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Electrochemical Water Purification

Electrochemical Alternatives for Drinking Water Disinfection

Carlos A. Martínez-Huitle and Enric Brillas*

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Chlorination is the most common method worldwide for the disinfection of drinking water. However, the identification of potentially toxic products from this method has encouraged the development of alternative disinfection technologies. Among them, electrochemical disinfection has emerged as one of the more feasible alternatives to chlorination. This article reviews electrochemical systems that can contribute to drinking water disinfection and underscores the efficiency of recently developed diamond films in chlorine-free electrochemical systems.

1. Drinking Water Disinfection

Disinfection generally constitutes the final step in the water reuse cycle. Since it represents the last barrier against pathogen microorganisms, its effectiveness is a crucial point in ensuring public health.[1,2] Without doubt it is the most important step in the production of safe drinking water. Water-borne diseases (diarrhea, cholera, typhoid, amoebiasis, and schistosomiasis) and deaths are still a problem in a large number of countries. These diseases contribute considerably to the morbidity and mortality rate in developing countries. Effective elimination of pathogenic microorganisms in drinking water is essential in fighting these diseases and this has made a major contribution to the reduction of mortality rates worldwide during the last century.[1] Drinking water disinfection typically includes multibarrier water treatment processes such as settlement, coagulation, and filtration as well as chemical processes such as ozonation and chlorination. Disinfection processes have two main purposes: primary disinfection for removal or inactivation of microbiological contaminants in the raw water supply[3] and the provision of a residual in the distribution network. Drinking water disinfection represents the most important topic in water purification, although the production of sterile water for medical, biological, and food safety applications is also of great importance.[4,5]

[*] Dr. C. A. Martínez-Huitle
DiSTAM
Università degli Studi di Milano
via Celoria 2, CAP-20133 Milan (Italy)
Fax: (+39) 02-5031-9061
E-mail: carlos.martinez@unimi.it
Prof. Dr. E. Brillas
Laboratori d'Electroquímica dels Materials i del Medi Ambient
Departament de Química Física
Facultat de Química, Universitat de Barcelona
Martí i Franquès 1-11, 08028 Barcelona (Spain)

2. Chlorine Disinfection and Related Problems

The most popular method for drinking water disinfection is the addition of chlorine and/or chlorine by-products that are able to eliminate most harmful microorganisms. Despite the great effectiveness of chlorination as a water disinfection method, disadvantages like unfavorable taste and odor, its ineffectiveness when used alone against some resistant microorganisms, and the generation of potentially toxic or mutagenic products such as trihalomethanes[6] and chloroform (the most common chemical by-product of water disinfection)[1,7,8] instigated the search for alternative disinfection methods. A number of these by-products are a major health concern because of their carcinogenic properties. The World Health Organization has set guidelines for these compounds based on increased cancer risk. Several epidemiological studies have investigated the possible carcinogenic properties of chlorinated drinking water. However, the International Agency for the Research on Cancer considered the evidence for an association between chlorination and the occurrence of cancer to be inadequate.[2] In March 1998, owing to the adverse effects of chloroform, the Environmental Protection Agency released new data on disinfection by-products, and announced that it was considering changing the goal for its contamination in drinking water from 0 to 300 mg L^{-1}.[9,10] As a result of these disadvantages, numerous

alternatives to chlorination for drinking water disinfection have been proposed.

3. Alternatives for Drinking Water Disinfection

The most interesting alternatives to chlorination include: 1) chemical systems based on ozone, silver, copper, ferrate, iodine, bromine, hydrogen peroxide, and potassium permanganate,[11–13] 2) physico-chemical means such as photocatalysis with titanium dioxide and photodynamic disinfection,[14–16] 3) electrochemical disinfection, and 4) physical treatments such as ultraviolet irradiation, ultrasonication, pulsed electric fields, irradiation, magnetic-enhanced disinfection, and microwave systems.[1,17,18] Whilst ozone and ultraviolet irradiation have gained acceptance as the water treatment processes, most of the other alternatives at present do not fulfill the requirements for primary and residual drinking water disinfection.[1] For example, the use of titanium dioxide photocatalysis, high intensity pulsed electric fields, and ultraviolet light does not generate residual disinfection. Hence these methods are suitable only for primary disinfection in countries such as the Netherlands where residual disinfection is not required. In contrast, electrochemical disinfection has emerged as one of the most promising alternatives to chlorination providing both primary and residual disinfection.[1]

4. Electrochemical Disinfection of Drinking Water

In recent years effective electrochemical disinfection systems for conventional water treatment have been developed. The advantages of these procedures make them more attractive than other methods. The electrochemical technology is environmentally friendly, low-cost, easily operated, and known to inactivate a wide variety of microorganisms ranging from bacteria to viruses and algae.[1,19] The most useful systems for electrochemical disinfection of drinking water are based on the electrogeneration of disinfecting agents. Other technologies such as the electrosorption of bacteria on the electrode surface,[20] electrocution,[21] and electrophoresis[22,23] have also been explored. The potential use of electrochemical methods for disinfection has been discussed since the 1950s, but systems other than those electrogenerating chlorine[1,24–26] have yet to gain widespread acceptance within the water treatment industry. Although the mechanism of electrochemical disinfection using chloride-containing solutions, so-called electrochlorination, has been mainly attributed to the action of electrogenerated active chlorine, conflicting research concerning the generation of other disinfecting agents in water treated with these systems has been considered. However, the debate as to whether electrochemical systems can replace chlorination is still open.

