) addition of salts as supporting electrolytes,
(iv) disparities with the real water-matrices composition which can cause variations on the inactivation efficiency due to the competition between the natural organic matter, organics or bacterial reduction,
(v) generation of organic residuals (suspension sludge) by degrading microorganisms, and
(vi) disinfections restrictions due to the surface-layer character of the heterogenous free-(•OH).

To solve these problems, novel designs of electrochemical systems has been recently developed to operate at different flow modes. An increasing research at lab scale has also been accomplished in the last years about the effect of water matrix compositions alongside the consideration of different chloride solutions to demonstrate the disinfection diamond viability over chlorination, as it will be described in the next Sections. It is important to note that GilPavas et al. [52] considered, for first time, to investigate the inactivation of 80 mL of a suspension of 6750 CFU mL^{-1} of total coliforms and 5600 CFU mL^{-1} of fecal coliforms in free-chloride surface water (pH 6.6, 18 mg L^{-1} TOC, 0.870 and 0.183 mg L^{-1} of NO_3^- and NO_2^-) in a Plexiglas, continuously stirred, batch jacketed reactor with two vertically-placed Ti|BDD plates. Relevant disinfection results were obtained, achieving 92%, 96%, and 100% of disinfection for 2, 11, and 20 mA cm^{-2}, respectively. A 25% of TOC removal, 79% of NO_2^- decay, and 65% of NO_3^- increase were obtained after 20 min at $j = 10$ mA cm^{-2}. No significant effects were registered due to the surface water composition because the inactivation was mainly due to the action of heterogeneous free-($^{\bullet}$OH), even when dissolved organic matter competes with the oxidants during the disinfection process. Then, this study allowed opening new horizons to apply electrodisinfection-based ROS species.

More studies have been developed to inactivate a greater number of bacteria to corroborate the effectiveness of EO as disinfection approach, as well as to validate the efficacy of other disinfectant agents than ROS. It is important to remark that the inactivation mechanism involving heterogeneous free-($^{\bullet}$OH) depends on the diffusion coefficient of bacteria in the solution, the diffusion distance of microorganisms, the thickness of diffusion layer and mixing rate [9,50]. However, the limiting step, in terms of inactivation rate and time, can be regarded as the diffusion of microorganism cells in the diffusion layer to react with the heterogeneous free-($^{\bullet}$OH) or ROS in the surface vicinity. This point is considerably important because the EO disinfection approach based on heterogeneous free-($^{\bullet}$OH) is a surface-layer-based process, different than electrochlorination, which mainly acts as a volume-based chemical process due to its reaction characteristics. Therefore, a more intense research related to electrodisinfection by EO with BDD should be potentiated and widely explored in the next years for its possible implementation and commercialization.

4.2.3. *Chloride medium*

Chloride media such as potable water, groundwater, urban wastewater, hospital wastewater, and so on are ubiquitous actual waters contaminated with pathogen agents. Electrodisinfection by EO with a BDD anode is a useful method for treating such aqueous matrices for possible reuse since it allows the generation of active chlorine as strong bactericide, needing the process to be deeply investigated to minimize the formation of toxic chlorinated products (ClO_3^-, ClO_4^-, and chloramines). Since the inactivation of *E. coli* has been the most largely process studied (see Fig. 1c), this section presents and discusses firstly the EO treatment with BDD in chloride media. A further Section will consider the analogous electrodisinfection process for chloride solutions without this pathogen.

4.2.3.1. Inactivation of E. coli. The most relevant results reported for the EO treatment with BDD of *E. coli* in chloride media are summarized in Table 2. The data are classified according to the kind of water tested, namely potable water, urban wastewater, synthetic urine, and other synthetic or real wastewaters. In general, large inactivation efficiency, related to the bacterial removal of various log units, can be observed in this table upon the application of relatively low I, j, or E_{cell} values. Small water volumes and great volumes up to 100 L were checked with undivided stirred tank reactors, pre-pilot plants with flow-by or flow-through filter-press cells, and commercial systems. In most cases, the evolution of active chlorine and other chlorinated products (ClO_3^-, ClO_4^-, and chloramines), as a function of time (t) or electric consumed charge (Q), was determined to show their role in the electrodisinfection process. TOC and COD decays using real wastewaters were also measured, as well as the EC$_V$ value, (in kWh m^{-3}) calculated as $E_{cell}\ I\ t/V$ [41]. However, two main drawbacks can be emphasized in these works. First, no techno-economic studies are reported, which are necessary to demonstrate the applicability of EO with BDD at industrial level in competence with other technologies, and second, neither information nor suggestions are given for the post-treatment of treated wastewaters before disposal for their possible reuse that is required to remove the toxic by-products generated. Future work should develop these aspects to strengthen the knowledge of the electrodisinfection technology for actual applications.

Regarding the papers related to the disinfection of potable water, Feng et al. [53,54] used an undivided stirred tank reactor like of Fig. 8a with a Si|BDD anode and a Ti mesh cathode to treat 400 mL of stormwater at neutral pH with *E. coli* contents up to 12,000 CFU (100 mL)$^{-1}$, along with other pathogens. Total disinfection was easily achieved after 6 min of electrolysis at $j = 4.2$ mA cm^{-2}, which was drastically reduced by adding *t*-butanol, a known scavenger of hydroxyl radical. In contrast, no inhibition was found when an alternative Ti|$Ir_{0.2}Ru_{0.4}Ti_{0.6}O_2$ anode was used, giving rise to overall inactivation in a shorter time of 2 min upon the same conditions (see Table 2). This means that active chlorine formed from Eqs. (2) and (3) is the preferential oxidant using the latter anode, whereas this species competes with BDD ($^{\bullet}$OH) generated from Eq. (1) when using the Si|BDD electrode. Operating with the cell of Fig. 12 equipped with two horizontal Nb|BDD electrodes, a fast and total disinfection of 800 mL of tap water contaminated with 10^4 CFU mL^{-1} of *E. coli*, *P. fluorescens*, *P. aeruginosa*, and *B. subtilis* spores was reached after 5.5 min of electrolysis at $j = 2.0$ mA cm^{-2} with low Q and EC$_V$ values of 0.017 Ah L^{-1} and 0.104 kWh m^{-3}, respectively, much smaller than those determined at lower j [37] (see Table 2).

The use of flow systems allowed the disinfection of higher volumes of water, with electrodes of greater size and using high current, thus presenting a better approach for industrial application. In this way, Yao et al. [28] treated 2 L of artificially contaminated river water with 10^7–10^8 CFU mL^{-1} of *E. coli*, *P. aeruginosa*, and *L. pneumophila* using the flow plant of Fig. 8b containing a Diachem® W cell with 2Si|BDD electrodes. These authors found a quicker disinfection rate for *E. coli* in front *P. aeruginosa*, 96 min vs. 150 min for total inactivation at 3 V, whereas *L. pneumophila* was much slowly removed, needing a superior E_{cell} of 4 V for its overall inactivation in about 64 min (see Table 2). This means that the nature of the cell membrane determines the ability of the oxidizing agents for its death. A similar system with two Si|BDD electrodes was used to treat 3 L of drinking water polluted with 10^8 CFU mL^{-1} of *E. coli*, *Enterococcus faecium*, and *P. aeruginosa* [55]. Very high j up to 333 mA cm^{-2} were applied to enhance the production of O_3 as bactericide, only needing 10 min for total disinfection at $j = 208$ mA cm^{-2} with a very small EC$_V$ = 0.0048 kWh m^{-3}, demonstrating the effectiveness of the procedure (see Table 2). Diacell® cells like of Fig. 9a equipped with Si|BDD electrodes have also been utilized to disinfect 5 L of tap water with 10^5 CFU mL^{-1} *E. coli* [55]. In this case, the addition of 1 g L^{-1} NaCl strongly accelerated the total inactivation of the bacteria, disclosing the key role of generated active chlorine during the electrodisinfection process (see Table 2). Naji et al. [56] reported the electrolysis of a large volume (100 L) of swimming water with 10^2 CFU (100 mL)$^{-1}$ of *E. coli* and *P. aeruginosa* using an undivided flow-through cylindrical cell equipped with a Nb|BDD or Ti|Pt anode and a carbon-felt cathode by applying an $I = 1.5$ or 3.0 A, respectively. Fig. 15a highlights that both bacteria were completely inactivated in about 30 min for Nb|BDD and 60 min for Ti|Pt. This behavior was ascribed to the much higher production of total oxidants by the former anode, as can be seen in Fig. 15b, in agreement with the higher production of BDD($^{\bullet}$OH) from Eq. (1) and $S_2O_8^{2-}$ from Eq. (9) and/or (20). It is interesting to note the results of Fig. 15c showing that active chlorine (ClO^-) practically disappeared after 120 min of electrolysis since it was converted into ClO_4^- ion. However, these authors did not attempt to remove the latter ion from the treated water, a necessary post-treatment to show the viability of this electrodisinfection method for swimming pools.

The electrodisinfection of urban wastewaters from WWTPs has been more extensively studied due to the interesting possibility for their reuse for agricultural activities. Apart from pathogens, these wastewaters contain a low content of NOM (measured by their COD and/or TOC), which can also be substantially reduced by the attack of generated oxidants. Following their study on tap water disinfection with a Diachem® cell with Si|BDD electrodes, Heim et al. [57] analyzed the analogous treatment of 3 L of a secondary WWTP effluent with 6–13 mg L^{-1} TOC and 10^8 CFU mL^{-1} of *E. coli*, *Enterococcus faecium*, and *P. aeruginosa*. The application of a high $j = 208$ mA cm^{-2}, with O_3 production, yielded again an excellent performance, even superior to that of tap water, since only 10 min were needed for complete bacterial inactivation, with very low $Q = 0.127$ Ah L^{-1} and EC$_V$ = 0.0010 kWh m^{-3}. Good results have been described by Frontistis et al. [58] as well, who used an undivided stirred Si|BDD/Zr tank reactor for electrolyzing 115 mL of an urban wastewater with 27 mg L^{-1} COD, 1250 CFU mL^{-1} *E. coli*, and 100 μg L^{-1} 17α-ethynylestradiol (EE2). Total disinfection and EE2 removal were attained after 5 min of electrolysis at $j = 2.1$ mA cm^{-2}, but a longer time of 30 min was needed for the abatement of 85% COD (see Table 2). The treatment of a secondary WWTP effluent with a suspension of 10^6 CFU mL^{-1} *E. coli* using an undivided flow-through filter-press cell with Nb|BDD plates was compared with the behavior of model waters without pollutants and Cl$^-$ ion in the presence and absence of HCO$_3^-$ ion at different j values and temperatures [59]. Table 2 shows a quicker inactivation in the model waters due to the consumption of oxidizing agents to destroy NOM in the WWTP effluent, as well as a significant effect of HCO$_3^-$, at least as scavenger of BDD($^{\bullet}$OH). The increase of temperature also enhanced the disinfection power of the electrolytic system by the acceleration of the oxidant attack. This same effect has been reported by Haaken et al. [60] for the total reduction of 10^5 CFU (100 mL)$^{-1}$ *E. coli* in the EO process of 5 L of urban wastewater with addition of 173 mg L^{-1} NaCl using a similar electrochemical cell at j from 15 to 105 mA cm^{-2} and raising the temperature from 6 to 30 °C. The growth of Q enhanced the production of free chlorine, and high EC$_V$ values between 2.0 and 2.6 kWh m^{-3} were determined for overall inactivation at Q values between 0.10 and 0.15 Ah L^{-1} (see Table 2). Using a Mini Diacell ® 101 PP, Pérez et al. [61] disinfected 20 L of WWTP effluents taken during a period of eight months with 1.3 × 10^4–5.2 × 10^5 CFU mL^{-1} *E. coli*. They reported a gradual cell reduction with increasing j from 40 to 120 mA cm^{-2} and Cl$^-$ content from 60 to 1050 mg L^{-1} as result of the production of more BDD($^{\bullet}$OH) and primordially active chlorine, along with the generation of undesirable trihalomethanes (see Table 2).

It is remarkable the extensive work of the Rodrigo's group to disinfect WWTP effluents using different electrolytic systems and experimental conditions. Undivided flow-through filter-press reactors [62–65] several Diacell® cells [30,66], and commercial CabECO® and ConDiacell® ECWP cells [67,68], equipped with Si|BDD or Nb|BDD electrodes, were used to treat effluent volumes from 600 mL to 100 L. Relevant results obtained for the assays made are summarized in Table 2, where it can be seen that *E.coli* and in some cases, *P. aeruginosa* [67,68], and *Klebsiella pneumoniae* and *Enterococcus faecalis* [65], were largely or completely reduced by applying low j values, typically <2.5 mA cm^{-2}. The characteristics of the electrodisinfection process were analyzed from the undivided flow-through filter-press reactors operating with wastewater volumes up to 3 L. As enhancement of the inactivation of 16,000 CFU mL^{-1} *E. coli* in 600 mL of urban wastewater was observed when j grew from 0.13 to 0.91 mA cm^{-2}, reaching 4.2 log cell units reduction in 40 min, with EC$_V$ values <0.2 kWh m^{-3}, due to the generation of more BDD($^{\bullet}$OH) and active chlorine, as pointed out above [63]. However, the use of a higher j of 1.30 mA cm^{-2} did not improve the performance of the system because of the loss of the above oxidizing agents by parasitic non-oxidant reactions. The much lower disinfection ability of a DSA anode discarded its application in front of BDD [64]. The works also clarified that active chlorine and chloramines (primary (NH$_2$Cl), secondary (NHCl$_2$), and/or tertiary (NCl$_3$)) were the main oxidants, whereas active chlorine evolved to ClO$_3^-$ and ClO$_4^-$ ions. Fig. 17a shows the quick and total disinfection of 10^7 CFU mL^{-1} *E. coli*, *K. pneumoniae*, and *E. faecalis* achieved at similar rate after the consumption of $Q = 0.03$ Ah L^{-1} at $j = 1.0$ mA cm^{-2} using an undivided flow-through Si|BDD/SS filter-press cell [65]. Fig. 17b illustrates that the remaining content of both, active chlorine and ClO$_3^-$ increased progressively with increasing Q, whereas chloramines appeared for Q values >0.12 Ah L^{-1}. The formation of these undesirable products was also found operating with 4 L of WWTP effluents using Diacell® 101, 401, and 1001 cells (see Fig. 9a and b) [30,66], whereas they were practically undetected when the assays were performed with a pilot plant that treated 300 L of wastewaters at the same $j = 1.20$ mA cm^{-2} [30]. Similar results were found with the CabECO® cell (see Fig. 10a and b) yielding good disinfection efficiency and small production of chlorinated products for the treatment of up to 300 L of WWTP effluents, since the SPE between electrodes practically avoids the reaction of active chlorine with BDD($^{\bullet}$OH) to form chloramines and enhances O$_3$ generation [67,68]. Even better results have been reported for a ConDiacell® cell type ECWP operating in continuous mode at $j = 19.04$ mA cm^{-2}, which showed at least one log cell unit reduction of 10^4 CFU mL^{-1} *E. coli* and 10^5 CFU mL^{-1} *P. aeruginosa* higher than in recirculation or batch mode, without detection of ClO$_3^-$ and ClO$_4^-$ ions (see Table 2). On the other hand, De Battisti et al. [69] analyzed the excellent performance of a CabECO® cell for inactivating 5 L of groundwater with ~ 200 MPN (100 mL)$^{-1}$ of *E. coli* (and coliforms), *Enterococcus faecalis*, *P. aeruginosa*, and *Legionella pneumophila* by applying between 0.31 and 2.30 A for 120 min. Fig. 18a depicts the progressive O$_3$ production at higher j, whereas Fig. 18b highlights that overall inactivation was easily attained for *E. coli*, coliforms, and *E. faecalis* at $Q = 0.045$ Ah L^{-1}, whereas *P. aeruginosa* and *L, pneumophila* were more slowly reduced. These authors remarked that no COD, i.e., organic matter, was removed and followed the time course of active chlorine, total chorine, and the low contents of ClO$_3^-$ and ClO$_4^-$ produced (see Table 2).

