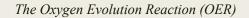


- Nonactive anodes (e.g., PbO₂, SnO₂, and BDD), which present high oxygen evolution overpotential, are
- poor electrocatalysts for the OER, and
- direct electrochemical oxidation is expected to occur for these electrodes.
- They present no higher oxidation state available and
- the organic species are directly oxidized by *nonadsorbed hydroxyl radicals*, giving *complete combustion* (so-called electrochemical combustion or incineration)
- For "nonactive" electrodes there is a weak interaction between electrode M and hydroxyl radicals (•OH). In this case, the oxidation of organics is mediated by hydroxyl radicals. This reaction occurs in competition with oxygen evolution by hydroxyl radical discharge. This case is typical for boron doped diamond electrodes.

- The comparison of the oxygen overpotential shows that lead dioxide, tin dioxide, and BDD have electrochemical windows larger than that of platinum.
- This means that under anodic polarization in the region of water oxidation, the production of strong oxidative species that are weakly adsorbed on the electrode surface are particularly active for oxidation. From this results a remarkable electrocatalytic activity toward organic compounds.
- In other words, the oxygen overpotential increases as the adsorption strength of hydroxyl radicals on the electrode surface decreases. So, electrode materials that favor the chemisorption emphasize the selective oxidation, like platinum, IrO₂, or RuO₂.
- Conversely, BDD exhibits a lower adsorption capacity, and hydroxyl radicals which are quasi free on the electrode surface react very quickly and strongly, and favor complete mineralization.



- The OER is the primary electrochemical reaction in water electrolysis. The standard electrode potential for this reaction at 25°C is 1.299 V vs the normal hydrogen electrode (NHE) in acid media and 0.401 V in alkaline media. The pertinent reactions are
- $2H_2O \rightarrow O_2 + 4H^+ + 4e$ (acid media)
- $40H^{-} \rightarrow O_2 + 2H_2O + 4e$ (alkaline media)
- According to the thermodynamics, all organic pollutants should be oxidized at potentials below the theoretical potential of OER ($E^0 = 1.23$ V).
- However, the complete mineralization of pollutants can only be achieved for simple organic molecules while using highly reactive catalysts such as Pt.
- In this regard, there is a need to use electrocatalytic anodes with the high overpotential toward OER.

Disinfection

- Disinfectants action usually implies cell lysis, that is, the dissolution of the cell membrane of the target organism, thus causing a change in cell permeability and inhibition of enzyme activity.
- The added chemicals affect membrane functions—they change osmotic pressure, permeability, and the transport processes of molecules and ions through the membrane while also inhibiting metabolic processes, bio-oxidation, and cell division.

How Can Electrochemistry Be Useful for Disinfection?

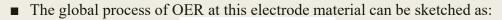
- EO in electrodisinfection is based on the anodic generation of strong oxidants such as oxygen, ozone, or hypochlorite during water electrolysis.
- Similar to conventional chemical disinfection, electrodisinfection can be used for the removal and deactivation of different microorganisms from water and often it is more efficient than chemical disinfection.
- The main advantages of electrochemical disinfection compared with conventional chemical disinfection is to
- I. keep the working areas required for the storage and dosage of chemicals substances;
- II. compact reactors allowing to operate in situ the main line of treatment facilities and
- III. no side generation of hazardous intermediates, which are typical for chemical disinfection.

- In electrochemical disinfection processes, the production of oxidants (disinfectants) may occur directly by
- i. water discharge (i.e., hydroxyl radicals, ozone),
- ii. dissolved species (i.e., active chlorine or hydrogen peroxide via oxygen reduction), or
- iii. anode dissolution (i.e., ferrate).

Types and concentrations of the formed oxidants strictly depend on the adopted operating conditions, mostly on the used electrode material.