5. Electrochemical Disinfection Systems

Numerous electrochemical systems and electrode materials have been tested against a variety of microorganisms, and their effectiveness to the abatement of bacteria, viruses, and protozoa is largely dependent on the electrochemical reactor, anode material, electrolyte composition, and electrolysis conditions. Table 1 summarizes these parameters for the most relevant research in the context of the inactivation of microorganisms in chloride-containing water by electrochlorination.[27–35] Similar data obtained for tap water samples with a very low chloride content ($< 4\ mg\,L^{-1}$) and chlorine-free water samples[1,31,34–45] are collected in Table 2. Application of alternating current or potential, pulse voltage, and mainly direct current to a large variety of undivided electrochemical cells can be observed. As anode material, which is the most important parameter in the disinfection process, metals, carbon electrodes, mixed metal oxides, and conductive boron-doped diamond films have been utilized. Tables 1 and 2 also list the electrolyte and concentration of cells treated, the applied anode potential, cell voltage and/or current density, and the kinds of bacteria, viruses, and algae inactivated.

6. Electrochlorination

The most popular method of electrochemical disinfection is electrochlorination. Its main advantage is the on-site generation of disinfectants. Thus the problems of standard chlorination—transport and storage of dangerous chlorine gas—are avoided.[19] There are two types of electrochlorination procedures: the synthesis of free chlorine from brine in an electrolytic generator and the direct production of oxidants from the water to be treated by the electrolyzer (Table 1).

Carlos A. Martínez-Huitle was born in México City in 1977. He graduated in chemistry from the Universidad de las Américas—Puebla, México (2000). After working in industry and academia, he moved to the University of Ferrara, Italy (2002), and earned a PhD in chemistry (2005) for work conducted under the supervision of Prof. Achille De Battisti. Currently, he works at the University of Milan. His research interests include electrochemical oxidation, electrocatalysis, and electroanalysis.

Enric Brillas was born in Barcelona, Spain, in 1951. He obtained his PhD in chemistry in 1977 at the Universitat Autònoma de Barcelona and has been Full Professor of Physical Chemistry at the Universitat de Barcelona since 1987. He was elected President of the Electrochemistry Group of the Real Sociedad Española de Química in 2004. His research is centered on organic electrochemistry, electrocatalysis, and electrochemical treatment of organic pollutants. He has published 175 peer-reviewed papers, four books, and seven book chapters.

Table 1: Microorganisms inactivated in chloride-containing water by electrochlorination.

Electrochemical cell	Anode	Effluent	Electrolysis conditions	Inactivated microorganisms	Ref.
Pulse voltage					
flow-through cell	Ti/RuO_2 plate (30 cm^2)	500 mL of water with germinated brown rice and NaCl (pH 5.5) containing 10^2–10^7 CFU mL^{-1}; batch treatment at 87 mL min^{-1}	cell voltage of 1.0 or 1.5 kV at 5 Hz	*Legionella*	[27]
Electrochemically assisted photocatalysis					
stirred tank reactor with a quartz window for anode illumination	Ti/TiO_2 foil (1.35 cm^2) irradiated with a 150-W Xe lamp	10 mL of 5×10^5 CFU mL^{-1} bacterial suspension in a Ringers solution[a]	1 V vs. SCE[b]	*E. coli*	[28]
Direct current					
stirred tank reactor	Pt wire	10 mL of EE buffer (pH 8.3)[c] with a suspension of 10^3 CFU mL^{-1}	25–350 mA (cell voltage of 25–350 V)	*E. coli*, *Ps. aeruginosa*, bacteriophage MS2	[29]
tubular reactor	Ti/RuO_2 rod (260 mm length, 5 mm diameter)	600 mL of 3×10^6 CFU mL^{-1} algal suspension in water with Cl^- (pH ≈ 7); batch treatment	1–10 mA cm^{-2} (cell voltage of 3.5–9.2 V)	*Mycrocystis aeruginosa*	[30]
	Ti/RuO_2–TiO_2 rod (87 cm^2)	265 mL of deionized water with bacterial suspension and up to 0.1 M NaCl	11 mA cm^{-2}	*E. coli*	[31]
flow-through cell	Ti/IrO_2–TiO_2 plate (30 cm^2)	potable water with 50 mg L^{-1} Cl^-, 240 mg L^{-1} SO_4^{2-}, and a suspension of 10^5–10^7 CFU mL^{-1}; continuous flow at 3 L min^{-1}	0.5–4 A (cell voltage of 4–14 V)	*Bacillus subtilis*, *E. coli*, *Saccharomyces cerevisiae*	[32]
typical dual-electrode cell	Ti/IrO_2–Sb_2O_5–SnO_2 pellets (919.6 mm^2)	synthetic solutions with a suspension of 10^7–10^8 CFU mL^{-1} and 0.016–0.032 wt% or 0.5–1.0 wt% NaCl	0–2 A (cell voltage of 0 to 18 V)	bacteriophage MS2	[33]
Zappi cell	Pt–Nb mesh (522 cm^2)	10 L of contaminated 0.010 M NaCl; batch treatment at 6 L min^{-1}	4 mA cm^{-2} (cell voltage of 5 V)	*E. coli,* bacteriophage MS2	[1]
DiaCell reactor	Si/BDD plate (65 cm^2)	tap water with 75 mg L^{-1} Cl^- or deionized water with 330 mg L^{-1} NaCl; continuous flow at 160 L h^{-1}; used subsequently for disinfection	25–150 mA cm^{-2}	*Legionella pneumophila*	[34, 35]