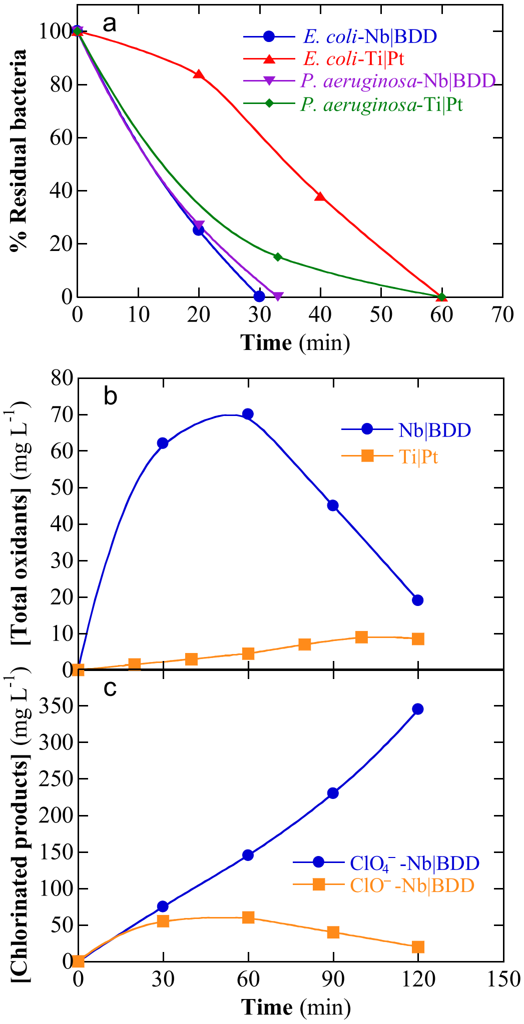

Fig. 15. EO treatment of 2 L of a swimming pool water with an undivided flow-through parallelepipedic cell with a Nb|BDD or Ti|Pt anode (45 cm^2 area) and a carbon-felt cathode by applying I = 1.5 or 3.0 A, respectively. Change with electrolysis time of: (a) percentage of residual *E. coli* and *P. aeruginosa* ($N_0 = 10^2$ CFU (100 mL)$^{-1}$), (b) concentration of total oxidants, and (c) chlorinated products. Adapted from [56].

Synthetic urine with inoculated *E. coli* was also chosen to be disinfected by EO with BDD. Raut el al. [33,70,71] used a Diamonox 40 cell, a flow-through filter-press reactor equipped with a Nb|boron doped ultrananocrystalline diamond (UNCD) or Nb|BDD plate as anode and a W plate as cathode, to treat 2 L of synthetic urine spiked with $\leq 10^{10}$ CFU (100 mL)$^{-1}$ *E. coli* (see Table 2). Operating in the presence of fecal matter, increasing disinfection efficiency was obtained with raising the E_{cell} from 4 to 12 V with Cl^- oxidation enhancement giving more oxidants. Total disinfection was found in 30 and 6 min at 6 and 12 V, respectively, with high EC_V values of 5 and 10 kWh m^{-3}. The effect of pulse or continuous mode over the process performance was assessed as well [71]. The pulse mode resulted much more efficient, achieving 6 log cell units reduction in 35 min for a 10% duty cycle pulse in front of 100 min needed during the continuous mode. This was ascribed to the fact that pulsing allowed the mixing of oxidants and improved the contact time with the pathogens during the OFF time of the pulse, thus giving rise to a more energy-efficient disinfection. Cotillas et al. [72] confirmed the applicability of EO with BDD to disinfect synthetic urine. These authors electrolyzed 1 L of such wastewaters with 700 mg L^{-1} TOC and 5×10^4 CFU mL^{-1} of *E. coli* and *P. aeruginosa* with an undivided flow-through filter-press cell with two Si|BDD electrodes by applying j values between 1.0 and 10 mA cm^{-2}. Total inactivation of both bacteria was attained in 20 min at $j = 10$ mA cm^{-2}, although a notable TOC reduction required much long treatment. NO_3^-, NH_4^+, ClO^-, and ClO_3^- ions were generated during the assays, the two formers proceeding from the N-components of the synthetic urine, and chloramines were undetected (see Table 2). This is a surprising result because chloramines are formed from the reaction of NH_4^+ with ClO^-, suggesting that the latter oxidant attacks preferentially the high amount of organic matter of the wastewater. This hypothesis has been recently confirmed by Herraiz-Carboné et al. [65] when treated a synthetic hospital urine with much lower organic load of 2.3–6.7 mg L^{-1} TOC and greater bacteria content of 10^7 CFU mL^{-1} of *E. coli*, *K.* pneumoniae, and *E. faecalis* (see Table 2). For this wastewater, Fig. 16a depicts a complete disinfection at $Q = 1.25$ Ah L^{-1}, a value much>0.03 Ah L^{-1} consumed by an urban wastewater with the same bacterial charge, making in evidence the competitive attack of oxidants over the organics of the synthetic hospital urine to produce NO_3^- and NH_4^+ ions. Under these conditions, Fig. 16b reveals a large production of chloramines with consumption of all generated ClO^- because of its reaction with NH_4^+. Using a similar electrochemical system, Dbira et al. [73] electrolyzed 600 mL of synthetic urine with 90 mg L^{-1} TOC, 80 mg O_2 L^{-1} COD, and 9000 MPN *E. coli* at $j = 15$ mA cm^{-2} using four anodes and a SS cathode. Fig. 19a-19c present the evolution of these parameters with Q. As can be seen, the disinfection efficiency decreased in the order: Si|BDD > Ti|RuO$_2$ ~ Ti|IrO$_2$ > Pt, and for the most powerful Si|BDD, total disinfection at $Q = 5$ Ah L^{-1} and overall reduction of TOC at 9 Ah L^{-1} and COD at 5 Ah L^{-1} were achieved. The time course of all species released, i.e., PO_4^{3-}, SO_4^{2-}, NO_3^-, NO_2^-, NH_4^+, ClO^-, ClO_4^- ions and chloramines, was determined for the four anodes.

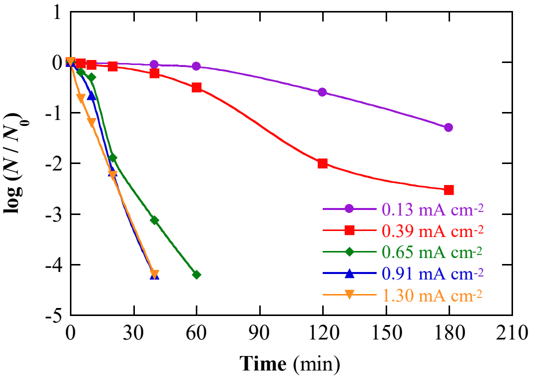

Fig. 16. Effect of current density over the logarithmic reduction of *E.coli* (N_0 = 16,000 CFU mL^{-1}) in 600 mL of an urban wastewater using an undivided flow-through Si|BDD/SS filter-press cell (78 cm^2 area). Adapted from [63].

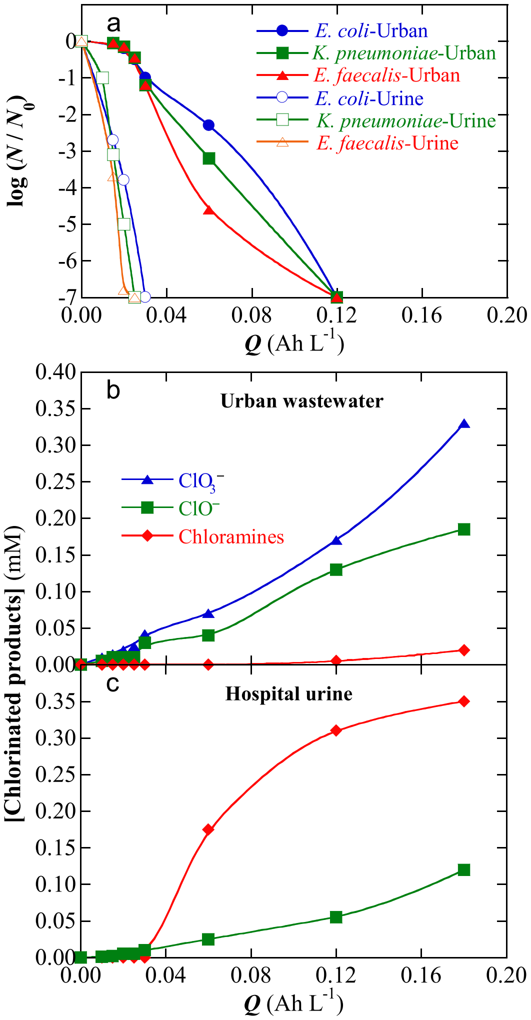

Fig. 17. EO treatment of urban wastewater and synthetic hospital urine with an undivided flow-through filter-press cell with a Si|BDD anode and a SS cathode (78 cm^2 area) at $j = 1.0$ mA cm^{-2}. Variation with electrical consumed charge of: (a) logarithmic reduction of *E. coli*, *K. pneumoniae*, and *E. faecalis* (N_0 = 10^7 CFU mL^{-1}), and concentration of chlorinated products for (b) urban wastewater and (c) synthetic hospital urine. Adapted from [65].

The inactivation of *E. coli* has been evaluated with synthetic chloride solutions to show the influence of its anodic oxidation products, as detailed in Table 2 [20,74,75]. Vacca et al. [74] developed a theoretical model to describe the ClO_3^- evolution in a 200 mg L^{-1} SO_4^{2-} + 100 mg L^{-1} Cl^- solution with a commercial EC Electro MP-Cell containing Si|BDD and SS plates operating in continuous and recirculation modes, as a function of the liquid flow rate characterized by the Reynolds number. The recirculation mode showed more efficiency to remove 10^4 CFU mL^{-1} *E. coli* inoculated in the solution and optimum conditions were established to minimize ClO_3^- production. Continuous and batch modes were also analyzed by Lacasa et al. [75] for the treatment of 30 L of a synthetic ballast water with 10^6 CFU mL^{-1} *E. coli* and 3.0 or 30 g L^{-1} NaCl using a Diacell® 100 cell with a Si|BDD anode. As expected, the higher production of active chlorine at 30 g L^{-1} NaCl enhanced the total inactivation of bacteria for both modes, with an EC_V value as low as 0.005 kWh m^{-3} at $j = 12.7$ mA cm^{-2} in continuous, disclosing the industrial interest of the BDD technology for the electrodisinfection of marine waters.

Finally, Gómez-López et al [76] explore the reuse of wash waters of iceberg lettuce and other vegetables by means of EO with BDD. As an example, they reported the overall microbial inactivation of 10^5 CFU

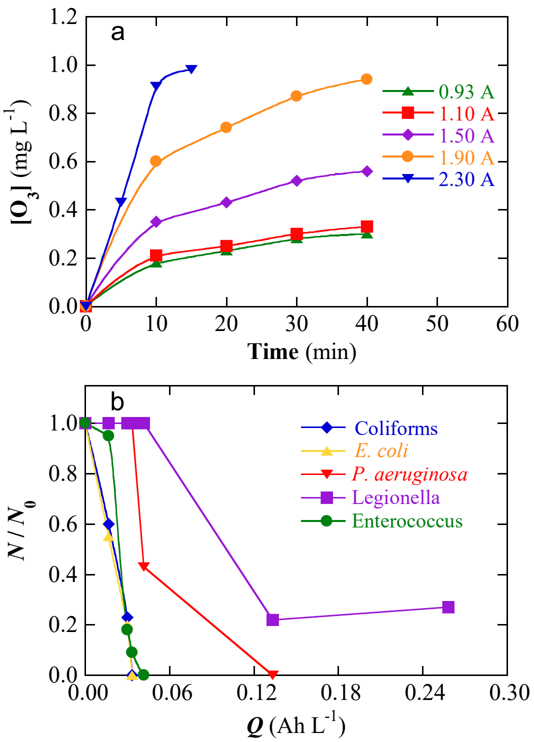

Fig. 18. (a) Time course of ozone concentration as a function of applied *I* for the EO process of 5 L of groundwater using a CabECO® cell (see Fig. 10a), 24 cm^2 electrode area) operating in batch. (b) Normalized bacterium concentration (N_0 ~ 200 MPN (100 mL)$^{-1}$) vs. electrical consumed charge for the same system operating in continuous mode. Adapted from [69].

mL^{-1} *E. coli* in 5 L of such wastewaters with 115 mg L^{-1} NaCl in 40 min using a Diacell® 101 cell with two Si|BDD plates at high B-doping levels and j = 180 mA cm^{-2} (see Table 2). Although they found the technology suitable for disinfecting and saving water consumption in fresh-cut industries, no techno-economic studies were described to support their industrial viability.

4.2.3.2. Inactivation of other bacteria. Despite the non-active diamond anodes can be considered as the best option for the inactivation of *E. coli* in chloride media by EO; a significant number of investigations have been devoted to clarify the electrochemical inactivation of several bacteria with BDD anodes in different aqueous matrices containing chloride in their compositions, to develop an efficient disinfection approach. These studies have been mainly centered in the inactivation of *P. aeruginosa, total coliforms, marine bacteria*, and others (*M. aeruginosa,* enterococci, *Campylobacter, C. perfringens,* Lactobacillus, Escherichia, Bacillus, Streptococcus, Eubacterium, Clostridium, Propionibacterium, *Legionella pneumophila, S.* aureus, and *Rhizoctonia solani*), whose main results are summarized in Table 3. Note that *P. aeruginosa,* in the same way as *E. coli* and *total coliforms,* has also been considered as model pathogen in several comparative studies regarding the electrodisinfection of bacteria in free-chloride or chloride synthetic and real wastewaters by using BDD as anode (see Fig. 1c).

According the results discussed in Section 4.2.3.1, NaCl strongly accelerated the *E. coli* inactivation rate respect to the EO of free-chloride solutions (Section 4.2.2, see Table 1), which is due to the key role of electrogenerated active chlorine species (see Table 2). Thus, it disclosed the great interest of the applicability of diamond technology to remove other bacteria.

Undivided flow reactors (pre-pilot plants with flow-by or flow-through filter-press cells and commercial systems, as described in Figs. 8-12) have been the predominant electrochemical systems employed to disinfect different water matrices (see Table 3), although some studies have also used agitated beaker or stirred tank reactors, divided or undivided. This strategy has also allowed to treat higher water volumes up to 10 L, achieving diverse bacterial inactivation efficiencies with lower values of j, I or E_{cell}. At this time, dissolved organic matter was measured by TOC, active chlorine species, and their by-products were also monitored, and the electric requirements were estimated, as already described in Section 4.2.3.1 [41].