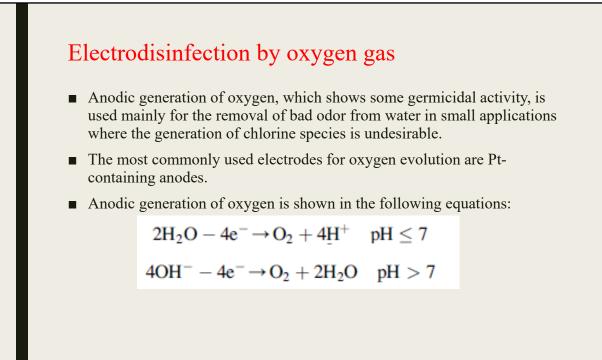
The main advantage provided by electrochemical disinfection is the possibility of producing the species involved in situ, thus avoiding all the hazards correlated to the manipulation of highly concentrated oxidants, very often without a requirement of additional chemicals.

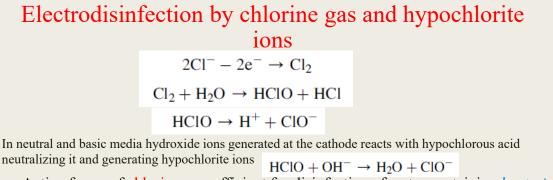
Electrodisinfection by reactive oxygenated species In particular, diamond electrodes exhibit high overpotential for water oxidation, allowing the electrogeneration of hydroxyl radicals directly from an aqueous solution. Because OH• radicals are scarcely adsorbed at the BDD surface, they are quickly desorbed and may react either with oxidizable compounds or with each other to give oxygen. Moreover, other bulk oxidizing agents such as hydrogen peroxide and ozone can be produced. Thus, reactive oxygenated species (ROS) may be generated during water oxidation, which can be exploited for a *chlorine-free disinfection process*.



$$\begin{split} H_2O &\rightarrow OH^{\bullet} + H^+ + e^- \\ OH^{\bullet} &\rightarrow O^{\bullet} + H^+ + e^- \\ 2O^{\bullet} &\rightarrow O_2 \\ 2OH^{\bullet} &\rightarrow H_2O_2 \\ H_2O_2 &\rightarrow O_2 + 2H^+ + 2e^- \\ O_2 + O^{\bullet} &\rightarrow O_3 \end{split}$$

• Due to their high reactivity, the radicals desorbed from the electrode surface remain confined near the anode in a thin layer of solution δr , (thickness of 10–40 nm), where they rapidly give rise to oxygen or other *reactive oxygen species* (ROS) such as ozone or hydrogen peroxide.





- Active forms of chlorines are efficient for disinfection of water containing *bacteria*, *viruses, fungi, and spores*. For example, Candida albicans fungi die within 30 seconds while exposed to 5% NaOCl solution.
- It is worth noting that not only is *hypochlorous acid* endowed with higher oxidizing power, but it also behaves as a *stronger disinfectant than hypochlorite*.
- In fact, with the cell wall of pathogenic microorganisms being naturally negatively charged, it can be entered more easily by the neutral hypochlorous acid than the negatively charged hypochlorite ion

- The superior disinfecting power of electrochlorination with respect to chemical chlorination can be explained by considering that, during the electrolysis, a number of different oxidants (i.e., hydroxyl radical, hydrogen peroxide, ozone) can be easily electrogenerated by water discharge at the anode.
- Anodes used for the process of electrodisinfection by hypochlorite ions should have low overpotential toward chlorine gas evolution such as Pt. However, pure Pt anodes are not used in industrial applications because of their high costs.
- Traditional electrodes for Cl₂ gas evolution are PbO₂ and MMO (mixed metal oxide) electrodes.