[a] Solution composed of 2.25 g L^{-1} NaCl, 0.105 g L^{-1} KCl, 0.120 g L^{-1} $CaCl_2$, and 50 mg L^{-1} $NaHCO_3$. [b] Applied anode potential in a three-electrode cell. [c] Buffer composed of 30 mM tris(hydroxymethyl)aminomethane (Tris) and 150 mM KCl

Active chlorine species such as Cl_2, HOCl, OCl^-, and ClO_2 are widely recognized as key oxidants responsible for inactivating cells in electrochlorination. These species can be produced at the anode by the reactions in Equations (1)–(3).[30,46]

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^- \quad (1)$$

$$Cl_2 + 2\,OH^- \rightarrow H_2O + OCl^- + Cl^- \quad (2)$$

$$Cl_2 + 4\,H_2O \rightarrow 2\,ClO_2 + 8\,H^+ + 8\,e^- \quad (3)$$

Some researchers have pointed out that the disinfecting efficacy of this method is much higher than that of chlorination because other oxidants are also formed by electrogeneration. Thus, Venczel et al.[48] found more rapid inactivation kinetics for *Escherichia coli*, the rugose strain of *Vibrio cholerae*, *Clostridium perfringens* spores, and bacteriophage MS2 in pH 6–10 with on-site electrogenerated oxidants from brine than with free chlorine. Similarly, Son et al.[47] reported that electrochemically generated oxidants displayed better disinfecting efficacy than free chlorine for *Escherichia coli* and *Bacillus subtilis* spores at pH 8.2 considering the same content of total oxidants. Recent studies have attributed the higher disinfecting power of electrochlorination to the oxidant role of reactive oxygen species (ROS) such as hydroxyl radical (•OH), atomic oxygen (•O), hydrogen peroxide, and ozone, which can be generated from water by discharge at the anode [Eq. (4)–(8)].[44,49,50]

$$H_2O \rightarrow {}^{\bullet}OH + H^+ + e^- \quad (4)$$

$${}^{\bullet}OH \rightarrow {}^{\bullet}O + H^+ + e^- \quad (5)$$

$$2\,{}^{\bullet}O \rightarrow O_2 \quad (6)$$

$$2\,{}^{\bullet}OH \rightarrow H_2O_2 \quad (7)$$

$$O_2 + {}^{\bullet}O \rightarrow O_3 \quad (8)$$

The hydroxyl radical is the second most oxidizing species known after fluorine and has a high standard potential (E° = 2.8 V vs. NHE) that ensures its fast reaction with most organic materials. However, the short lifetime of •OH and other ROS in solution makes only possible to underline their possible role in disinfection using direct current. Liang et al.[30] utilized a tubular electrochemical cell with a Ti/RuO_2 anode (see Figure 1) for the batch treatment of an aqueous chloride solution (600 mL, ca. pH 7) containing a suspension of the alga *Microcystis aeruginosa*. Under these conditions, the cell content of the algal suspension decreased rapidly and propor-

Table 2: Microorganisms in tap water with very low chloride content or in chlorine-free water inactivated by electrochemical disinfection.