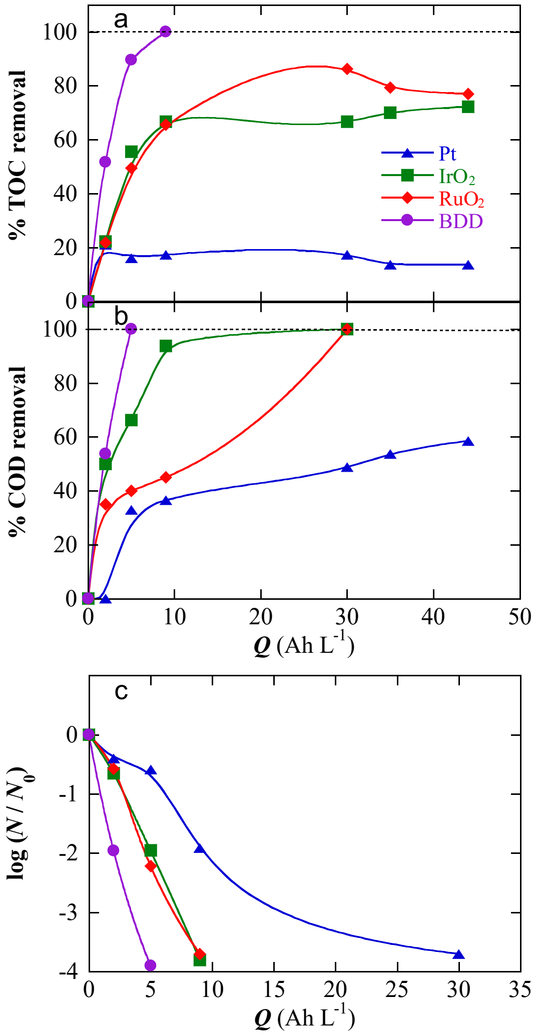

Fig. 19. Decay of (a) TOC, (b) COD, and (c) logarithm of normalized *E. coli* concentration (N_0 = 83–87 MNP mL^{-1}) with electrical consumed charge in 600 mL of synthetic urine wastewater (pH 8.1) by EO using an undivided flow-through filter-press cell with different anodes and a SS cathode (78 cm^2 area) at j = 15 mA cm^{-2} and 25 °C. Adapted from [73].

Concerning the studies related to the inactivation of *P. aeruginosa*, Griessler et al. [29] used a bench-scale unit at flow rate of 12 L h^{-1} equipped with a bed of bipolar diamonds (0.4 mL) with titanium-iridium-oxide as contact electrodes, as shown in Fig. 8c, to electrolyze 1 L of a bacterial suspension of 10^6 CFU mL^{-1} with ≈8 mg L^{-1} NaCl by applying a j ranging from 140 to 210 mA cm^{-2} for 30 min. The inactivation effect by applying direct current (DC) or alternating current (AC) was investigated, achieving better results for DC mode. Depending on the contact time by applying 140 mA cm^{-2}, the DC mode reduced between 0.9 and 4.0 log cell units, whereas the AC mode removed between 0.4 and2.9 log cell units. The *P. aeruginosa* inactivation ranged between 1.6 and 3.6 log units at the higher flow rate and 2.4–4.4 log units at the lower rate by using DC mode. These results were similar to those obtained by Jeong, et al. [9,50] for *E. coli* inactivation, in terms of efficiency. However, different electrochemical systems were employed in these investigations and active chlorine was the most important disinfectant in [29], which allowed efficiently achieving larger inactivation in short times (few seconds or <30 min in some experiments).

Undivided flow-through [77] and flow-through filter-press [72] reactors with Si|BDD anodes in disc-planar arrangement (78 cm^2 of geometric area), like in Fig. 9, were used for the inactivation of *P. aeruginosa* and other waterborne pathogens like *Aeromonas hydrophila* and *L. pneumophila* [77], and *E. coli* [72], as detailed in Table 3. In the first case, solutions of 500 mL with 900–4500 mg L^{-1} of NaCl and cell suspensions of 6.6×10^8 CFU mL^{-1} at pH = 7.2 and 25 °C were electrolyzed at $j = 50$ mA cm^{-2}. A total disinfection in shorter times of 120, 60, and 45 min for increasing 900, 2300, and 4500 mg L^{-1} of NaCl, respectively, was attained at a liquid flow rate of 250 mL min^{-1}. This gradual enhancement in inactivation can be ascribed to a greater of active chlorine as result of the inhibition of its oxidation to ClO_3^- and ClO_4^- ions via reactions (25)-(27). Other effects including bacterial density (10^7-10^8 CFU mL^{-1}), bacteria survival, and liquid flow rate (250–1250 mL min^{-1}) were also investigated considering all microorganisms. In this context, a complete waterborne pathogens reduction was found regardless of the bacteria nature. However, noticeable inactivation differences were achieved on the bacterial survival as a function of disinfection time because the inactivation of *P. Aeruginosa* and *A. hydrophila* was faster (<30 min) than that of *L. pneumophila* (up to 60 min to be totally inactivated). These facts highlight that the bactericidal activity of the disinfection process is related not only to the oxidation power of electrogenerated active chlorine species, but also to the damage of the cell walls of bacteria (Gram-negative or Gram-positive, and the subcellular mechanism followed), as already described by Bruguera-Casamada et al. [16] and Yao et al. [28]. As shown in Table 3, Bensalah and Abdel-Wahab [77] also monitored the evolution of Cl^-, ClO^-, ClO_3^-, and ClO_2^- concentrations with electrolysis time when a solution containing 2250 mg L^{-1} NaCl was electrolyzed by applying 50 mA cm^{-2} under neutral pH conditions. They found that Cl^- decreased linearly as a function of time, whereas ClO^- increased up to 540 min, whereupon it decreased. Negligible amounts of ClO_3^- and ClO_2^- were measured, but their concentration rapidly increased after 120 min of electrolysis. These behaviors are in agreement with the data reported in the literature [78,79], evidencing the relevance of active chlorine as a volume-oxidation process.

Cotillas et al. [72] electrolyzed a synthetic human urine (1 L with 700 mg L^{-1} of TOC), which was polluted with a cell suspension of 10^4 CFU mL^{-1} of *E. coli* and *P. aeruginosa*, with an undivided flow-through filter-press cell with two Si|BDD electrodes by applying j values between 0.5 and 10 mA cm^{-2}. For *P. aeruginosa*, a total disinfection was achieved after 120 min at 0.5 and 1.0 mA cm^{-2} ($Q = 0.25$ Ah L^{-1}) and after 60 min at 5 and 10 mA cm^{-2} ($Q = 1$ Ah L^{-1}). When compared the rates, *E. coli* was more rapidly removed than *P. aeruginosa*, which was related to its antibiotic-resistant bacteria character. Also, the *E. coli* and *P. aeruginosa* inactivation was unaffected by the complexity of the synthetic effluent, i.e., the amount of chloride in the composition of the synthetic urine, favoring the electrosynthesis of oxidant HClO from Eq. (2) and (3). Additionally, other ions such as sulfate, phosphate, and carbonate were present in the urine matrix, which can also be electrochemically oxidized, generating powerful oxidants such as peroxodisulfate from Eq. (9), peroxodiphosphate from Eq. (10) and peroxodicarbonate from Eq. (11).

Bruguera-Casamada et al. [80] utilized an undivided two-electrode (geometric area = 3 cm^2) stirred tank reactor like of Fig. 8a, to treat 100 mL of 7 mM Na_2SO_4 or 7 mM Na_2SO_4 + (1–7) mM NaCl, with cell suspensions of 10^6 CFU mL^{-1} at pH 5.8 and 25 °C by applying a $j = 33.3$ mA cm^{-2} for 60 min. BDD, and IrO_2-based or RuO_2-based DSA were used in the electrolytic cell as anode and SS as cathode. Primordially, BDD ($^{\bullet}OH$) and active chlorine promoted the electrochemical inactivation of *P. aeruginosa*. A total inactivation and damage of the cell wall were achieved after 60 min at 33.3 mA cm^{-2} using a BDD anode in sulfate medium; whereas for the IrO_2- or RuO_2-based anodes, a faster cell reduction was achieved in 30 min because of the adsorption of microorganisms onto the BDD surface, enhancing their reaction with BDD ($^{\bullet}OH$) and consequently, attaining complete inactivation (see Fig. 20a). Conversely, higher disinfection rates were obtained in the presence of NaCl, requiring 5 and <30 min for complete inactivation, caused by HClO with both DSA and BDD electrodes, respectively, at $j = 33.3$ mA cm^{-2} (see Fig. 20b). The authors indicated that, the concentration of active chlorine increased with increasing j from 8.3 to 33.3 mA cm^{-2} and NaCl concentration from 1 to 7 mM by using a BDD/SS system. The best performance was found for a solution of 7 mM Na_2SO_4 + 7 mM NaCl and a cell suspension of 10^6 CFU treated with a BDD anode by applying 8.3 mA cm^{-2}, completing the disinfection in only 2 min and requiring an $EC_V = 0.059$ kWh m^{-3}. However, DSA electrodes always reached a most favorable inactivation result. *P. aeruginosa* suspensions were also treated by EO with BDD/BDD flow systems by Griessler et al. [29], but only a cell reduction close to 4 log cell units from a 10^6 CFU mL^{-1} bacterial suspension in tap water containing 7.8 mg L^{-1} SO_4^{2-} + 7.0 mg L^{-1} Cl^- was attained after 30 min of electrolysis. The results reported by Bruguera-Casamada et al. [80] were then superior for microorganism removal.

The use of commercial disinfection devices has also been reported in the literature to treat *P. aeruginosa* suspensions [81,82] and other bacteria. Relevant results obtained for the laboratory experiments are summarized in Table 3. Rajab et al. [81] described the disinfection of 10 L of a particular water matrix with 10^7–10^9 CFU mL^{-1} bacterial suspensions under recirculation at 10 L min^{-1}. Inactivation levels of 3.2 log cell units were obtained by applying 42 mA cm^{-2} for 60 min, whereas total inactivation (≅ 8 log cell units) was found after 15 min at 167 mA cm^{-2}. Under these conditions, 0.07 and 0.46 mg L^{-1} O_3, respectively, were produced using a CONDIAPURE® cell equipped with two Nb|BDD/two Nb|BDD arrangement in contact with a cation exchange membrane. Better results were found after 10 min when 250 mg L^{-1} NaCl were added, since 5–7 log cell unit inactivation at 167 mA cm^{-2} were reached, while ≈ 3–6 log cell unit inactivation after 60 min at 42 mA cm^{-2} were attained in the presence of 20 mg L^{-1} NaCl in solution. In this study, ClO_3^- and ClO_4^- determination was also performed, indicating that these toxic by-products can be generated. Recently, Isidro et al. [82] treated a secondary WWTP effluent with a *P. aeruginosa* suspension of 2.7×10^8 CFU $(100\ mL)^{-1}$ by using a MIKROZON® cell that is designed to produce O_3 in low conductivity media. This cell operated with a Si|BDD/Si|BDD arrangement in contact with a cation exchange membrane (see Fig. 10e and f) by applying from 0.3 to 1.0 A with a liquid flow rate of 66 L h^{-1}, achieving 6, 3.5, and 5 log cell reductions at 0.3, 0.6, and 1.0 A, respectively, as result of the greater oxidant production. In this context, the authors demonstrated that this innovative polymer exchange membrane-electrolyte–electrode electrolyzer was efficient enough to disinfect chloride-water matrices in continuous and discontinuous operating mode (see Fig. 10d and 10e), attaining several log removals of pathogens as a consequence of the attack of active chlorine species, like $HClO/ClO^-$, produced. Inactivation levels depended on the liquid flow rate used and the electric charge applied, as reported in Table 3. As illustrated in Fig. 10c, a structured silicon substrate and a double sided BDD coatings were used in ten slots that allow the total contact area of membrane, BDD coating, and water, thus favoring an efficient O_3 production in continuous mode as well as the lower contact time in the MIKROZON® cell to prevent the ClO_3^- formation. However, when the discontinuous operation mode was employed (see Fig. 10) with several passes of the water matrix through the cell or an increase of residence time and lower flow rates below the recommended values, significant ClO_3^- concentrations were detected. Conversely, a crucial advantage of MIKROZON® cell is that thanks to its novel configuration, the formation of toxic ClO_4^- ion is prevented in any operating condition.

Electrochemical systems flow-through cells such as CabECO® or MIKROZON®, containing a SPE or a polymer exchange membrane-electrolyte–electrode assembly, respectively, have also been utilized for

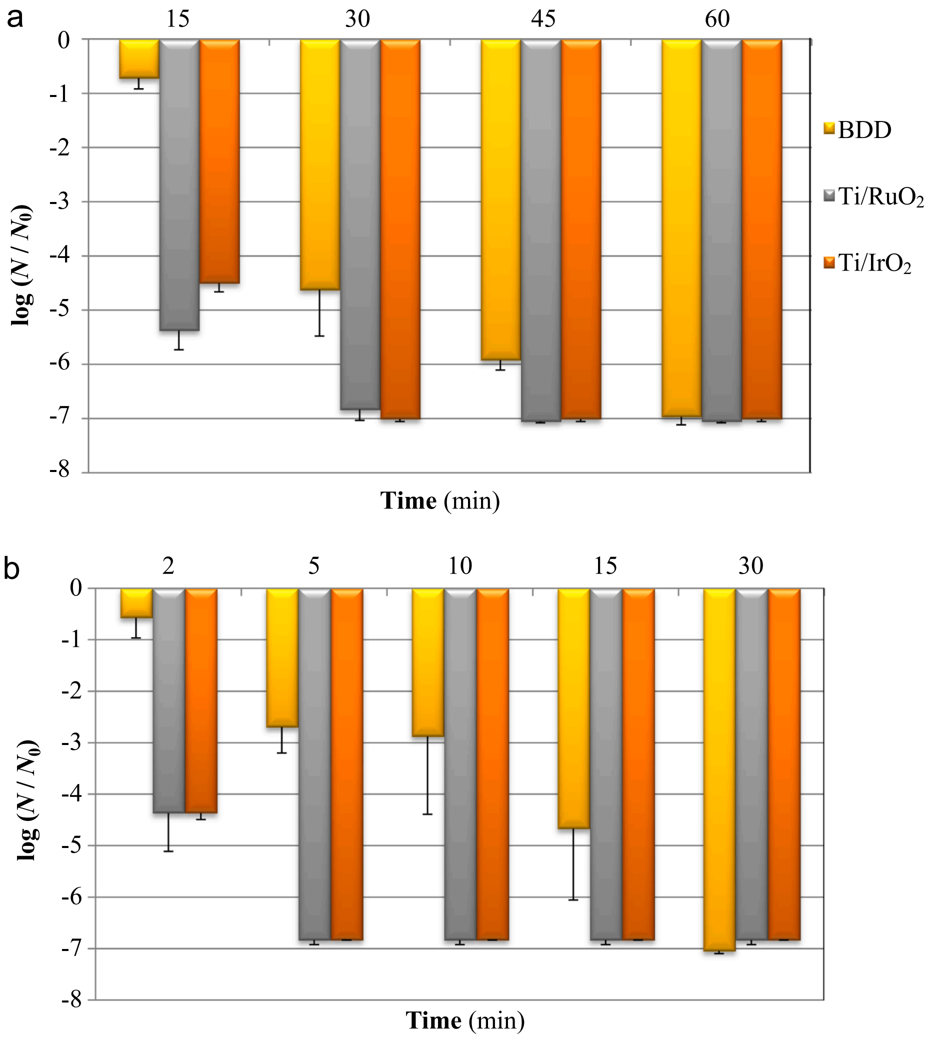

Fig. 20. Logarithmic reduction of 10^6 CFU mL^{-1}*P. aeruginosa* suspensions with electrolysis time for the EO of 100 mL of (a) 7 mM Na_2SO_4 and (b) 7 mM Na_2SO_4 + 1 mM NaCl at pH 5.8 using an undivided stirred tank reactor with a Si|BDD, Ti/RuO_2-based or Ti/IrO_2-based anode and a SS cathode, all of 3 cm^2 area, at $j = 33.3$ mA cm^{-2} and 25 °C. Adapted from [80].

total coliforms disinfection [34,35]. In both commercial devices, significant reductions of coliforms population were achieved when WWTP effluents were disinfected. Table 3 illustrates that CabECO® cell was used to treat 5 L of water collected at the inlet of municipal WWTP merged with the effluent of secondary clarifier (ratio 95/5 v/v) with 4,935 CFU (100 mL)$^{-1}$ coliforms at j ranging from 0.083 to 83.3 mA cm^{-2}, achieving a quasi-complete disinfection (≈ 90%) at 83.3 mA cm^{-2}. At least, about 50% of TOC removal was achieved in 2 h at all j values applied, with a production of trihalomethanes very low, below 100 ppb. Nevertheless, the evolution of toxic disinfectant by-products like ClO_3^- and ClO_4^- was detected, as well as of F^-, NO_3^-, Br^-, and SO_4^{2-}. On the other hand, a MIKROZON® cell with a liquid flow rate of 66 L h^{-1} was employed to treat a secondary WWTP effluent, with suspension of 3.2×10^8 CFU (100 mL)$^{-1}$ of total coliforms [35]. As can be seen in Table 3, the removal attained with this cell depended on the flow rate and current charge passed ($Q = 0.3$, 0.6, and 1.0 Ah L^{-1}), giving rise to 5–7 log cell reduction. No ClO_4^- was detected in any of the tests and low ClO_3^- concentrations below 5.0 μg L^{-1} were measured in the case of operating at 22.5 L h^{-1}. From these findings, the CabECO® cell has been considered a promising technology to avoid problems with disinfection by-products.