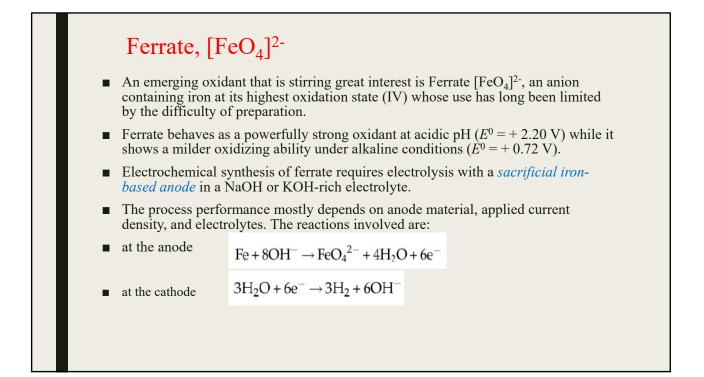
 Different concomitant effects, such as irreversible permeabilization of the cytoplasmic membrane caused by the electrical field, led to cell lysis by reaction of the biopolymers with electrogenerated oxidants, a release of highly reactive atomic oxygen thus contributing to effectively inactivating a broad range of microorganisms

 $HClO \rightarrow O + Cl^{-} + H^{+}$ $ClO^{-} \rightarrow O + Cl^{-}$

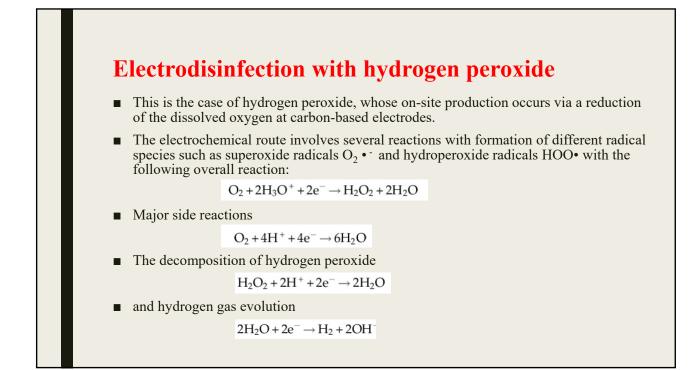
A paper also reports the removal of Staphylococcus aureus by active rutheniumbased electrodes in the absence of chloride Only a few species such as Giardia and Cryptosporidium are known to be chlorination resistant

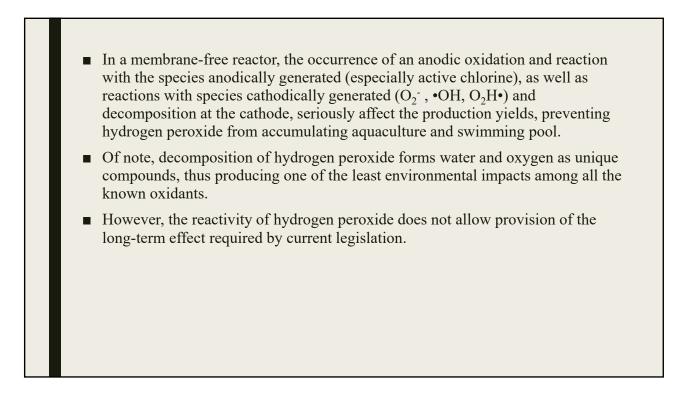
- An issue of serious concern related to electrochlorination is the occurrence of side reactions leading to the formation of hazardous by-products. Although trihalomethanes (THMs) and haloacetic acids (HAAs) are considered as the main DBPs, hundreds of different chemicals have been identified *in treated drinking water*; for many of them, mutagenic or carcinogenic behavior has been verified.
- The World Health Organization (WHO) recommends very low concentrations of ClO₃⁻ and ClO₄⁻ in drinking water. A correct choice of anode material and operative conditions are key parameters to obtain a powerful mixture of disinfectant, limiting the production of DPBs.
- Despite concerns raised by toxic by-product formation along with unpleasant odor and taste, active chlorine remains hardly replaceable due to its high reactivity and relatively low-cost production and mostly for its capacity to provide a long-term biocidal action.