Electrochemical cell	Anode	Effluent	Electrolysis conditions	Inactivated microorganisms	Ref.
Alternating current or potential					
stirred tank reactor	Ti plate (25 cm^2)	350 mL of tap water (pH 8.1) with a suspension up to 26800 cells per milliliter	2.5–5.0 $mA\,cm^{-2}$ (45–100 V cell voltage) at 0.5 Hz	coliform bacteria	[36]
flow-through cell	activated carbon fiber (34 mm diameter, 100 mm length, 9 mm thickness)	tap water with a suspension of 2.3×10^3 cells per milliliter; continuous flow at 300 $mL\,min^{-1}$	1.0 V vs. SCE for 20 min and cycling from 0.2 to −0.8 V vs. SCE for 10 min[a]	*E. coli*	[37]
	TiN mesh (2 cm^2)	tap water with a suspension of 73 cells per milliliter; continuous flow at 15 $mL\,min^{-1}$	1.2 V vs. Ag/AgCl for 60 min and −0.6 V vs. Ag/AgCl for 30 min[a]	*Aenomas hydrophila*, *Bacillus subtilis*, *E. coli*, *Saccharomyces cerevisiae*, *Klebsiella pneumoniae*, *Ps. cepacia*, *Ps. fluorescens*	[38]
Direct current					
flow-through cell	carbon-cloth sheet (260 or 1170 cm^2)	tap water with a suspension of 10^2 cells per milliliter; continuous flow	0.5–0.7 V vs. SCE[a]	*E. coli*	[39]
	activated carbon fiber (18 mm diameter, 100 mm length, 5 mm thickness)	drinking water with 22 cells mL^{-1}; continuous flow at 2 $mL\,min^{-1}$ (12 h); after an interruption for 24 h, it was started again at 1 $mL\,min^{-1}$ (6 h)	0.8 V vs. SCE[a]	*E. coli*	[40]
stirred tank reactor	Pt sheet (4.6 cm^2)	50 mL of 0.1 M phosphate buffer (pH 7.1) with a suspension of 2×10^6 CFU mL^{-1}	0.1–1 A	*Saccharomyces cerevisiae*	[41]
	Nb/BDD plate (6 cm^2) or Pt sheet (5 cm^2)	80 mL of 0.2 M phosphate buffer (pH 7.1) with a suspension of 10^5 CFU mL^{-1}	0.1–100 $mA\,cm^{-2}$	*E. coli*	[42, 43]
	Si/BDD plate (30 cm^2)	1 mM Na_2SO_4 with a suspension of about 10^2 CFU mL^{-1}; batch or continuous flow up to 100 $mL\,min^{-1}$	1.5–13.3 $mA\,cm^{-2}$ (2.8–3.1 V vs. SCE)[a]	*E. coli*, *Enterococcus faecalis*, coliform *Enterobacter*, coliform *Acinectobacter*	[44]
tubular reactor	Ti/RuO_2–TiO_2 rod (87 cm^2)	265 mL of deionized water with bacterial suspension and 0.01 M $NaNO_3$ or 0.1 M Na_2SO_4	11 $mA\,cm^{-2}$	*E. coli*	[31]
Zappi cell	Pt–Nb mesh (522 cm^2)	10 L of contaminated 0.030 M Na_2SO_4 or 0.036 M NaH_2PO_4; batch treatment at 6 $L\,min^{-1}$	24–27 $mA\,cm^{-2}$ (cell voltage of 5 V)	*E. coli*, bacteriophage MS2	[1]
DiaCell reactor	Si/BDD plate (65 cm^2)	tap water or deionized water with 476 $mg\,L^{-1}$ $NaHCO_3$ or 440 $mg\,L^{-1}$ Na_2SO_4; continuous flow at 160 $L\,h^{-1}$; used subsequently for disinfection	25–150 $mA\,cm^{-2}$	*Legionella pneumophila*	[34, 35]
not specified	IrO_2, Pt, BDD–diamond	tap water with 1.4×10^8 CFU of bacterial suspension and glucose (9 $g\,O_2\,L^{-1}$ of COD)	not specified	*E. coli*	[45]

[a] Applied anode potential in a three-electrode cell.

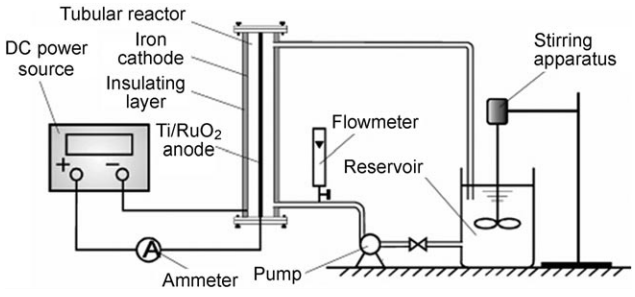

Figure 1. Setup for the inactivation of the alga *Microcystis aeurinogosa* using a tubular electrochemical cell with a Ti/RuO_2 anode. Adapted from Liang et al.[30]

tionally to the current density and electrolysis time. After 52 min of treatment at 10 $mA\,cm^{-2}$, the population of *Microcystis aeruginosa* was reduced from 3×10^6 to 0.6×10^6 colony-forming units (CFU) per milliliter. Scanning electron microscopy revealed surface damage and apparent leakage of intracellular contents after electrochemical disinfection (Figure 2). As a result, chlorophyll *a* was released from the cells and degraded up to 96% by electrochemically generated oxidants; oxidation with ozone gave similar results.[30]