The efficiency of the CabECO® technology equipped with diamond electrodes in the direct disinfection of surface water containing highly faecal pollution has been mainly investigated by the Rodrigo's group, as shown in Table 3. Using this cell in continuous mode for the disinfection of highly fecal-polluted surface water [67], an efficient removal of total coliforms was achieved up to 4 log cell units when using a liquid flow rate of 90 L h^{-1} with a single cell (diamond geometric area = 24 cm^2). Disinfection efficiency (≈3–4 log cell units) was relied to j from 41.67 to 166.67 mA cm^{-2} where less than $Q = 0.05$ Ah L^{-1} was required, because only 2 log cell units were obtained at higher Q values. It is important to remark that the strongly polluted water conditions in this study contributed to diminish the disinfection efficiency due to the electrode fouling observed. The further electrochemical disinfection process [83] was made with a flow commercial plant like of Fig. 9a with a Diacell® 101 (one Si|BDD/Si|BDD flow-compartment) to treat 10 L of WWTP effluent with a suspension of 2.2×10^4-5×10^5 CFU (100 mL)$^{-1}$ of total coliforms and 10^4-1.3×10^5 CFU (100 mL)$^{-1}$ of fecal coliforms by applying 1 and 2 A for 10 min at a liquid flow rate of 10 L min^{-1}. Under these experimental conditions, >95% of disinfection was achieved after 9 and 4 min at 1 and 2 A, respectively, with modest electric requirements of EC_V of 0.40 and 0.65 kWh m^{-3}, respectively. Undivided stirred tank reactors have also been employed to eliminate total coliforms (see Fig. 9a). For example, Rajasekhar et al. [84] treated 250 mL of influent of sequence batch reactor and effluent of constructed wetland containing suspensions of 2.9×10^5 and 3.2×10^4 CFU mL^{-1} of total coliforms and fecal coliforms, respectively, by applying a high *j* value of 30 mA cm^{-2} for 60 min. Fast inactivation was found, but much slower than that reported by Polcaro et al. [48] for 1 M Na_2SO_4 (see Tables 2 and 3). However, a more detailed study on the evolution of COD and NO_3^-, NH_4^+, and active chlorine species was done, which allowed to comprehend the cell damages and the by-products released in the final effluent.

A great interest has been shown by some research groups related to the treatment of seawater because these water matrices are used in industrial activities such as aquaculture or shipping. The problems due to waterborne agents or undesired biofouling imply to control risks by disinfecting preventions. A reduced number of studies have been devoted to the inactivation of marine bacteria (see Table 3), and these investigations have mainly used flow-through (Diaclean cell and Electro-MP-cell) systems as well as batch stirred reactors. Real or synthetic ballast waters were treated by Moreno-Andrés et al. [85], Petrucci et al. [86], and Mascia et al. [87]. Natural marine heterotrophic bacteria were used as an indicator of disinfection efficiency in [85] when real ballast water (pH 7.94, 2.13 mg L^{-1} TOC, and 16.26 g L^{-1} Cl^-) with 10^6 CFU mL^{-1} of such bacteria was disinfected in continuous mode at 200–1000 L h^{-1}. At *I* values ranging from 0.7 to 7.3 A, which corresponded to *j* values between 9.72 and 101.38 mA cm^{-2}, significant log cell unit reductions were achieved with EC_V values from 0.009 to 0.264 kWh m^{-3}. However, this report did not clearly detail the disinfection efficiencies obtained at each applied *I*. A biphasic inactivation kinetic model was developed and the disinfection data were well-fitted with experimental points, which showed that a 4.5 log cell reduction was attained at liquid flow rates >0.22 A h L^{-1}, assessing higher bacterial damages under these operating conditions when it was compared to chlorination. Evolution of total residual oxidant was monitored, making in evidence, as expected, that the active chlorine species acted efficiently to remove microorganisms from real ballast water. In some cases, ClO_4^- was detected as disinfectant by-product at high *I* values and low liquid flow rates, whereas no ClO_4^- was formed at liquid flow rate >200 L h^{-1} as a consequence of the very small residence time [67].

Because of their easy adaptability to the different operating conditions, divided stirred reactors have also been used to inactivate marine bacteria [86], limiting its application to the knowledge of the effectiveness of the treatment by comparing the effect of experimental parameters over the cell reduction and the detection of by-products. Petrucci et al. [86] obtained a total inactivation of *A. minutum* and *A. taylori* after 15 min at 5 mA cm^{-2} and that of *P. Aeruginosa* in 60 min at 10 mA cm^{-2} when 200 mL of synthetic ballast water (pH 8.0–8.2, conductivity 45 mS) inoculated with a suspension of two marine bacteria, 16,500 CFU mL^{-1} of *Alexandrium minutum* and 12,000 CFU mL^{-1} of *A. taylori*, along with 4.7 × 10^8 CFU mL^{-1} of *P. aeruginosa*, was electrochemically treated by EO. The disinfection system was equipped with a BDD plate as anode and an air-diffusion electrode as cathode, which were separated with a cation exchange membrane, by applying different *j* values from 5 to 15 mA cm^{-2} for 60 min. In this case, good inactivation performances were disclosed because the addition of NaCl strongly accelerated the process, and the acidic pH conditions that were reached in the anodic compartment of the divided cell contributed to killing the waterborne agents due to the key role of HClO, while ensuring a low-active chlorine concentration. A complete cell reduction was achieved by extending the contact time of the remaining microorganisms in the solution with the disinfectant agents electrochemically generated at the anodic material, which remained in the bulk after the electrolysis. This behavior was considered an innovative successive treatment. Since H_2O_2 originated from the air-diffusion cathode was accumulated in the catholyte, a sequential treatment was adopted by mixing cathodic and anodic solutions after the electrolysis, allowing the contact of remaining cells with H_2O_2 to enhance the cell inactivation. A large cell reduction of 88% was already attained in the catholyte solution during the cathodic pre-treatment.

A commercial flow-through filter-press 1 reactor (Electro-MP-cell) was efficiently utilized to treat 300 mL of synthetic ballast water containing 1 × 10^9 CFU mL^{-1} of *Chlorella vulgaris* (see Table 3) in recirculating batch continuous mode from 190 to 670 mL min^{-1} at *j* values from 25 to 100 A cm^{-2}, related to E_{cell} values from 4 to 6 V at 25 °C [87]. The effect of *j* and reactor hydrodynamics were studied, as well as the production of active chlorine and other oxychorinated by-products. Under that operating conditions, significant algae inactivation efficiencies at batch mode were obtained at $Q = 8$ Ah L^{-1}: 45% at 25 A cm^{-2} (Re = 20), 93% at 25 A cm^{-2} (Re = 100), 79% at 100 A cm^{-2} (Re = 20), and 80% at 100 A cm^{-2} (Re = 100). Meanwhile, 97% of algae inactivation efficacy was attained in batch mode after $Q = 7$ Ah L^{-1} in 100 mg L^{-1} Cl^- at Re = 100 and $j = 7.5$ A cm^{-2}. Then, the complete inactivation was a consequence of the main mechanism associated to active chlorine, which promotes the algae destruction by long life oxidants generated. Finally, it was confirmed a smaller formation of oxychlorinated by-products in the presence of algae due to the consumption of active chlorine to destroy such microorganisms.

The majority of disinfection studies related to the inactivation of other bacteria have been made with undivided stirred tank reactors [53,88], undivided flow reactors [36], undivided plug-flow micro-reactors [89], undivided flow-through cells [77], and undivided flow-through filter-press cells [90]. In the first case, total disinfection of 400 mL of 4 stormwater samples, with suspension of 5140–8090, 3950–37170, and 43–267 MPN (100 $mL)^{-1}$ of enterococci, *Campylobacter*, and *C. perfringens* at pH 6.7–7.6, was reached with a two-electrode undivided tank reactor (see Table 3) by applying 4.2 mA cm^{-2} for 8–30 min, depending on the stormwater [53]. On the other hand, 10Si|BDD plates and a graphite rod cathode were submerged in an undivided stirred tank reactor for treating 300 mL of hospital effluent wastewater containing 29 pharmaceuticals, illegal drugs and their metabolites, and resistant types of microorganisms (total coliforms: 5.5–7 log CFU mL^{-1} and *S. aureus*: 2.7–3.8 log CFU mL^{-1}) by applying a $j = 45$ mA cm^{-2} [88]. >60% of efficiency resulted as the optimum achievement for the elimination of pharmaceuticals, drugs, and bacteria in 30 min. Gentamicin-resistant coliforms especially *E. coli*, *S. aureus*, and drugs such as ampicillin and penicillin, were eliminated under these conditions.

The flow electrochemical cell design was strategically chosen by several authors to use different mode operations (discontinuous or continuous as well as single pass or batch flow) [36,77,89,90] and diverse operating conditions [5,24] aiming the scaling-up of the process. Mascia et al. [36] used a fixed bed reactor, in continuous and in batch recirculated mode, with three-dimensional conductive diamond anodes like of Fig. 11 to investigate the electrochemical treatment of 300 mL of water containing 1 × 10^6 CFU mL^{-1} *M. aeruginosa* at *j* ranging from 10 to 60 A m^{-2}, liquid flow rates corresponding to Re values from 10 to 160, and Cl^- content from 100 to 1000 g m^{-3} (see Table 3). In the continuous mode trials and without adding the algae in the inlet stream, a total oxidant concentration of about 0.7 g Cl_2 m^{-3} was measured, with maximum values at Re = 1.0 and $j = 2.5$ mA cm^{-2}, strongly dependent on the Cl^- concentration. In the presence of microorganisms, an 80% of cell reduction at different times was always achieved. At Re = 10, $j =$ 6.0 mA cm^{-2} and 1000 g m^{-3} Cl^-, maximum removal was reached after 6–20 ks under the weakest condition. From 1.0 to 4.0 mA cm^{-2}, the apparent kinetic constant increased a 50%, but only a 10% was raised for Re values from 10 to 4.0 at $j = 6.0$ mA cm^{-2}. The absorbance of Chl-a pigment and the concentration of by-products were also measured, demonstrating that the presence of *M. aeruginosa* resulted in a lower ClO_3^- accumulation and from 1 to 7% of total oxidants, usually found during electrolysis with BDD anodes in continuous and in batch recirculated modes. Other bacteria, such as *L. pneumophila and Rhizoctonia solani* were electrochemically treated with undivided flow-through (see Fig. 9a) and undivided flow-through filter-press (see Fig. 9f) cells by Bensalah and Abdel-Wahab [77] and Levésque et al. [90], respectively. A solution with 2250 mg L^{-1} of NaCl and a suspension of 4.4 × 10^7 CFU mL^{-1} of *L. pneumophila* was electrolyzed by applying *j* values between 20 and 100 mA cm^{-2} for 120 min at pH 7.2, 25 °C and liquid flow rate of

250 mL min^{-1}, resulting an inactivation of 7 log cell units after 120 min at 20 mA cm^{-2}, 7.5 log cell units after120 min at 50 mA cm^{-2}, and 7.5 log cell units after 60 min at 100 mA cm^{-2} [77]. On the other hand, fertigation solutions in continuous mode were electrolyzed with an undivided flow-cell like of Fig. 9f, by adding or not 20 mg L^{-1} of KCl, with a suspension of 3.5×10^4 CFU mL^{-1} *Rhizoctonia solani* at j values between 1.14 and 9.09 mA cm^{-2}, 25 °C and liquid flow rates ranging from 127 to 720 mL min^{-1} [90]. Without KCl as supporting electrolyte, 1 log cell unit inactivation was attained in 6 min. The addition of this salt accelerated the disinfection that was completed in only 1–2 min from 2.37 to 9.09 mA cm^{-2}, demonstrating again that active chlorine species participate actively in the cell reduction by inactivation or lysis. Evolution of active and total chlorine, NH_4^+, NO_3^-, and SO_4^{2-} was monitored. Low j values promoted chloramines formation, decreasing with contact time, whereas the concentration of these by-products was strongly increased at high j and longer electrolysis time. Low ClO_4^- concentration was always formed. Additionally, total bacterial count for diverse anaerobic and aerobic bacteria (initial population concentration = 2.2×10^6 CFU mL^{-1}) was reduced up to 5.7×10^3 CFU mL^{-1} after 250 min at 600 mA (see Table 3), although longer treatment times were required for TOC reduction [89].

The above findings demonstrated that bacteria inactivation by using diamond anodes in chloride water matrices can be performed with different efficiencies, which are dependent on the operating conditions. The studies over this approach present as major advantages:

(i) Understanding on the crucial role of active chlorine and chloride-based oxidants in the cell inactivation,
(ii) comprehension of the effects of cell integrity and damage cell walls when active chlorine species are in-situ electrochemically produced by using diamond electrochemical systems,
(iii) no addition of salts as supporting electrolytes,
(iv) preventing production of the toxic disinfection by-products such as ClO_3^- and ClO_4^-,
(v) development of novel diamond technologies (including design, dimensions, electrode arrangements, electrode-gap distance, membrane improvements, flow rates, and so on) that can be used to disinfect higher volumes of real water matrices,
(vi) higher inactivation effectiveness removing several bacteria from water matrices respect to the conventional chlorination treatment, and
(vii) disinfection action by chloride-water matrices as a volume-based chemical approach due to its reaction characteristics

Important drawbacks should also be remarked when chloride media are electrolyzed, as already pointed out with free-chloride solutions:

(i) Undivided or divided stirred tank reactors should be avoided, whereas electrochemical flow- systems must be preferentially utilized to fabricate other commercial devices,
(ii) electric requirement estimations and costs should be determined considering all parameters to a full-scale application and techno-economic studies should be developed,
(iii) variations on the inactivation efficiency due to the competition between NOM, organics or bacterial reduction when real water matrices are treated with active chlorine,
(iv) generation of organic residuals or disinfection toxic by-products from chloride oxidation species that need to be removed before water disposal, and
(v) restrictions due to the volume-based chemical process by using active chlorine.