Oxidation number	Examples	
	Chloride ion	Cl-
0	Elemental chlorine	Cl ₂
1	Hypochlorous acid/Hypochlorite	HClO/OCl-
	Chlorine oxide	Cl ₂ O
3	Chlorous acid/Chlorite	HClO ₂ /ClO ₂
4	Chlorine dioxide	ClO ₂
5	Chlorate	ClO_3^-
6	Chlorine trioxide	ClO ₃
7	Perchlorate	ClO_4^-
	Chlorine heptoxide	$Cl_2 \vec{O}_7$
8	Chlorine tetroxide	ClO ₄



- Anode materials generally consist of iron, carbon steel, or cast iron.
- Porosity and composition of electrodes greatly affect the ferrate electrogeneration.
- Outstanding performance of ferrate (VI) relies on its multifunctional action:
- i. it can inactivate a variety of microorganisms including some viruses while oxidizing a wide range of compounds (including emerging contaminants);
- ii. moreover, due to the release of ferric ions, it also provides coagulant action. For example, Jiang et al., indicate that 0.5 mg/L of ferrate (VI) is sufficient to oxidize many chemicals and to achieve complete disinfection, with the performance unaffected by the initial content of the microbial load.





Electrodisinfection by ozone

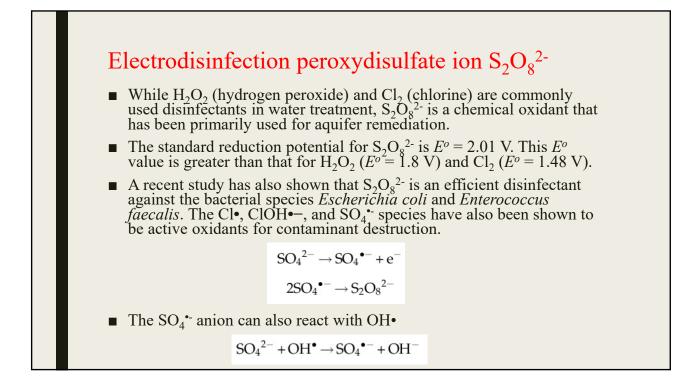
 Ozone can be allocated at the anode having high overvoltage toward OERs, for example, BDD electrodes. Electrode reaction of O₃ anodic generation is described as follows:

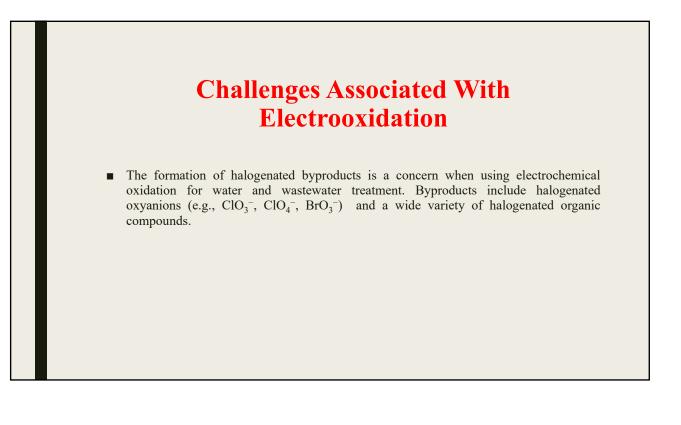
$$3H_2O - 4e^- \rightarrow O_3 + 6H^+$$

- Bactericidal effect of ozone is associated with its high oxidation potential (2.076 V) and the ease of diffusion through the cell walls of microorganisms. For example, polio virus dies within 2 min when ozone dosage is equal to 0.45 mg/L, while chlorine kills the virus only after 3 h with a dosage of 2 mg/L.
- Because both ozone and chlorine species are highly corrosive, corrosion resistant materials should be used for the construction of equipment and pipelines.