The kinetics of the different series/parallel steps in reactions (1)–(8) depends on the anode material and determines the predominant oxidants produced. Thus, the electrochemical production rate of free chlorine at IrO_2 and IrO_2/RuO_2 anodes is higher than that at boron-doped diamond (BDD) and Pt anodes under comparable conditions.[32,51] Mixed-metal oxides of Ir and/or Ru are then preferable as anodes for electrochlorination to enhance the generation of active chlorine species as the main disinfectants. In contrast, a

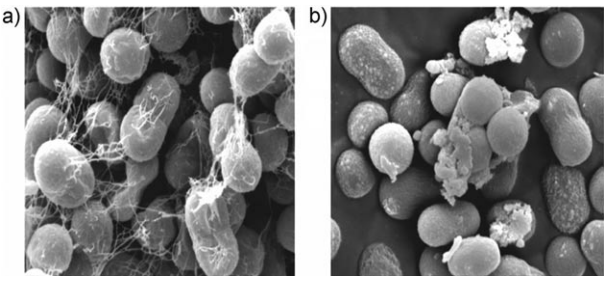

Figure 2. Scanning electron micrographs of *Microcystis aeurinogosa* obtained before (a) and after (b) disinfection using the electrochemical tubular cell of Figure 1. Reprinted with permission from Ref. [30] Copyright 2005, American Chemical Society.

BDD anode produces much more appreciable amounts of ROS and other oxidizing species such as peroxodisulfate, peroxodicarbonate, and peroxodiphosphate; these species arise from the oxidation of ions present in the solution and also allow rapid, long-lasting disinfection.

A different method of electrochemical inactivation based on the direct electron transfer between the electrode surface and the microbial cells under low alternating or direct potential (or current) has been reported by Matsunaga et al.[37–40] They showed, for example, that inactivation of *Escherichia coli* using a carbon cloth anode is a result of the electrochemical oxidation of intracellular coenzyme A, leading to decreased respiration and consequent cell death.[39]

7. Diamond Films for Wastewater Treatment

Recently, BDD thin-film electrodes have been found to be particularly attractive as anodes owing to their outstanding properties including large potential window, low species adsorption, corrosion stability in very aggressive media, high efficiency in oxidation processes, and very low double-layer capacitance and background current. These properties differ significantly from those of conventional anodes including Pt and PbO_2, doped and undoped SnO_2, IrO_2, and RuO_2.[35,49] Diamond films are suitable materials for industrial applications such as chemical synthesis and electroanalysis and can be used in sensors and biosensors, although they have been mainly applied in anodic oxidation to destroy refractory organic pollutants and toxic substances for wastewater treatment.[45,51–55] The great effectiveness of diamond films in anodic oxidation has been confirmed in the degradation of ammonia, cyanide, phenol, chlorophenols, aniline, dyes, surfactants, alcohols and many other pollutants.[49,51,55,56] In addition to ROS, weak oxidants such as peroxodisulfate, peroxodicarbonate, and peroxodiphosphate can also be formed from the oxidation of sulfate or bisulfate,[57] bicarbonate,[58] and phosphate[59] at the BDD surface [Eq. (9)–(11)].

$$2\,HSO_4^- \rightarrow S_2O_8^{2-} + 2\,H^+ + 2\,e^- \quad (9)$$

$$2\,HCO_3^- \rightarrow C_2O_6^{2-} + 2\,H^+ + 2\,e^- \quad (10)$$

$$2\,PO_4^{3-} \rightarrow P_2O_8^{4-} + 2\,e^- \quad (11)$$

Unlike PbO_2, SnO_2, and TiO_2, BDD thin films deposited on Si, Ta, Nb, and W by chemical vapor deposition have shown excellent electrochemical stability.[51–53] The application of BDD electrodes for wastewater treatment has been mostly studied with Si-supported devices, despite their fragility and the relatively low conductivity of the Si substrate. Although BDD films synthesized on Nb, Ta, and W are promising, their large-scale preparation is prevented by the high costs of these metal substrates. Titanium is a possible alternative support since it possesses all of the required features. Ti/BDD anodes have been already used for the destruction of some pollutants. However, diamond deposition on Ti must be greatly improved because cracks appear and cause the detachment of the diamond film during long-term electrolysis. For these reasons, Si/BDD electrodes are currently applied to drinking water disinfection, where smaller anodes suffice, in contrast to those required for wastewater treatment.