As possible answers to these drawbacks, novel designs of the electrochemical systems are being developed to operate at different flow modes, and consequently, high current efficiencies could be attained without formation of toxic disinfectant by-products. From an analytical inspection of the results summarized and discussed in this section, we concluded that further investigations to evaluate the diamond electrodisinfection technology should be performed in terms of techno-economic analysis and post-treatment proposals. These aspects are necessary to prove the applicability of EO with BDD at industrial level in competence with conventional disinfection approaches as well as to envisage the translation from lab experiments to commercial devices.

4.3. Combined processes

Several simple combined processes, namely hybrid or sequential, have been proposed to upgrade the bacterial inactivation by EO with a BDD anode and reduce the energetic requirements of treatment. Electrocoagulation (EC) has been utilized in both kinds of processes due to its ability to remove colloidal particles such as bacteria. The hybrid treatments also include adsorption/electrosorption, photoelectrolysis (PE), sonoelectrolysis (SE), and electro-Fenton (EF). Pre-disinfection with biofiltration, coagulation-flocculation, sedimentation, or filtration has been tested in sequential treatments, as well the use of EF and photoeletro-Fenton (PEF). This section is devoted to explaining the fundamentals and characteristics of such combined processes. Table 4 collects selected results obtained in these assays.

4.3.1. Hybrid processes

Addition of suspended carbonaceous materials to the wastewater, with ability to be polarized upon the electric field produced between the two electrodes of the electrolytic reactor, has shown a large improvement of bacterial inactivation. rGO [19] and granular activated carbon [91]) have been checked for this coupling between adsorption/electrosorption and EO with a BDD anode. As detailed in section 3, Qi et al. [19] used an undivided stirred Nb|BDD/SS tank reactor to treat a suspension of 10^7 CFU mL^{-1} *E. coli* in 0.050 M Na_2SO_4 in the presence and absence of solid rGO. Fig. 21a and Table 4 highlight that after 30 min of electrolysis, the presence of 1.0 μg mL^{-1} rGO only yielded less than 1 log cell unit inactivation, which grew up to 4 log cell units by EO with a Nb|BDD/SS cell at $j = 15$ mA cm^{-2}. In contrast, the use of a 3D Nb|BDD/SS system, i.e., with the solution containing 1.0 μg mL^{-1} rGO, led to total inactivation with 7 log cell units reduction. Based on these findings, the authors proposed the disinfection mechanism of Fig. 6 involving two parallel attacks to the adsorbed cell membrane by means of charge transfer to the electronic acceptor rGO and disruption by sharp edges of rGO nanosheets, along with oxidation by BDD(˙OH) formed at the Nb|BDD anode from Eq. (1). Fig. 21b–d show the effect of j from 10 to 20 mA cm^{-2}, Na_2SO_4 content from 20 to 100 mM, and rGO concentration from 0.5 to 2.0 μg mL^{-1} over the inactivation process in the 3D BDD/SS system. The inactivation enhancement observed with increasing j and Na_2SO_4 content can be ascribed to the production of more oxidizing agents, BDD(˙OH) and $S_2O_8^{2-}$, respectively. The best inactivation power was achieved for 1.0 μg mL^{-1} rGO, which allowed the attack of a higher number of bacteria than 0.5 μg mL^{-1}. The lower efficiency for 2.0 μg mL^{-1} can be accounted for by the hydrophobic character of rGO favoring its aggregation that limits its inactivation power. However, in this study the reusability of the rGO after treatment was not assessed. This is a valuable issue needed to disclose the viability of this interesting material for industrial application.

Similar results have been described by Garcia et al. [91], who utilized a recirculation plant with an undivided 3D flow-through filter-press Si|BDD/SS cell with suspended GAC to treat a synthetic greywater spiked with 10^5 CFU mL^{-1} *E. Coli*, 10^4 CFU mL^{-1}*C. perfringens* spores, and 10^4 CFU mL^{-1} somatic coliphages (see Table 4). Comparative trials showed the synergy of the 3D system, which resulted in 21% COD removal and 23% TOC decay, higher than the sum of the individual GAC and EO processes after 5 h of treatment at $j = 1.5$ mA cm^{-2}, due to the efficient combination of GAC adsorption and electrogenerated oxidizing agents. While GAC alone did not removed any bacteria, the 3D system led to the total inactivation of *E. Coli*, but only reduced the content of

C. perfringens and somatic coliphages by 0.6 and 3.3 log cell units, respectively. The low electrodisinfection power of the 3D system can then be ascribed to the parallel oxidation and adsorption over the GAC particles of the organic components of the wastewater, which inhibits the microorganism removal. However, it was found that the electric field polarized the surface of the GAC particles causing a notable enhancement of the killing of microorganisms and their electrochemical regeneration. After 31consecutive runs of 5 h, a 65% of GAC regeneration efficiency was achieved, demonstrating the good performance of the proposed 3D arrangement for long-term operation.

Other interesting hybrid process is PE. It consists in the irradiation of an UVC light (λ_{max} = 254 nm) to the wastewater treated by EO. This irradiation upgrades the oxidation power of EO since photolyzes the photoactive species and helps to inactivate the microorganisms, in conjunction with the electrogenerated oxidizing agents. The effectiveness of PE has been checked with different arrangements like an undivided flow-by filter-press cell equipped with a Nb|BDD or Ir|Ru as anode and cathode upon 20 W UVC [92], an undivided flow-by filter-press Si|BDD/SS cell upon 4 W UVC [93], and commercial Diacell® 101 and Diacell® 1001 (see Fig. 9a and 9b) also upon 4 W UVC [30]. In all these works, secondary WWTP effluents were tested and the evolution of *E. coli* was monitored to characterize the electrodisinfection potentiality of PE (see Table 4). As an example, Fig. 22a highlights the direct and indirect electrogeneration of oxidants formed at the Si|BDD anode from water oxidation and that of inorganic ions such as Cl^-, PO_4^{3-}, and CO_3^{2-} present in a secondary effluent [93]. The initial oxidants can be recombined and the resulting species are further photoactivated by the incident UVC light, originating a large variety of oxidizing agents, mainly very reactive radicals. Apart from these photoreactions, UVC light also photolyzes the photoactive organics in solution and can inactivate the existing microorganisms. Fig. 22b and Table 4 make in evidence the synergism of PE respect to EO and direct photolysis for the electrodisinfection of 4 L of a secondary effluent with <16,000 CFU (100 mL)$^{-1}$ *E. coli* at j = 0.13 mA cm^{-2} for 180 min [93]. While total disinfection was reached in 120 min by PE, much poorer reductions of 1.2 and 2.1 log cell units can be observed by EO and photolysis, respectively, meaning that the photoactivation reactions in PE become very effective to kill the bacteria. Also, all TOC was completely removed. In these works, the time course of several generated ions like ClO^-, ClO_3^-, and ClO_4^-, as well as primary, secondary, and tertiary chloramines initiated from reaction between ClO^- and NH_4^+ proceeding from the organic matter degradation, was determined. No ClO_3^- and ClO_4^- ions were detected owing to the very low j applied, which represents a clear advantage over the treatment of concentrated wastewaters where the high j used provokes the accumulation of such undesirable ions. Fig. 22c shows that ClO^- was more largely accumulated by EO than by PE, because of its photoactivation in the latter method (see Fig. 22a). This fact is also reflected in Fig. 22d, where NH_2Cl is formed to smaller extent in PE, whereas similar accumulation can be observed for $NHCl_2$, without NCl_3 detection, in both treatments. Overall, one can conclude than UVC irradiation inhibits the generation of toxic by-products, which is a positive factor for PE application. However, the main drawback of this procedure is the high electric cost requirement of the UVC light. This allows proposing the alternative use of free sunlight as energy source in future works to make PE viable at industrial level.

SE is other hybrid process explored by Llanos et al. [94]. Fig. 23 shows the recirculation plant utilized by this team for SE [95]. The undivided flow-by filter-press contained a Si|BDD anode and a SS cathode while an ultrasound (US) generator of 12 W cm^{-2}, 200 W, and 24 kHz was introduced in the reservoir. US is typically used in sonolysis and produces hot spots by cavitation forming ROS from water oxidation in the wastewater bulk. Moreover, the disinfection process is favored by the additional destruction of agglomerates of bacterial flocs. The good coupling of US with EO was tested to inactivate up to 24,000 CFU (100 mL)$^{-1}$ *E. coli* in 2 L of domestic wastewater at j = 0.127 mA cm^{-2} and 25 °C during 120 min. For 16,000 CFU (100 mL)$^{-1}$ bacteria, only 0.02 log units decay was determined by simple sonolysis, whereas the use of EO led to 92% inactivation, upgraded by the total disinfection achieved by SE (see Table 4). At the low j applied, only ClO^- and chloramines were found to be accumulated, to smaller proportion in SE and EO. Despite of these positive results for SE, the very high energetic requirements of the US generator hinders its practical application.

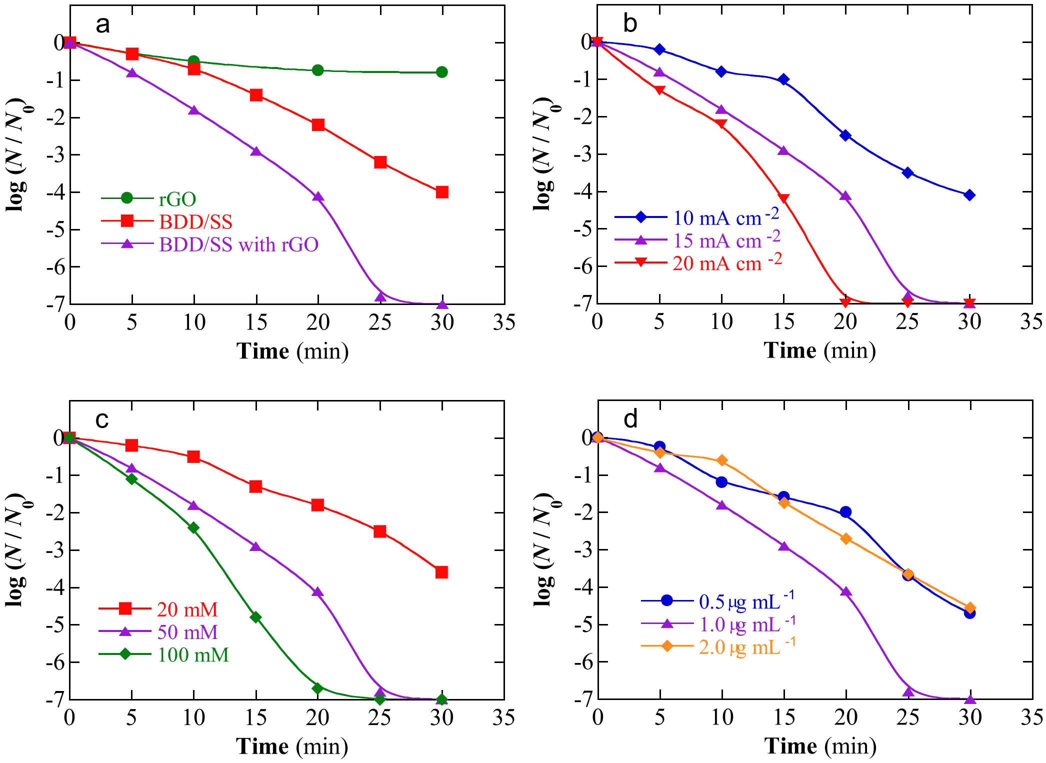

Fig. 21. (a) Inactivation of 250 mL of suspensions of 10^7 CFU mL^{-1} *E. coli* in 0.050 M Na_2SO_4 using 1.0 μg mL^{-1} rGO, an undivided Nb|BDD/SS cell (4 cm^2 area) at j = 15 mA cm^{-2}, and a 3D Nb|BDD/SS cell with 1.0 μg mL^{-1} rGO at j = 15 mA cm^{-2}. Influence over the performance of the 3D Nb|BDD/SS cell from the change of: (b) applied current density with 0.050 M Na_2SO_4 with 1.0 μg mL^{-1} rGO, (c) Na_2SO_4 concentration with 1.0 μg mL^{-1} rGO at j = 15 mA cm^{-2}, and (d) rGO content in 0.050 M Na_2SO_4 at j = 15 mA cm^{-2}. Adapted from [19].

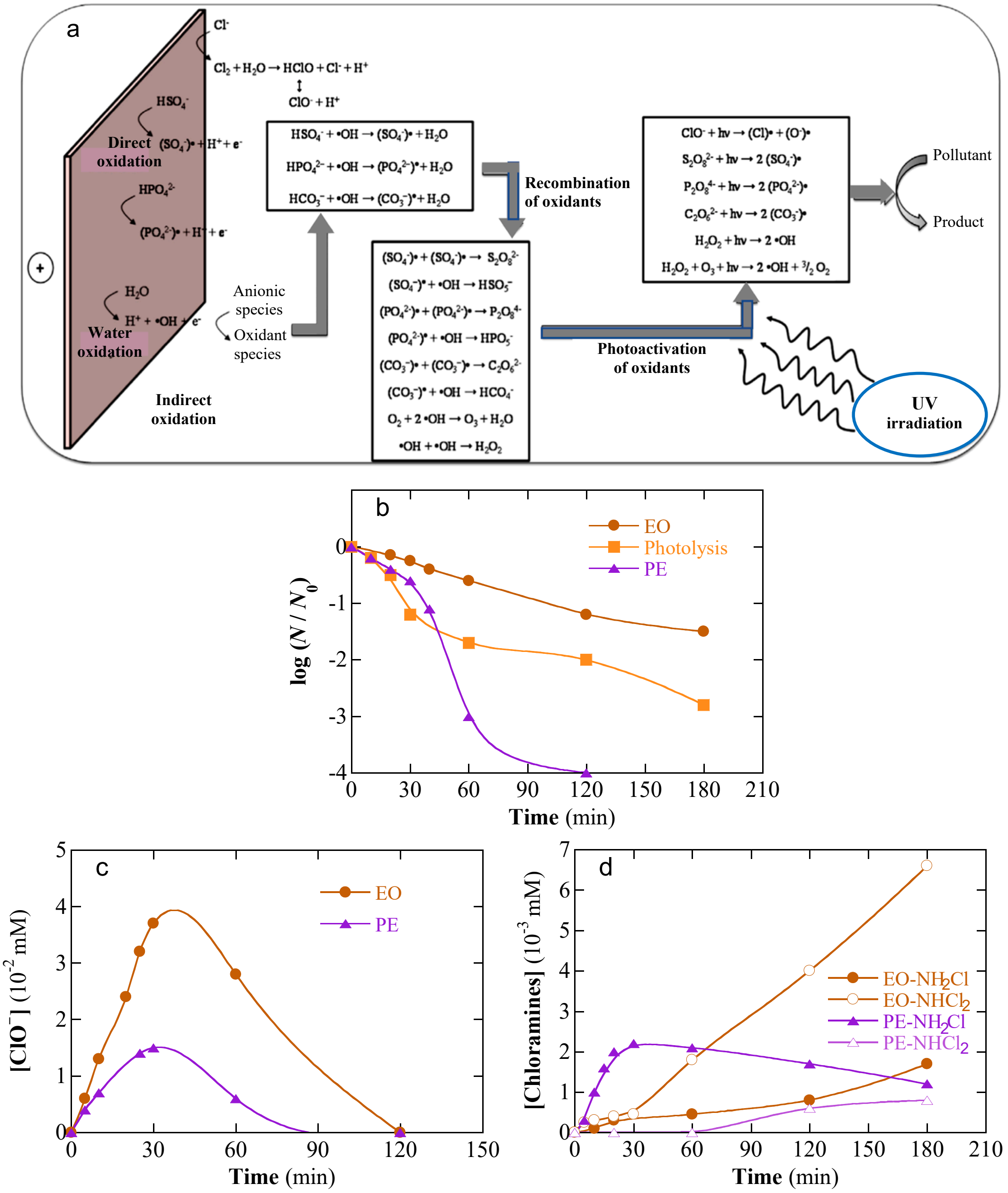

Fig. 22. (a) Mechanisms expected for the PE process of a secondary wastewater effluent. (b) Evolution of *E. coli* concentration (N_0 = 16,000, 5,400 and 9,100 CFU (100 mL)$^{-1}$) during the EO, photolysis and PE treatments of 4 L of such effluent using an undivided flow-by filter press BDD/SS cell (78 cm^2 area) coupled to a 4 W UVC light at j = 0.13 mA cm^{-2} and 25 °C. Change of (c) hypochlorite and (d) chloramines in the above trial. Adapted from [93].