Electrodisinfection by silver

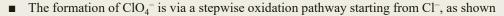
- Along with oxygen, ozone, and chlorine species, silver ions have highantibacterial properties toward Staphylococcus, Streptococcus, typhoid, dysentery, and coliform bacteria.
- There are few hypotheses explaining the mechanism of silverantibacterial properties. One of the mechanisms states that silver interacts with bacterial cell enzymes and violate cell exchange with the environment thus killing it. Another mechanism claims that silver ions penetrate the cell and bind with cell's protoplasts thus killing it. It is also suggested that silver adsorbs on the surface of cells and catalyzes reactions of cell plasma oxidation by oxygen.
- Anodic dissolution of silver anodes occurs by the following mechanism:
- $\blacksquare Ag^0 + e \rightarrow Ag^+$





Inorganic Byproduct Formation

- The formation of halogenated oxyanions, including ClO₃⁻, ClO₄⁻, and BrO₃⁻, has been detected in numerous studies. Of these oxyanions, ClO₄⁻ is especially problematic because it is a terminal oxidation product, its consumption has been linked to adverse health risks, and Cl⁻ is ubiquitous in natural and wastewater streams, making it especially challenging to control its formation.
- The EPA has issued a health advisory level for ClO₄⁻ of 15 µg/ L for drinking water sources, and Massachusetts and California have set even lower drinking water standards of 2 and 6 µg/L, respectively.



$$Cl^- \rightarrow OCl^- \rightarrow ClO_2^- \rightarrow ClO_3^- \rightarrow ClO_4^-$$

■ The rate-determining step for the formation of is the oxidation of ClO₃⁻ to ClO₄⁻. The conversion of ClO₃⁻ to ClO₄⁻ on BDD anodes has been shown to be a two step process. The first step is a direct electron transfer reaction of ClO₃⁻ at the electrode surface

$$ClO_3^- \rightarrow ClO_3^\bullet + e^-$$

• The second step is the homogeneous reaction between ClO_3^- and OH• to form $HClO_4$

$$ClO_3^{\bullet} + OH^{\bullet} \rightarrow HClO_4$$

It was shown that formation on BDD electrodes is approximately 50–100 times higher than on Pt and mixed-metal oxide electrodes. These results are likely due to the fact that OH• is not formed at high quantities on these active electrode materials.

- The formation of BrO₃⁻ during electrochemical oxidation is also of concern, as the EPA has set a maximum contaminant level (MCL) of 0.01 mg/L for drinking water. The Br⁻ content of natural waters is often at least an order of magnitude lower then Cl⁻, but BrO₃⁻ formation has been shown in numerous electrochemical studies.
- In some cases, BrO₃⁻ was further oxidized to BrO₄⁻. There have not been any mechanistic studies that focused on the electrochemical formation of BrO₃⁻ and BrO₄⁻. However, initial studies have suggested that the formation of BrO_x⁻ species follows a stepwise pathway, which is similar to ClO_x⁻ formation.

 $Br^- \! \rightarrow \! OBr^- \! \rightarrow \! BrO_2^- \! \rightarrow \! BrO_3^- \! \rightarrow \! BrO_4^-$

BrO₃⁻ accumulates in solution and slowly oxidizes to BrO₄⁻, which suggests the rate determining step for BrO₄⁻ formation is the oxidation of BrO₃⁻.

Halogenated Organic Compound Formation

- The formation of halogenated-organic compounds (HOCs) has been detected during the application of EAOPs to a variety of solution conditions.
- HOC formation is attributed to addition and substitution reactions between organic compounds and in situ formed halogenated oxidants. These oxidants include active chlorine (e.g., Cl₂, OCl⁻, HOCl/OCl⁻) and bromine (e.g., Br₂, OBr⁻, HOBr/OBr⁻) species, chlorine radicals (Cl[•], Cl₂^{••}), and bromine radicals (Br[•], Br₂^{••}).
- Studies indicated that
- (1) HOCs were continuously formed during electrolysis while halogens and organics were both present,
- (2) HOCs were completely oxidized to inorganic end products (i.e., CO_2 , ClO_3^- , ClO_4^- , BrO_3^- , BrO_4^-) after elimination of halogen ions or halogenated oxidants, and
- (3) the incorporation of halogens into organic compounds increased in the following order: Cl < I < Br.