8. Diamond Films for Drinking Water Disinfection

Electrochemical disinfecting methods with generation of oxidants at diamond films are still under investigation, but the efficient direct in situ production of common chlorine-based disinfection agents,[34,35,51,60] along with the high generation of ROS,[51,61–63] by the reactions in Equations (1)–(11) may achieve more accurate dosage and simplify the handling of chemicals. Electrochemical production of oxidants at the diamond surface can thus be exploited for the disinfection of drinking water and removal of color and odor (see Tables 1 and 2).A DiaCell reactor (Figure 3) with a Si/BDD anode has been applied to prepare electrolyzed water with residual oxidants for inactivation of *Legionella pneumophila* (10^4–10^6 CFU mL^{-1}).[34,35] The cell was operated in continuous-flow mode by circulating either tap water (without or with addition of 75 mg L^{-1} Cl^-) or deionized water (with 330 mg L^{-1} NaCl, 476 mg L^{-1} $NaHCO_3$ or 440 mg L^{-1} Na_2SO_4) at 160 L h^{-1}. Total inactivation of *Legionella* cells (> 90 %) was achieved when the tap water was electrolyzed at more than 150 mA cm^{-2} and the contact time was longer than 1 h. The bacteria abatement in tap water (with 3.5 mg L^{-1} Cl^-) was at least three times faster with the electrochemical disinfection from the diamond cell than with conventional chlorine

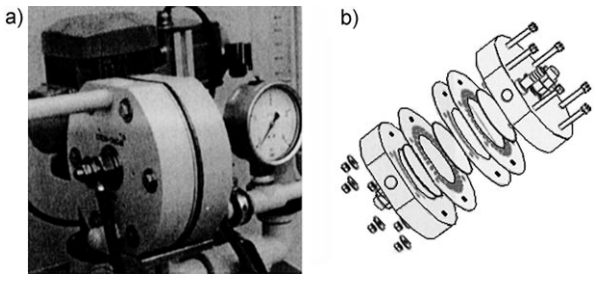

Figure 3. a) DiaCell reactor with Si/BDD electrodes used for wastewater treatment and disinfection. b) Magnified view of the basic bipolar module of the electrochemical cell with two compartments containing two current feeders and a bipolar electrode separated by 5 mm. Adapted from Haenni et al.[60]

treatment. A low level of electrogenerated oxidant ($<1\,mg\,L^{-1}$) was sufficient for a rapid disinfection. The inactivation efficacy increased gradually as the electrolyzed water contained more chloride, even at low current densities. Using $80\,mg\,L^{-1}\,Cl^-$, for example, *Legionella* cells were completely inactivated by applying a current density as small as $50\,mA\,cm^{-2}$ with contact times of 1 min. Bicarbonate solutions electrolyzed in the diamond cell also inactivated the bacteria as a result of the formation of a low content of oxidant peroxodicarbonate [Eq. (10)]. The generation of this oxidant can then explain the rapid abatement of *Legionella* attained with electrolyzed tap water, which contains a high HCO_3^- concentration of $324\,mg\,L^{-1}$. In contrast, water electrolyzed with sulfate had no impact on *Legionella* cells owing to the low oxidizing power of peroxodisulfate formed by the reaction in Equation (9).

Tröster et al.[45] also reported that a diamond anode performed better than common electrode materials like Pt and IrO_2 for the treatment of a solution containing 1.4×10^8 CFU of *Escherichia coli* and glucose with a chemical oxygen demand (COD) of $9\,g\,O_2\,L^{-1}$. The use of diamond anode led not only to a considerable reduction in bacteria population but also to the simultaneous removal of COD by combustion of the sugar. These effects result in greatly improved disinfection and simultaneous decontamination of water.

Haenni et al.[60] showed that the diamond electrodes in the DiaCell reactor generate oxidants such as ROS by the reactions in Equations (4)–(8). These species at diamond electrodes can be efficiently utilized for the disinfection of chloride-containing water in swimming pools. The Si/BDD anode exhibits continuous chlorine productivity and higher disinfection performance against bacteria in comparison to directly added NaOCl.

Other interesting electrochemical applications of diamond films include the disinfection of water circuits and process water in industrial and power plants, air-conditioning systems, cooling towers (inactivation of algae, *Legionella*, and germs), warm-water systems in hotels and hospitals (*Legionella* removal), biologically cleaned wastewater (sewage), and ballast water, and the disinfection of medical instruments.[45,64,65]

9. Electrochemical Chlorine-Free Systems

New evidence on the oxidizing action of ROS (·OH, ·O, H_2O_2, O_3) in the electrochemical disinfection with diamond films has been obtained by electrolyzing chlorine-free waters. Polcaro et al.[44] recently reported the treatment of suspensions of *Escherichia coli*, *Enterococcus faecalis*, and coliform bacteria in 1 mM Na_2SO_4 using the system depicted in Figure 4 with a stirred tank reactor containing a Si/BDD anode. Figure 5a shows that the concentration of oxidants accumulated in electrolyzed solution (H_2O_2, O_3, and peroxodisulfate formed from the reactions in Equations (7)–(9)) under continuous treatment depends on effluent flow rate. A decay in oxidant species can be observed with increasing effluent flow. However, higher concentrations of oxidants are produced when high current density is applied and low stirring