Long et al. [21] tested the ability of electro-Fenton (EF) process to disinfect 100 mL of (3–4) × 10^6 CFU mL^{-1} *M. aeruginosa* in 20 mM Na_2SO_4 at pH 3–9 using an undivided stirred tank reactor with a Nb|BDD anode and a carbon felt (CF) or SS as cathode at 200 mA for 60 min. The EF process became effective when the CF cathode was utilized and an air flow was bubbled through the solution to originate H_2O_2 from the cathodic reduction of dissolved O_2 via Eq. (29) [96]. A concentration from 0.1 to 0.5 mM of catalytic Fe^{2+} was added to the solution to generate homogeneous $^{\bullet}OH$ as oxidant by the classical Fenton's reaction (30). The catalytic loop of Fe^{3+}/Fe^{2+} was ensured by the continuous reduction of Fe^{3+} to Fe^{2+} at the cathode according to Eq. (31). Under these conditions, heterogeneous BDD($^{\bullet}OH$) and homogeneous $^{\bullet}OH$ are the main electrogenerated oxidants.

$$O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (29)$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O \quad (30)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (31)$$

The authors found that under optimum conditions of 0.2 mM Fe^{2+} and pH 3, the EF process with the Nb|BDD/CF system yielded overall inactivation (3.2 log cell unit reduction) in 60 min. This result was independent of the flow rate of injected air, probably because the solution always remained O_2 saturated. Note that at this pH = 3 the highest rate for Fenton's reaction (30) is achieved [96], thereby producing the maximum quantity of homogeneous $^{\bullet}OH$. The role of this radical in front of BDD($^{\bullet}OH$) was determinant for microorganisms removal, since only 1.2 log cell units were destroyed by the EO treatments with the Nb|BDD/CF (without Fe^{2+}) and Nb|BDD/SS (with an without 0.2 mM Fe^{2+}) (see Table 4), where only BDD($^{\bullet}OH$) acted as main oxidizing agent. These findings indicate that EF is a valuable process for electrodisinfection that needs to be much more developed in the next future.

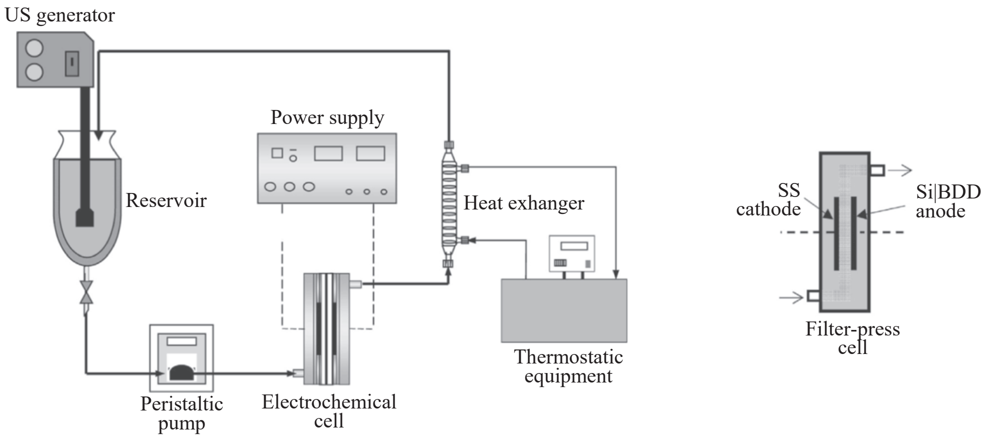

Fig. 23. Hybrid system for electrodisinfection with a BDD anode, showing the sketch of the flow plant and the undivided filter-press reactor for bacteria disinfection by sonoelectrolysis (SE) with ultrasound (US). Adapted from [95].

Finally, the Rodrigo's group proposed a curious hybrid treatment for urban wastewater from simultaneous electrodisinfection by EO and turbidity (from colloids) removal by EC (see Table 4). Fig. 9f presents a scheme of the undivided flow-through filter-press cell utilized that was equipped with plates of a Si|BDD anode, a SS cathode, and an intermediate perforated bipolar Al electrode to permit the liquid current pass [31]. These electrodes were rectangular or circular relied to the recirculation plant utilized. When a current was applied to this arrangement, electrogenerated oxidants able to kill bacteria were formed at the BDD anode (see Fig. 22a), whereas the intermediate Al was dissolved originating an $Al(OH)_3$ precipitate from Eq. (32) and (33) that coagulates the colloidal organic and inorganic components of the wastewater.

$$Al \rightarrow Al^{3+} + 3\ e^- \tag{32}$$

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3(s) \tag{33}$$

Llanos et al. [97] compared the use of intermediate perforated bipolar Fe or Al electrodes for the coupled EC to the EO process. In the case of the sacrificial Fe, $Fe(OH)_2$ and/or $Fe(OH)_3$ precipitates with ability for colloid coagulation can be formed from Eq. (34)-(36) depending on the operating conditions:

$$Fe \rightarrow Fe^{2+} + 2\ e^- \tag{34}$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2(s) \tag{35}$$

$$4\ Fe^{2+} + 10\ H_2O + O_2(g) \rightarrow 4\ Fe(OH)_3(s) + 8H^+ \tag{36}$$

These authors treated 4 L of secondary WWTP effluents (25 mg L^{-1} COD, 30 mg L^{-1} TOC) with suspensions < 90,000 CFU (100 mL)$^{-1}$ *E. coli* at pH 8.05 by applying low j values between 0.190 and 0.980 mA cm^{-2} upon recirculation mode at liquid flow rate of 50 L h^{-1}. They found total disinfection and a loss of 80–90% of the initial 14 NTU turbidity by using the perforated Fe electrode after applying Q values of 0.01 and 0.05 Ah L^{-1} at 0.670 and 0.938 mA cm^{-2} for 22,000 and 31,000 CFU (100 mL)$^{-1}$ bacteria, respectively (see Table 4). This corresponded to EC_V values as low as 0.030 and 0.080 kWh m^{-3}. Passivation of the intermediate Al electrode under the same conditions was observed. The authors remarked that no disinfection effects were promoted by the intermediate bipolar electrodes (Al or Fe). The electrodisinfection process was ascribed to the attack of ClO^- and chloramines and, as expected, undesirable ClO_3^- ions were detected at $j > 0.670$ mA cm^{-2} and $Q > 0.020$ Ah L^{-1}, meaning that $Q = 0.010$ Ah L^{-1} resulted optimal for the hybrid EO/EC with intermediate Fe. The Rodrigo's group has shown the interest of this promising integrated technology by recently reporting the application of the pilot plant schematized in Fig. 24 [98]. As can be seen, an urban treated wastewater (a secondary WWTP effluent) was circulated to the EO/EC unit from a feed tank to be finally accumulated in a storage tank as reclaimed water. This unit was composed of 3 parallel undivided flow-through filter-press cells equipped with a Si|BDD anode, a SS cathode, and 5 intermediate perforated bipolar Fe electrodes, all them of 78.5 cm^2 area, at liquid flow rate of 50 L h^{-1}. The system allowed a total inactivation of 2,200 MPN (100 mL)$^{-1}$ *E. coli* present in the secondary effluent of pH 7.6 after applying Q values of 0.10 and 0.07 Ah L^{-1} for 0.5 and 0.7 mA cm^{-2}, with EC_V values of 2.41 and 2.24 kWh m^{-3} and energy costs of 0.18 and 0.17 € m^{-3}, respectively (see Table 4). The electrodisinfection was ascribed again to the attack of ClO^- and chloramines generated. The main drawback of this system in practice is the continuous release of Fe ions, which remained dissolved in the solution or precipitate as hydroxide and that need to be removed from the reclaimed water before disposal with the consequent increase of the operating cost.

4.3.2. Sequential processes

Biofiltration has been envisaged as a potential method for pollutant remediation of greywater because it offers aesthetic and amenity benefits, along with a small footprint in the dense and land-limited urban environment. However, this procedure does not allow a large bacterial disinfection power, and for this reason, Bakheet el al. [99] explored its sequential coupling with EO to more effectively remove the bacteria content of such kind of wastewater. Fig. 25 shows the sketch of the sequential biofiltration-EO process proposed by these authors. The biofiltration system was composed of a green wall with 5 replicates of 3 vertical planter pots that mimic natural phenomena such as root growth and water flow paths. The greywater was dosed at the top of the green wall and dripped by gravity to be collected at its bottom. The resulting wastewater was then introduced in the anolyte reservoir of a divided flow electrochemical plant where it was treated by EO. The filter-press cell contained a Nb|BDD anode and the anolyte was separated of the catholyte (50 mg L^{-1} NaCl, SS cathode) by a SPE. The assays were initiated with 4 L of greywater of pH 6.62 with 54.9 NTU turbidity, 449Pt/Co units color, 66.5 mg L^{-1} TOC, 322 mg L^{-1} COD, 140 mg L^{-1} BOD_5, 29,100 MPN (100 mL)$^{-1}$ *E. coli*, and 61,300 MPN (100 mL)$^{-1}$ total coliforms (see Table 4). Biofiltration was very effective to remove about 90% of turbidity, color, TOC, COD, and BOD_5, but it only reduced 1 log unit of *E. coli* and total coliforms. The following EO treatment was able to completely inactivate both bacteria after 10–15 min of electrolysis at $j = 25$ mA cm^{-2} upon liquid flow rate of 50 mL min^{-1}, giving rise to a treated wastewater with < 2 MPN (100 mL)$^{-1}$. For this treatment, low EC_V values of 0.63–0.83 kWh m^{-3} were determined, demonstrating the viability of the sequential biofiltration-EO as an environmental-friendly method for pollutant removal and disinfection of greywater.

Isidro et al. [100] developed a novel pre-disinfection column

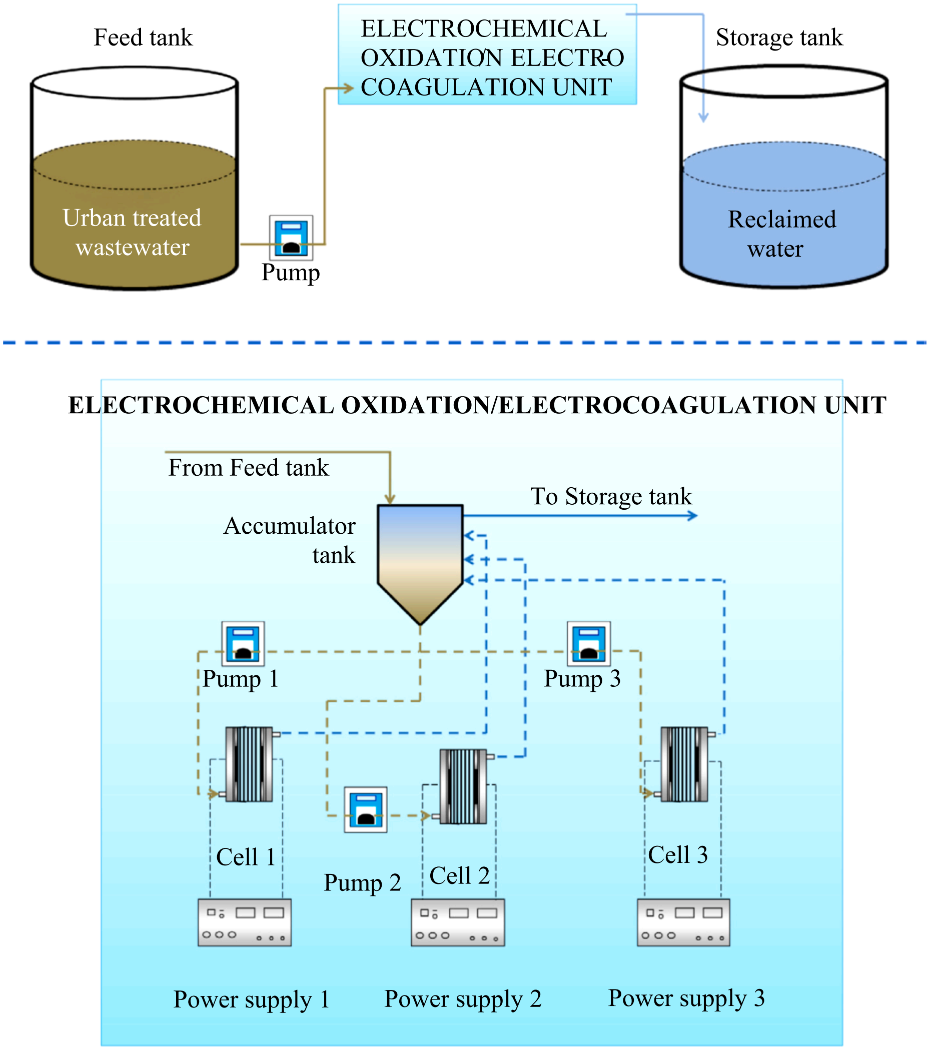

Fig. 24. Hybrid EO/EC pilot plant for wastewater reclamation. Adapted from [98].