Targeted Pollutant	Anode Type	Working Parameters	Rem oval Efficiency	Referen
Organic Compounds				
Reactive Blue 109 (1000 mg/L)	Pt	NaCl (0.1 M) $j = 20 \text{ mA/cm}^2$ pH 4 t = 1.25 h	96% COD	[6]
Dimethyl phthalate (0.03 mM)		$\begin{array}{l} Na_2 SO_4 \; (0.2 \; \text{M}) \\ j = 20 \; \text{mA/cm}^2 \\ \text{pH } 7 \\ t = 18 \; \text{h} \end{array}$	20% 10% COD	[27]
Diethyl phthalate (0.03 mM)		$ \begin{array}{l} Na_2 SO_4 \; (0.2 \; \text{M}) \\ j = 20 \; \text{mA/cm}^2 \\ pH \; 7 \\ t = 18 \; \text{h} \end{array} $	50% 30% COD	
Diheptyl phthalate (0.03 mM)			100% 100% COD	
Phenol (490 mg/L)		$Na_2SO_4 (0.25 M)$ t = 20 h $j = 20 mA/cm^2$ pH 5	100% 20% TOC	[28]

Methylene blue (40 mg/L)	Pt/MnO ₂	$Na_2SO_4 (0.05 M)$ $j = 7 mA/cm^2$ pH 8 t = 2 h	90% 70% COD	[29]
Landfill leachate (COD 1414 mg/L)	Graphite carbon electrode	$Na_2SO_4 (1 g/L)$ $j = 79 mA/cm^2$ t = 4 h	68% COD 84% color	[30]
Amoxicillin (19.6 mg/LTOC)	Ti∕Ti₄O ₇	$Na_2SO_4 (0.05 M)$ $j = 5 mA/cm^2$ t = 8 h	69% TOC	[31]
Phenol (100 mg/L)	Ti/SnO ₂ —Sb—Mo	$Na_2SO_4 (0.25 M)$ $j = 10 mA/cm^2$ t = 3.5 h	99.6% 82.7% TOC	[32]
Aniline (2.7 mM)	PbO ₂	pH 2 I = 2 A t = 1 h	>90%	[33]
Sanitary landfill leachate (COD 6.2 g/L)	Ti/Pt/PbO ₂	I = 0.3 A t = 6 h	40% COD	[34]
Sanitary landfill leachate (COD 6.2 g/L)	${\rm Ti/Pt/SnO_2-Sb_2O_4}$	I = 0.3 A t = 6 h	40% COD	[34]
4-chlorophenol (100 mg/L)	Ti/IrO ₂ —RuO ₂	$\begin{array}{l} Na_2 SO_4 \; (0.1 \; mM) \\ j = 39 \; mA/cm^2 \\ t = 2 \; h \end{array}$	100% >70% COD	[35]
Phenol (0.05 mM)	Ti/Ta ₂ O ₅ —IrO		99%	[36]
	Ti/SnO-RuO2-IrO2			
	Ti/RhO ₂ -IrO ₂			
Methylene blue (0.025 mM)	Ti/Ta ₂ O ₅ —SnO ₂	$Na_2SO_4 (0.1 M)$ $j = 9.1 m A/cm^2$ t = 3 h	38.6% TOC 95% color	[37]

