Joana Cristina Taveira Fernandes

Licenciada em Ciências de Engenharia do Ambiente

Water treatment with boron-doped diamond electrodes. A review on by-products formation

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Orientador: Dr. J.G. (Ivan) Buijnsters, Associate Professor, TU Delft

Co-orientador: Prof. Doutora Leonor Miranda Monteiro do Amaral,
Professora Associada, FCT NOVA

Júri:

Presidente: Prof. Doutora Rita Maurício Rodrigues Rosa

Arguente(s): Prof.dr. Jan Peter van der Hoek, TU Delft

Vogal(ais): Dr. Yasmina Doekhi-Bennani, postdoctoral researcher, TU Delft
Prof. Doutora Leonor Miranda Monteiro do Amaral

FACULDADE DE
CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

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Abstract

The formation and identification of by-products is crucial for understanding the possible environmental and public health risks of applying electrochemical advanced oxidation processes (EAOPs) in water treatment, involving boron-doped diamond (BDD) anodes. Despite the substantial research work concerning the use of BDD technology in water treatment review articles with a specific focus on by-products formation and their hazardous effects in the major environmental fields of application in water treatment are not available. This comprehensive review provides the current knowledge on the reactive species and by-products formed during electrochemical oxidation with BDD in municipal landfill leachate treatment, industrial wastewater treatment, disinfection of drinking water, municipal wastewater treatment, and removal of micropollutants. The reactive species electrogenerated in EAOPs with BDD, including the reactive oxygen species (ROS), reactive sulfate species (RSS), reactive chlorine species (RCS) and other oxidant species, are systematically discussed. In general, halogenated and perhalogenated compounds are the common by-products identified in the different fields of application. The concentration and type of by-products were influenced by process conditions and the BDD anode material itself. Recommended conditions to minimize the formation of halogenated and perhalogenated compounds are acidic pH, low current densities, high chloride concentrations, $NaNO_3$ as a supporting electrolyte and avoiding active cooling temperatures (e.g., 5ºC). The few available toxicological studies reported that BDD lowered the toxicity. However, in terms of toxic effects in mammalian's (i.e., rats and humans) health, there is a considerable number of by-products classified as possible carcinogenic, endocrine disruptive and mutagenic. This review paper provides better understanding of the by-products formed during electrochemical oxidation with BDD anodes and raises awareness of the improvements that still need to be made when applying this technology in water treatment plants.

Keywords

By-products; Reactive species; BDD anode; Electrochemical advanced oxidation processes; Water treatment

Resumo

A formação e identificação de sub-produtos resultantes da utilização de processos eletroquímicos avançados de oxidação de diamante dopado com boro (BDD), para o tratamento de água, é essencial para a compreensão dos respetivos riscos para a saúde pública e o ambiente. Contudo, apesar da considerável bibliografia relativa à utilização desta tecnologia em tratamento de água, um estado da arte sobre a formação de sub-produtos e respetivos efeitos nocivos nas principais áreas de tratamento de água, ainda não foi elaborado. Esta dissertação tem como objetivo apresentar o conhecimento atual sobre as espécies reativas e sub-produtos formados durante a oxidação eletroquímica com BDD no tratamento de lixiviados de aterro municipal, água residual industrial, água potável, água residual municipal e remoção de micropoluentes. Foram abordadas as principais espécies reativas, nomeadamente, de oxigénio (ROS), de sulfato (RSS), de cloro (RCS) e, outras espécies oxidantes. Relativamente aos sub-produtos identificados, a presença de compostos halogenados e per-halogenados é recorrente nas diferentes áreas de tratamento de água. A concentração dos mesmos foi influenciada por condições experimentais e pelo material do BDD. Consequentemente, para minimizar a formação destes compostos, é recomendável a utilização de um pH ácido, baixa densidade de corrente, concentrações elevadas de cloretos, $NaNO_3$ como eletrólito e evitar o uso de temperaturas baixas (e.g., 5ºC). A diminuição da toxicidade com esta tecnologia foi verificada em alguns dos estudos. No entanto, em termos de efeitos tóxicos em mamíferos (i.e., roedores e humanos), existe um número considerável de sub-produtos classificados como possíveis carcinogénicos, disruptor endócrinos e mutagénicos. Esta dissertação contribui para uma melhor compreensão dos sub-produtos formados durante a oxidação eletroquímica com BDD, e proporciona um aumento da consciencialização sobre os progressos a realizar na implementação desta tecnologia em estações de tratamento de água.