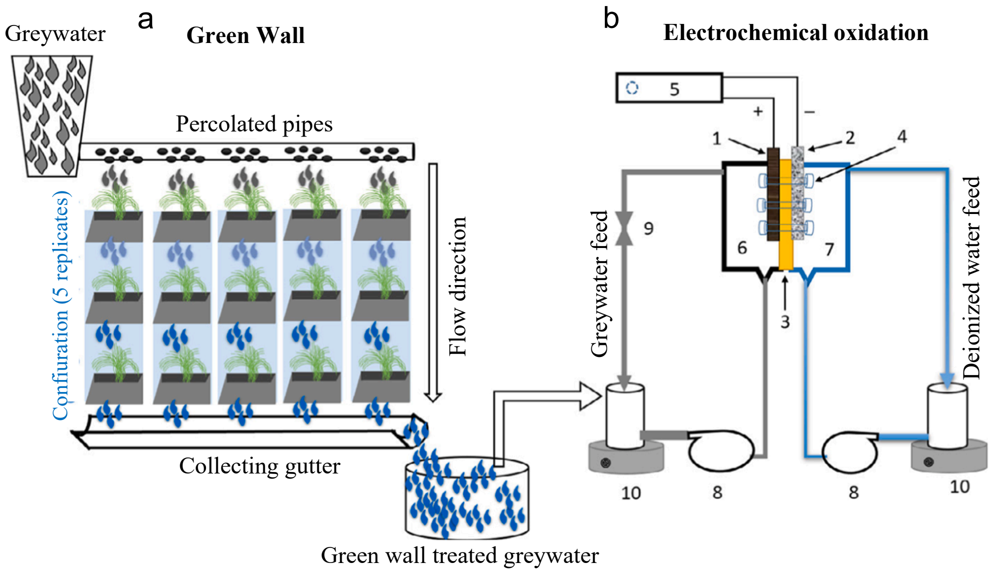

Fig. 25. Sequential biofiltration-electrochemical oxidation system for greywater treatment. (a) Green wall biofiltration system, and (b) electrochemical disinfection process with a divided cell: (1) BDD anode, (2) SS cathode, (3) cation-exchange membrane (solid polymer electrolyte (SPE)), (4) polycarbonate bolts and nails, (5) power supply, (6) anolyte (i.e., biofiltered greywater by green wall), (7) catholyte (deionized water containing 50 mg L^{-1} NaCl, (8) pumps, (9) sampling point, and (10) magnetic stirrers. Adapted from [99].

(PREDICO system) to be coupled to a subsequent EO process for improving the electrodisinfection of a highly faecal-polluted surface water. The pre-disinfection column was a single-column unit in which coagulation-flocculation, lamellar sedimentation and filtration were consecutively associated. The efficiency of this unit relied to the hydraulic residence time (HRT) and surface loading rate (SLR). For the most suitable values of these parameters, HRT = 13.6 min and SLR = 20 cm min^{-1}, a large disinfection was found involving the removal of 3 log units of total aerobic microorganism and 4 log units of total coliform (see Table 4). The resulting wastewater was then electrolyzed in a CabECO® (BDD/Nafion®/BDD) cell (see Fig. 10a) at I values of 1–4 A and liquid flow rates of 150 and 300 L h^{-1}, resulting disinfections of about 4.5 log units without fouling of the electrochemical cell. However, in this study the lifetime of the pre-disinfection column, as well as the operating costs, were not analyzed.

Less information is known about a sequential EC-EO process, which has only been checked by Heffron et al. [101] when treating 200 mL of suspensions of 10^7 plaque-forming unit (PFU) mL^{-1} of human virus surrogates of MS2 and ΦX174 in model surface waters and groundwaters. Undivided stirred tank reactors were utilized in both cases, equipped with 4 steel rectangular plates for EC and with a BDD/Ti system for subsequent EO. A $I = 50$ mA for 5 min was applied in both treatments. Greater removal of the bacteriophage ΦX174 was achieved in both waters (see Table 4), but with a lower influence of EO respect to EC. Parameters such as TOC (proceeding from NOM) and turbidity inhibited the combined process due to the competition with the generated coagulants and oxidizing agents. The authors also compared these results with those obtained with conventional treatments such as chlorine disinfection and Fe^{3+} salt coagulant, concluding that the EO-EC system was more effective for model groundwaters, but less for model surface waters. More studies over other microorganisms are required to obtain a general disinfection overview of this coupled system that offers excellent results for hybrid treatments, as stated above.

It is noticeable the interesting papers published by Anfruns-Estrada et al. [102] and Bruguera-Casamada et al. [103] describing the sequential combination of EC with EF or PEF, which are expected to be more powerful treatments than EO, using undivided stirred tank reactors and with exhaustive analysis of actual microorganisms present in the wastewaters tested. Two Fe plates of 10 cm^2 area were employed in EC, whereas for the Fenton-based EAOPs, a Si|BDD or Ti|RuO_2 plate as anode and an air-diffusion cathode (all them of 3 cm^2 area) were selected. In the sequential system, the supernatant liquid of the EC process was treated by EF or PEF after addition of 0.25 mM Fe^{2+}, because of the very low concentration of dissolved iron species originated in EC. Anfruns-Estrada [102] treated 200 mL of a secondary wastewater effluent by EC at $j = 20$ mA cm^{-2} lasting 90 min and found total inactivation of somatic coliphages and eukaryotes, with reduction up to 5 log units of *E.coli* and smaller decay of heterotrophs, enterococci, and *C. perfringens* (see Fig. 26a). The EF process alone with a Si|BDD anode of 100 mL of the initial wastewater with 0.25 mM Fe^{2+} was performed at pH 3.0 or 7.0 and applying a $j = 33.3$ mA cm^{-2} lasting 30 min. After this time, total removal of all microorganisms was reached, except for the most resistant heterotrophs and *C. perfringens*, regardless of the pH tested (see Fig. 26b), showing the potent oxidation power of generated BDD($^\bullet$OH), active chlorine, and homogeneous $^\bullet$OH formed from Eq. (1), (2) and-(3), and (30), respectively, over all pathogens. A final assay involving 30 min of each process and pH 7.0 for EF revealed a faster removal of all microorganisms (see Fig. 25c and Table 4), confirming the excellent electrodisinfection efficiency of the sequential EC-EF system at neutral pH. Similar findings have been reported by Bruguera-Casamada et al. [103] for the treatment of a dairy wastewater that contained up to 5×10^6 CFU mL^{-1} of heterotrophic and lactic acid bacteria, *E. coli*, and enterococci. While the EC treatment of the initial dairy wastewater of pH 5.7 at $j = 10$ mA cm^{-2} during 60 min only allowed <1 log unit reduction of all bacteria, the sequential EF process with a Si|BDD anode at pH 3.0 and $j = 33.3$ mA cm^{-2} for 120 min yielded up to 5 log unit removal of all cells. In contrast, total disinfection was achieved using PEF upon illumination with a 6 W UVA light due to the additional oxidation with homogeneous $^\bullet$OH originated from the photolysis of Fe(OH)^{2+}, the most photoactive species of hydrolyzed Fe^{3+} ion, according to photo-Fenton reaction (37) [96]. Additional assays with EF alone of the wastewater at pH 5.7 showed > 6 log units reduction for all cells, always being the heterotrophic bacteria the most resistant, although the inactivation process was faster using a Ti|RuO_2 anode than a Si|BDD one as result of the greater production of active chlorine in the former case. The good performance demonstrated by the EC-EF and EC-PEF systems in these works opens the door to further research over their possible viability at industrial level.

$$\text{Fe(OH)}^{2+} + h\nu \rightarrow \text{Fe}^{2+} + {}^\bullet\text{OH} \qquad (37)$$

4.4. Endodontic applications

Over the last 5 years, a practical application of EO with BDD is being developed for removing the pathogens from the root canals reaching the tooth pulp. This dental therapy seems very promising since it has been found even more effective than NaClO sterilization, mechanical debridement, and air particle abrasion. The first work showing an useful arrangement for this treatment has been reported by Ochiai et al. [104]. Fig. 27 illustrates SEM images of the system proposed by these authors, formed by an anode of a metal wire coated with a BDD powder mixed with Nafion® (BDDP/polymer composite) and a Pt ribbon cathode with an ion-exchange membrane as separator that were spirally rolled up around the anode. This flexible pinpoint electrolysis unit was tested with root canals infected with biofilms of *Porphyromonas gingivalis* or *Enterococcus faecalis* extracted from bovine and human teeth, respectively. Total inactivation of such bacteria was attained after 120 and 15 s of electrolysis at $E_{\text{cell}} = 7.5$ V due to the effective production of O_3 and other ROS (see Table 5), disclosing an sterilization ability similar to a toxic solution of 1 wt% aqueous NaClO. The authors remarked that the BDD/polymer composite was very robust having excellent durability, without cracking or peeling in consecutive assays. Following this study, several arrangements of 2 Nb wires coated with very thin BDD films have been utilized for disinfecting dental implants [105] and root canals of extracted human teeth, both covered by bacterial biofilms [106], using a phosphate saline medium with NaCl and KCl as background electrolyte. Compared with conventional mechanical debridement and air particle abrasion, the EO process was more efficient for dental treatment due to the high bactericide action of electrogenerated ROS. It is noticeable that Bohm et al. [106] proposed a clinically integrated system, so-called Prototype 2, that can be directly introduced in the root canals and that was checked to completely disinfect biofilms of *Staphylococcus epidermidis* in 10 min or *Bacillus subtilis* in 25 min after application of an $E_{\text{cell}} = 6$ V (see Table 5). The authors remarked that this time could be notably shortened in clinical application by previous mechanical shaping of the root canal. A similar arrangement to the above Prototype 2 has also been tested for the disinfection of dental implants with 0.9 wt% NaCl [107] or phosphate saline solution [108] (see Table 5). For example, in the latter case, biofilms of 6 ubiquitous bacteria were completely or partially inactivated after 20 min of electrolysis at $E_{\text{cell}} = 6$ V. The disinfection results obtained by EO were again better than those found with air particle abrasion and mechanical debridement. All these excellent findings should encourage further research over the dental treatment by EO with BDD for achieving an actual clinical application.

4.5. Food control applications

Preventing any kind of food contamination in fresh fruits and vegetables by microbial pathogens, is considered as an effective strategy to

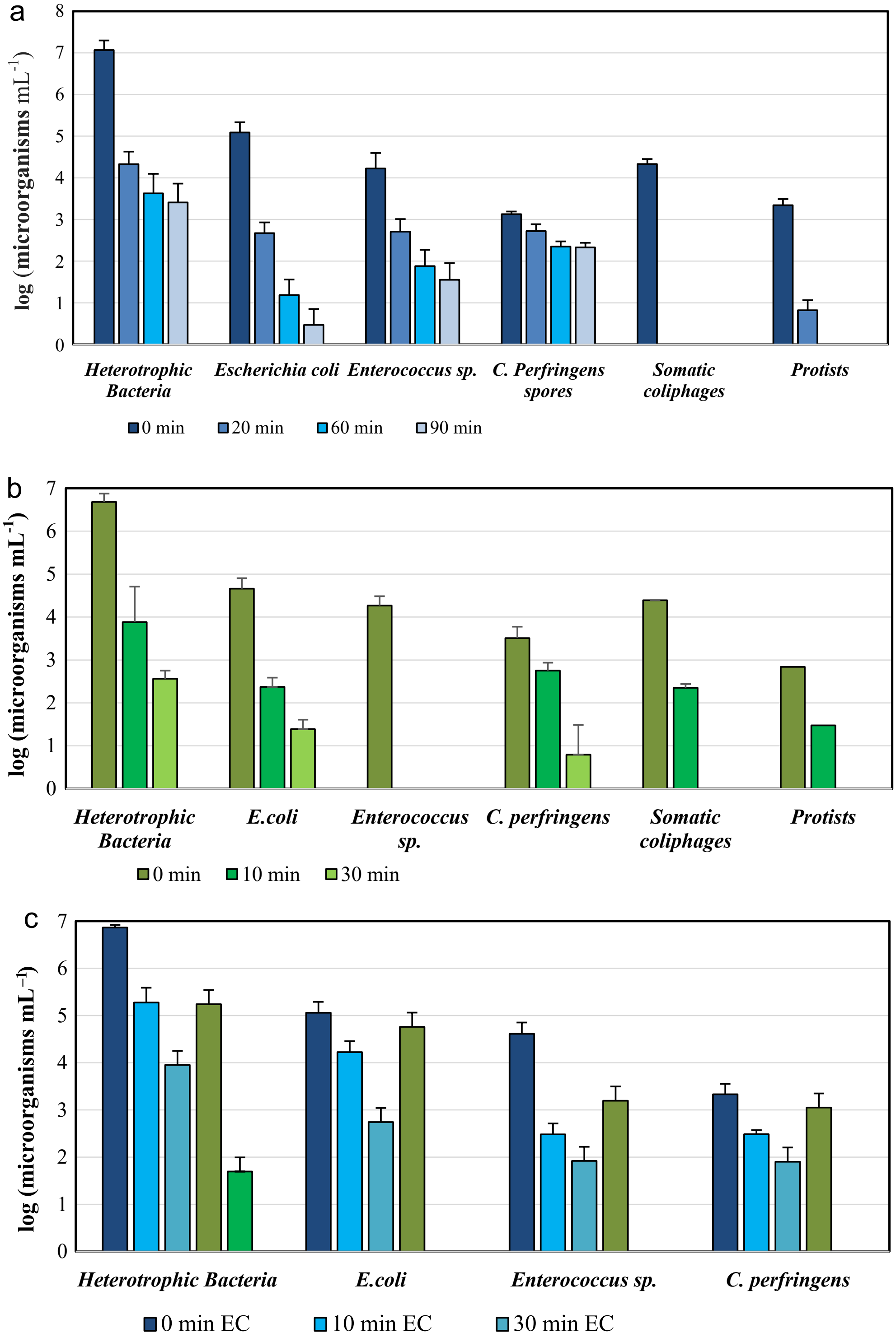

Fig. 26. Variation of the logarithm of concentration of different microorganisms of a secondary WWTP effluent with electrolysis time upon: (a) electrocoagulation (EC) of 200 mL using an undivided Fe/Fe cell (10 cm^2 area) at $j = 20$ mA cm^{-2} , (b) electro-Fenton (EF) of 100 mL at neutral pH (~7) with an undivided BDD/air-diffusion cell (3 cm^2 area) at $j = 33.3$ mA cm^{-2}, and (c) sequential EC-EF (30 min each). Temperature 25 °C. Adapted from [102].

guarantee that these foods are healthy and safe for human consumption [109]. One of the most important risk factors at the pre-harvest and post-harvest levels is the water quality. Since water is used for irrigation or during washing, facilitating cross-contamination [110], suitable ways to reduce the microbial risks are necessary, including: (i) water quality at irrigation or crop management products, (ii) a correct selection of wash water treatment, (ii) proper management of water, (iii) disinfection approaches, (iv) water quality for reuse, and (v) production of water-based sanitizers.