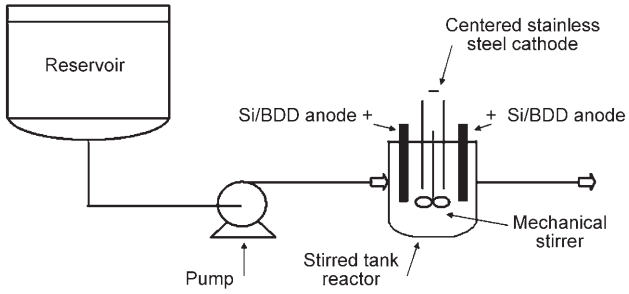

Figure 4. Experimental setup for the electrochemical disinfection of microorganisms in 1 mM Na_2SO_4 using a Si/BDD anode. Adapted from Polcaro et al.[44]

velocity (characterized by the Reynolds number) is used during the experiments. On the basis of these results, several disinfection trials were performed and fast inactivation of all bacteria was found by applying $10\,mA\,cm^{-2}$ under batch conditions (Figure 5b). The reduction of microorganism populations from $1\times10^3\,CFU\,mL^{-1}$ to the detection limit was achieved in 60, 100, and 300 s for *Escherichia coli*, coliform bacteria, and enterococcci cells, respectively. These results are significantly better than those achieved with similar electrochemical processes and other anode materials

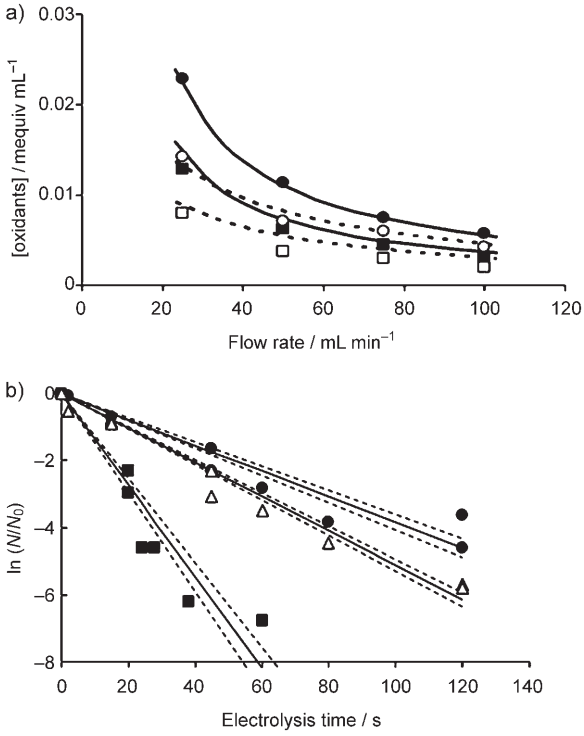

Figure 5. a) Plot of the concentration of oxidants (in milliequivalents per milliliter) as a function of the effluent flow rate under continuous treatment. Applied current density: 13.3 $mA\,cm^{-2}$ (filled symbols), 6.6 $mA\,cm^{-2}$ (empty symbols). Reynolds number: 1.5×10^3 (circles), 1.0×10^4 (squares). b) Survival ratio with electrolysis time for *Escherichia coli* (■), coliforms (△), and enterococci (●) under batch treatment at 10 $mA\,cm^{-2}$ and a Reynolds number of 1.0×10^4. $[E.\,coli]_0 = 6.4\times10^2\,CFU\,mL^{-1}$, $[coliforms]_0 = 2.3\times10^3\,CFU\,mL^{-1}$, $[enterococci]_0 = 4.4\times10^3\,CFU\,mL^{-1}$. Solid lines represent the least squares regression lines for the data, dotted lines represent the standard error of the regression. Adapted from Polcaro et al.[44]

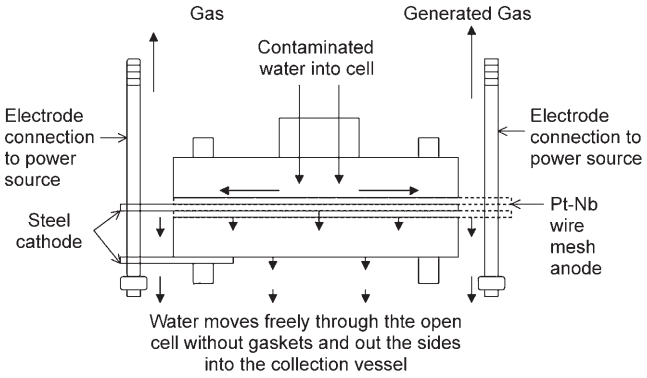

Figure 6. Representation of the Zappi cell used to disinfect water contaminated with *Escherichia coli* and the bacteriophage MS2. Adapted from Kerwick et al.[1]