Targeted Pollutant	Anode Type	Working Parameters	Removal Efficiency	Reference
Phenol (100 mg/L)	BDD	$ \begin{aligned} Na_2 SO_4 & (0.25 \text{ M}) \\ j &= 10 \text{ mA/cm}^2 \\ t &= 6 \text{ h} \end{aligned} $	100% 95.4% TOC	[42]
Sanitary landfill leachate (COD 6.2 g/L)		I = 0.3 A t = 6 h	40% COD	[34]
Dimethyl phthalate (0.03 mM)		$ \begin{array}{l} Na_2 SO_4 \; (0.2 \; \mbox{M}) \\ j = 20 \; \mbox{mA/cm}^2 \\ p H \; 7 \\ t = 0.5 \; \mbox{h} \end{array} $	100% 50% COD	[27]
Diethyl phthalate (0.03 mM)		$ \begin{array}{l} Na_2 SO_4 \; (0.2 \; \mbox{M}) \\ j = 20 \; \mbox{mA/cm}^2 \\ p H \; 7 \\ t = 0.5 \; \mbox{h} \end{array} $	100% 50% COD	[27]
Diheptyl phthalate (0.03 mM)		$ \begin{array}{l} Na_2 SO_4 \; (0.2 \; \mbox{M}) \\ j = 20 \; \mbox{mA/cm}^2 \\ p H \; 7 \\ t = 0.5 \; \mbox{h} \end{array} $	50% 10% COD	[27]
Amoxicillin (19.6 mg/L TOC)		$ \begin{aligned} Na_2SO_4 & (0.05 \text{ M}) \\ j &= 5 \text{ mA/cm}^2 \\ t &= 8 \text{ h} \end{aligned} $	36% TOC	[31]
Aniline (500 mg/L)	Ti/TiO _x H _y /Sb-SnO ₂	Na ₂ SO ₄ (5 wt.%) $j = 20 \text{ mA/cm}^2$ t = 5 h	85% 71% COD	[50]

Inorganic Compounds				
Na ₂ S (0.023 M)	Ti/RuO ₂	$j = 25 \text{ mA/cm}^2$ pH 13 t = 5 h	100%	[51]
Na ₂ S (60 mM)	BDD	j = 33 mA/cm ² t = 5h NaCl 1%	100%	[52]
Na ₂ S (30 mM)	$Ti/IrO_2 - Ta_2O_5$	$j = 13.5 \text{ mA/cm}^2$ t = 6 h NaOH (0.25 M)	83%	[53]
Thiocyanate, SCN ⁻ , (852.2 mg/L)	$\mathrm{Ti}/\mathrm{Ru}_{0.3}\mathrm{Ti}_{0.7}\mathrm{O}_2$	E = 8 V pH 9 t = 6 h NaCl 0.01M	90%	[54]
Cyanides (CN ⁻) including thiocyanate (SCN ⁻) (280 mg/L)	PbO ₂	j = 6.7 mA/cm ² pH 4 NaCl 1 g/L	99.6%	[55]
NaCN (250 mg/L)	Ti/SnO ₂ -Sb-Ce	$j = 30 \text{ mA/cm}^2$ pH 13 t = 4 h	98.2%	[56]

Toilet wastewater Escherichia coli Enterococcus	Bismuth-doped TiO_2	E = 4 V pH 6.7-8.3 t = 10 min	5-log ₁₀ reduction	[57]
Artemia salina	Si/BDD	$j = 255 \text{ mA/cm}^2$ NaCl 3 g/L t = 1 h	100%	[58]
Pseudomonas aeruginosa	BDD	j = 167 mA/cm ² t = 5 min NaCl 20 mg/L	6-log ₁₀ reduction	[59]
Escherichia coli	PbO ₂ /graphite	$j = 253 \text{ mA/cm}^2$	100% (8 min)	[60]
Enterococcus faecalis		NaCl 20 mg/L	100% (60 min)	
Artemia salina			100% (40 min)	
BBD, boron-doped diamond; COD, chemical oxygen deman	d; E, applied voltage at electrolysi	s (V); <i>I</i> , applied current (A); <i>j</i> , applied o	current density; t, elect	rolysis t