In fresh-cut vegetable production, a crucial processing step is the water disinfection [110]. In this context, hypochlorite solutions are widely used as chemical disinfectant, but the electrodisinfection of the wash water emerges as an effective alternative to eliminate/inactivate a wide spectrum of waterborne and/or foodborne pathogens [109]. By

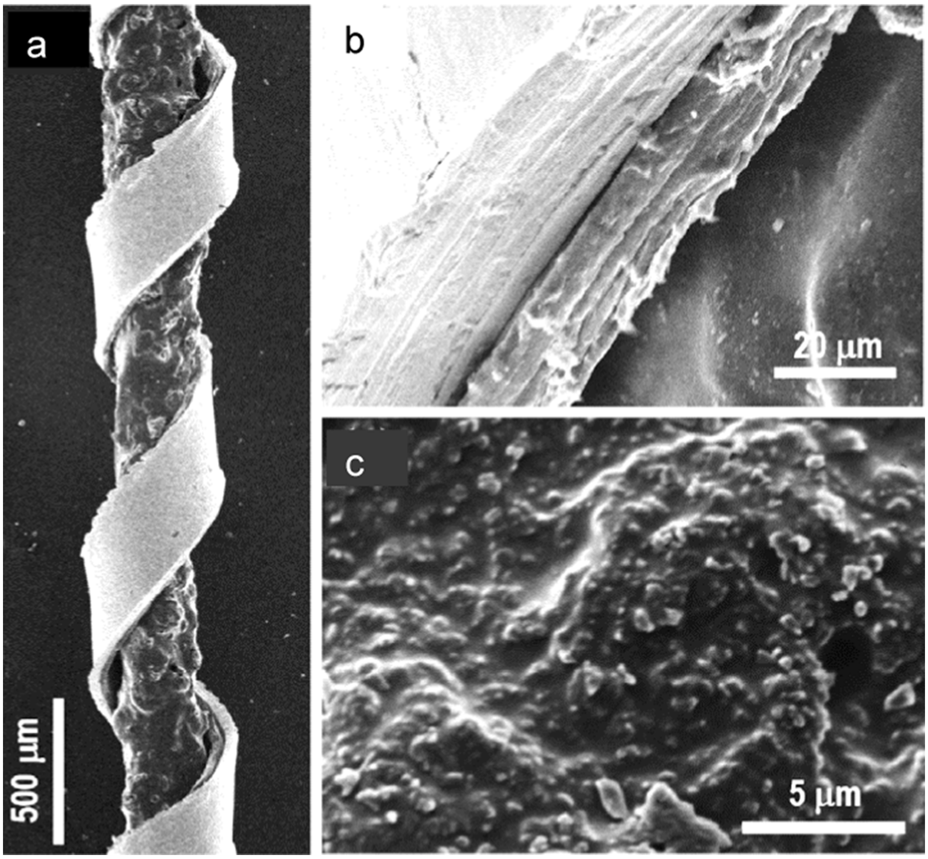

Fig. 27. SEM images of the EO system used to disinfect biofilms of *Porphynoromas gingivalis* in the root canals of extracted bovine teeth in phosphate buffer (pH 7). (a) BDDP/polymer composite with the spirally wound Pt ribbon. (b) Membrane electrode assembly with the Pt ribbon (left, white layer), ion-exchange membrane (middle, gray layer), and BDDP/polymer composite surface (right, black layer). (c) BDDP/polymer composite surface. Adapted from [104].

using adequate doses, hypochlorite solutions and active chlorine electrochemically produced (such as HClO) can be considered effective disinfectants. Among the electrocatalytic materials used to produce oxidizing species, the BDD anode appears as a novel food control alternative to enhance disinfecting capacity in the fresh-cut industry. Fresh-cut fruits and vegetables can become contaminated with disease-causing pathogenic bacteria, viruses, and protozoan parasites in different steps throughout the supply chain [110].

A limited number of contributions regarding foodborne pathogens inactivation is available in the existing literature by using BDD anodes [55]. These studies have focused their efforts on the implementation of electrochemical approaches for avoiding microbial cross-contamination by wash water treatments, disinfection approaches for water reuse, and preparation of water-based sanitizers.

Regarding the electrochemical disinfection of water for reuse, Gómez-López et al. [76] have reported relevant results when wash waters of iceberg lettuce and other vegetables were treated to inactivate a cocktail of *E. coli* microorganisms by EO with a Diacell® 101 cell in the presence of low NaCl concentrations, as already described in section 4.2.3.1 (see Table 2). López-Gálvez et al. [111] also evaluated the use of electrodisinfection diamond approach with a Diacell® 101 cell as a technology that helps to reduce the high water consumption of the fresh-cut produce industry because wash water was reused, having positive economic and environmental impacts.

Concerning the wash water treatments, López-Gálvez et al. [55] and Gómez-López et al. [112] demonstrated the effectiveness of water electrodisinfection by EO with a BDD anode and its appropriateness for the fresh-cut produce industry. Tap water containing or not NaCl with different concentrations of organic matter, in terms of COD (60, 300, 550, and 750 mg L^{-1}) obtained from lettuce, were inoculated with a suspension of *E. coli O157:H7* at 10^5 CFU mL^{-1} [55]. When tap water containing NaCl was electrolyzed in the absence of microorganisms, free chlorine was more quickly produced than in tap water without NaCl. This difference could be obvious because of the significant lower Cl^- content in tap water, as reported in [55]. When chloride electrolyzed-tap water was used as disinfectant, reduction of 5 log units of *E. coli O157:H7* was achieved in longer times of 0.17, 4, 15, and 24 min for increasing 60, 300, 500, and 750 mg L^{-1} of COD, respectively; whereas in electrolyzed-tap water, longer times of 0.9, 25, 60, and 90 min were needed for 60, 300, 600, and 800 mg L^{-1} of COD, respectively. Both solutions then showed potential for water disinfection and organic matter reduction. This behavior can be associated with the two methods critically discussed in this review, where a volume-based chemical process is attained in the former and a surface-layer-based approach is ascribed to the latter. In other study performed by Gómez-López et al. [112], NOM and *E. coli O157:H7* were removed and inactivated, respectively, from wash water in the washing tank by using electrolyzed waters obtained with different amounts of NaCl (1, 0.5, and 0.15 g L^{-1}). Total bacteria inactivation and a significant decrease on COD due to the organic matter depletion were achieved for vegetable wash water when electrolyzing a solution containing 0.5 g L^{-1} NaCl. However, low levels of chloroform and trihalomethanes were produced, but fortunately they remained lower than European limits (100 µg L^{-1}).

Diamond disinfection solutions is an actual alternative to chlorination, as a sanitizer, in the fresh-cut industry to maintain the microbiological and physicochemical quality of foods. For example, neutral electrolyzed water was generated from a 1 g L^{-1} NaCl solution at 4 °C with a pilot scale BDD-prototype (Adamant Technologies, Switzerland) by applying a j = 24 mA cm^{-2} with $E_{cell} \cong$ 26.4 A [113]. A sanitizer solution of 40 L of tap water with diluted chlorine (50 mg L^{-1}) was prepared at pH = 6.5, 4 °C (adjusted with citric acid), and an oxidation reduction potential >450 mV [55]. Then, 3.5 kg of *E. coli O157:H7*-inoculated lettuce were washed with the sanitizer solution, rinsed with cold tap water, and after that, lettuce was storage at different temperatures. The bacteria was not completely eliminated from lettuce after this treatment, with gradual increase at storage temperatures ≥ 8 °C. However, the growth of *E. coli O157:H7* was slower at all temperatures after the treatment with the sanitizer solution as compared to that observed after the treatment with chlorinated water. The longest lag time was 19 d at 8 °C, greater than the typical fresh-cut leafy green manufacturer's shelf-life time limit. The growth of pathogen was avoided if inoculated-lettuce was treated with the sanitizer solution, followed by storage at temperature below 8 °C.

Electrolyzed oxidizing waters, i.e., sanitizer solutions without or with 1 g L^{-1} NaCl, were also prepared with a Diacell® 101 at flow rate of 750 L h^{-1} by applying a $j = 216$ mA cm^{-2} (≅14.5 A), with changes in the electrode polarity each 20 min [114]. Two solutions of 10 L of acidified water with 80 mg L^{-1} citric acid and without and with 1 g L^{-1} of NaCl were electrochemically treated up to reach chlorine levels similar to those of used sodium hypochlorite (2–4 mg L^{-1} free chlorine). Then, 2 kg of baby spinach were washed with the sanitizer solutions containing a high organic load of 474 ± 8 mg L^{-1} COD, commonly found in the washing tanks of fresh-cut produce. Trihalomethanes were produced during the baby spinach washing process, although achieved values within the regulation limits. The storage quality after washing process by electrolyzed waters did not provoke impacts on microbial, nutritional, and sensory quality of baby spinach. From an economic point of view, electrolyzed chloride waters are the cheapest option among sanitizers, but no techno-economic analysis has been done to evaluate its applicability for commercialization.

5. Concluding remarks and prospects

The information available over electrochemical disinfection with diamond electrodes has been mainly obtained by treating free-chloride or chloride synthetic/real water matrices by using divided/undivided stirred tank or flow reactors. In the pioneering electrodisinfection studies, free-chloride synthetic solutions were tested aiming to assess the role of ROS generated at diamond electrode surface under specific experimental conditions, considering the use of phosphate, sulfate, or nitrate salts as supporting electrolytes. From the applicability of BDD in EO as approach to mineralize organic compounds, it is well-known that oxidation processes occur directly to the diamond surface by direct electron transfer, in its vicinity by the participation of reactive heterogeneous free-(•OH)), or in the bulk of solution by the action of stable oxidizing species. To clarify this point in the electrodisinfection technology because it is diverse, scientific researches have been conducted to understand the reactions that occur close to the anode surface, the inactivation role of the oxidants electrogenerated in free-chloride solutions and operating variables, and the mechanisms associated to the subcellular processes, lysis, and the damage of the cell walls. Based on the existing literature, only 8.1% of the papers published during the period 2006–2020 have dedicated research efforts for clarifying these concepts, whereas the rest of scientific communications have envisaged the applicability of this technology.

When microbial cells stopped their metabolic activity, which inhibits their pathogenicity but preserve their structures, their inactivation occurs. However, a reactivation upon appropriate physical and chemical conditions can be attained. The destruction of the cell structure arises from a disruption of the plasma membrane with lysis, as remarked in the works discussed on the section related to the mechanisms of bacteria inactivation by electrodisinfection with a BDD anode. Nevertheless, more sophisticated detection analysis and instrumental techniques should be used for solving the lacks on these mechanisms and for unrevealing the key role of the oxidants electrochemically generated with BDD anodes and their reactivity. Computational and theoretical calculations could also be taken into account for understanding conformational dynamic interactions that can be attained between the microorganisms and oxidizing species as well as the multi-point interactions between the diamond film and the microorganisms, the degradation reactions, and the factors that influence them.

The most important advantage of diamond electrodes is that they are considered as the best anode for EO of organics due to its high O_2-evolution overpotential, which is significantly greater than that of the rest of anodes, producing more significant quantities of reactive heterogeneous free-(•OH) or intensifying the production of other oxidizing agents. However, the high cost of BDD for industrial applications and the lower efficiencies achieved when low pollutant concentrations are present in the effluents are considered important disadvantages of this method. As a consequence, pros and cons are directly extrapolated to the suitability of electrodisinfection, and positive and negative technological significances are gained. For example, small BDD electrodisinfection devices can be designed, constructed, and commercialized, depending on the crucial operating conditions, where no substantial electrode dimensions would be needed, altering its techno-economic considerations. On the other hand, acceptable selection and adequate doses of oxidant precursors could direct the effective electrogeneration of oxidants, avoiding the loss in current/elimination efficiency when lower microorganism concentrations are checked. In fact, pioneering studies published by the Bergmann's group demonstrated the occurrence of toxic by-products, such as chlorate, perchlorate, bromate, and perbromate, on disinfection electrolysis of different water matrices using BDD anodes [27,46,115–117]. The investigations in this frame need to be encouraged in the next future, searching novel materials or defining operating conditions to avoid the formation of such undesirable by-products.l

The influence of the water matrix (natural organic matter, other organics, and inorganic ion composition) should be clearly elucidated to better understand the consequences of competitive reactions and generation of different oxidizing agents (ROS, active chlorine and others) on the electrodisinfection procedure. More critical operating conditions including materials that are used as the anode or cathode to improve the oxidation power of the process, electrochemical systems, the homogenous and heterogeneous nature of reactive species, the influence of each oxidant on others, the effect of precursors on the reactive species generated, their reactivity, and lifetime that are not completely explored yet, and the fundamental reaction mechanisms, should be investigated. More studies are also necessary to completely understand the synergistic or antagonist effects that can be promoted by using diamond films.

Stirred tank and flow reactors in divided or undivided setups have been widely adopted in most electrodisinfection studies, obtaining a great variety of achievements. The selection of the electrochemical systems is relied to the applicability, irradiation used, geometry of the electrodes, effluent properties, and volume treated. Preferentially, undivided electrochemical systems are used since they avoid the use of a membrane or separator that provokes an increase on the cell potential, affecting the production of oxidants, energy requirements, and electric costs. In the case of stirred tank reactors, only superficial information on the experimental conditions and treatment efficacy can be obtained, but these results could be not reproductible and well-defined, limiting the scale-up. For this reason, the correct strategy is to use electrochemical flow cells in discontinuous or continuous modes, allowing the scaling-up of the process. Mathematical descriptions, computational models, and simulations could be tools adopted to control the surface area/volume ratio to do a competent prototype-evaluation of the electrodisinfection approach. In undivided flow cells, the electrode material form, size and structure, and the operating cell mode and design, are factors that must be considered to assemble the internal cell compartment, aiming well-defined hydrodynamics and outstanding mass transfer rates to/from electrodes. Variants of electrode arrangements, multi-electrode systems, assembling numerous cell units, and reduced-gaps reactors, along with the use of mass transfer promoters should be widely explored in the next years to effectively translate the technology from lab to real applications and their possible commercialization.

The variability of electrochemical cells and the preparation of numerous diamond surfaces and supports have allowed to enhance the production of oxidizing species, favoring a more effective inactivation of pathogen agents and removal of toxic disinfection by-products. In fact, it is worth noting the development of electrochemical systems with BDD electrodes in contact with a membrane or the relevant role of the BDD composition expressed as the sp^3/sp^2 carbon ratio [78], i.e., the diamond/graphite structure ratio, over its oxidation power and/or its capacity to produce specific active chlorine species. Both features improve the electrogeneration of oxidants and avoid the production of chlorates and perchlorates from chloride-water matrices. The development of micro- and nanostructured materials with different BDD characteristics to provide new substrates and catalysts for improving ROS production in EO is also an exciting trend that must be approached.

Hybrid and sequential disinfection technologies to inactivate waterborne pathogens are dependent on the operating conditions. In this context, the composition of the water or other additives can play an essential role in the cell reduction and lysis of the microorganisms. Chemical/electrochemical phenomena can be attained upon pH conditions, dissolved cationic or anionic species, irradiation profiles or modes, ultrasounds, temperature, organic concentrations, viscosity, flow directions, and so on. Problems or challenges associated with each one of these factors should be also carefully considered during optimization and scale-up of the association of these combined technologies. It is important to indicate that no large scales are always necessary to achieve efficient commercial applications because sometimes the volume of the effluent to be treated is reduced, and consequently, the design, elaboration, and construction of small devices is only required. As a vital challenge, the design of autonomous electrodisinfection with systems powered by free renewable energy (wind, solar photovoltaic panels, etc.) with low maintenance should be developed to make the diamond disinfection technologies more attractive for their industrial use, even in remote regions. Techno-economic analysis for each process should be done to demonstrate their competitive respect to conventional disinfection methods like chlorination.

The diamond disinfection technology future is bright, even with predictable new actual endodontic and food control applications, as analyzed in this review. Future developments will rely upon the close collaboration of analytical chemists, engineers, and electrochemists to ensure an effective application and exploitation of these methods. Nevertheless, great efforts are mandatory. To do this, more bacteria in real effluents should be treated, more designs and construction of optimized reactors should be done, and novel alternatives should be explored, e.g., to prove the viability of sanitizer solutions respect to commercial technologies.

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CRediT authorship contribution statement

Carlos A. Martínez-Huitle: Conceptualization, Data curation, Formal analysis, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing. **Enric Brillas:** Conceptualization, Data curation, Formal analysis, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Papers of particular interest, published within the period of review, have been highlighted as: special interest (*) or outstanding interest (**)

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