(Table 2). Kerwick et al.[1] described the batch treatment of 10 L of 0.030 M Na_2SO_4 or 0.036 M NaH_2PO_4 at a flow rate of 6 L min^{-1} through a Zappi cell (Figure 6). In both media inactivation of *Escherichia coli* and bacteriophage MS2 cells was found only after long electrolysis times (60–75 min) at 24–27 mA cm^{-2} owing to the lower production of ROS at the Pt-Nb anode than at diamond films. Patermarakis and Fountoukidis[36] exposed tap water containing coliform bacteria at a total population density of 200–26800 cells per milliliter to alternating current of 2.5 mA cm^{-2} using Ti electrodes, but the culturable counts were reduced by only an order of magnitude in 15.7 min. Matsunaga et al.[39] reduced *Escherichia coli* from a population density of 100 cells per milliliter in tap water to less than 2% of the initial density after 10 min of electrolysis with a carbon-cloth electrode at 0.7 V. The good efficiency of the direct electrochemical disinfection with a Si/BDD anode in diluted Na_2SO_4 solutions corroborates the important role the anode material plays in producing ROS.

In a detailed study by Jeong et al.[42] *Escherichia coli* cells were inactivated with an electrochemical chlorine-free system containing 0.2 M phosphate buffer and using Nb/BDD as anode. The morphological changes in the cells after 5 min of electrolysis at 100 mA cm^{-2} were simultaneously followed by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The TEM images of the untreated and treated bacteria (Figure 7 a,b) indicate drastic changes in both the cell content and cell walls after electrolysis.[42] The cells are almost empty and their membranes are no longer uniform. Figure 7 c,d present AFM images of the same cells before and after electrolysis. While the surface of the untreated cells appears to be smooth and flat, the treated cells have a rough and sunken surface, as if they had shrunk when the contents escaped. These morphological changes can be interpreted by the attack of ROS, disrupting the integrity of the cell membrane and leading to the lyses of the cells. Greater inactivation was also found upon decreasing the temperature from 35 to 4 °C and the pH from 7.1 to 5.6; this was mainly related to the formation of more O_3 and $^{\bullet}OH$, respectively. This study clearly shows that strong oxidants as ROS formed by electrolyzing water at diamond films can cause a significant inactivation of microorganisms, comparable to that of chlorine in electrochlorination. The potential

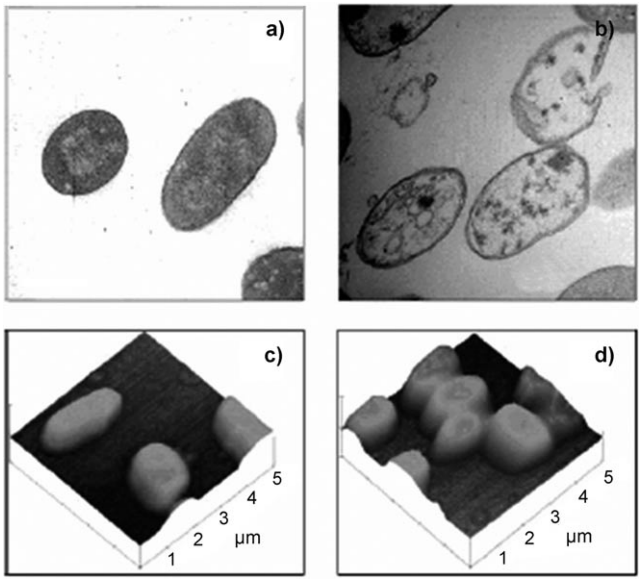

Figure 7. Morphological changes in *Escherichia coli* cells resulting from electrolysis at 100 mA cm^{-2} for 5 min using a Nb/BDD anode. $[E.\ coli]_0 = 10^8$ CFU mL^{-1}, $[KH_2PO_4]_0 = 0.2$ M, pH 7.1, 25 °C. TEM images before (a) and after (b) electrolysis; AFM images before (c) and after (d) electrolysis. Reprinted with permission from Ref. [42]. Copyright 2006, American Chemical Society.

role of these strong oxidant species, which have higher oxidizing power than chlorine, should be examined for the treatment of spore-forming microorganisms, which are difficult to inactivate by chlorination. Therefore, the development of new approaches to disinfecting water by using diamond films may lead to an entirely new class of electrochemical chlorine-free systems.

10. Conclusion and Outlook

The recent advances obtained with diamond film electrodes suggest that their application to the disinfection water should be rapidly developed. Diamond-coated electrodes have impressive commercial implications since the large amounts of ROS produced during water electrolysis result in fast bacterial abatement and total oxidation of organic substances. Imagine, for example, the use of such practical commercial technology for disinfection, washing, and sterilization of medical instruments, drinking water disinfection and treatment of purulent and septic diseases of humans and animals. Other applications include wastewater and/or sewage treatment, disinfection of swimming pools, poultry factories, livestock farms, and control of epidemics. This opens new perspectives for easy, effective, and chemical-free water treatment. More research is needed to assess possible problems involved with the formation of disinfection by-products having a high health risk like ClO_2, ClO_3^-, and ClO_4^-.[62]

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