Palavras-Chave

Sub-produtos; Espécies reativas; anodo de BDD; Processos eletroquímicos avançados de oxidação; Tratamento de água

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List of abbreviations

AB-210	Acid black 210 dye
AO	Anodic oxidation
AOBr	Absorbable organic bromine
AOCl	Absorbable organic chlorine
AOI	Absorbable organic iodine
AOPs	Advanced oxidation processes
AOX	Absorbable organic halogen
BCAA	Bromochloroacetic acid
BDCM	Bromodichloromethane
BDD	Boron-doped diamond
BOD	Biological oxygen demand
CMR	Carcinogenic, mutagenic and reprotoxic subtstances
COD	Chemical oxygen demand
CVD	Chemical vapor deposition
DBAA	Dibromoacetic acid
DBCM	Dibromochloromethane
DCAA	Dichloroacetic acid
DNA	Deoxyribonucleic acid
DW	Drinking water
EAOPs	Electrochemical advanced oxidation processes
EF	Electro-Fenton
EP	Ethyl paraben
EPA	Environmental Protection Agency
FAC	Free available chlorine
GC-MS	Gas chromatography – Mass spectrometry
HAAs	Haloacetic acids
HPHT	High pressure high temperature
HPLC	High pressure liquid chromatography
M	Electrode surface
MBAA	Monobromoacetic acid
MCAA	Monochloroacetic acid
MC	Microcrystalline
MPs	Micropollutants
NB	Novacron blue
NDMA	N-nitrosodimethylamine
PCBs	Polychlorinated biphenyl
PEF	Photoelectro-fenton
PS	Persulfate
R	Organic substances

R_{ads}	Adsorbed pollutant
RB5	Reactive black 5 dye
RCS	Reactive chlorine species
RO	Pollutant oxidation product
RO16	Reactive orange 16 dye
ROC	Reverse osmosis concentrate
ROS	Reactive oxygen species
RSS	Reactive sulfate species
RRB	Remazol red BR
SEM	Scanning electron microscopy
SMX	Sulfamethoxazole
SPEF	Solar photoelectro-fenton
TBM	Tribromethane
TCAA	Trichloroacetic acid
TCM	Trichloromethane
THMs	Trihalomethanes
TMP	Trimethoprim
TN	Total nitrogen
TOC	Total organic carbon
UNC	Ultra-nanocrystalline
UV	Ultraviolet
WHO	World Health Organization
WW	Wastewater
ze^-	Electrons exchanged

1. Scope of thesis

Electrochemical advanced oxidation processes (EAOPs) are gaining increasing interest for water treatment, particularly for micropollutants removal, when compared to conventional methods.[1]. This can be explained due to the limited efficiency of conventional methods (i.e. coagulation/sedimentation, filtration, and disinfection) to remove toxic and recalcitrant organic micropollutants and the capability of EAOPs to break down high molecular weight compounds to low molecular weight compounds with the *in situ* generation of strong and non-selective radicals like hydroxyl radical •OH.[2] EAOPs are able to mineralize organic material to relatively harmless substances such as CO_2, N_2 and other non-toxic compounds.[3]

Processes such as anodic oxidation (AO), anodic oxidation with electrogenerated H_2O_2 (AO-H_2O_2), electro-fenton (EF), photoelectro-fenton (PEF) and solar photoelectro-fenton (SPEF) are the main EAOPs discussed in the literature.[4] AO, also known as electro-oxidation, consists in the chemical conversion of energy into an electrochemical cell that contains one or more pairs of electrodes.[5] Figure 1.1 shows a schematic diagram of an electrochemical reactor comprising one pair of electrodes, called the anode and the cathode, respectively. Reduction processes (i.e., gain of electrons) occur at the cathode whereas oxidation processes (i.e., loss of electrons) take place at the anode.[5] The electrodes are connected to an electrical power supply, and electrons migrate from the power supply to the electrochemical system via the cathode.

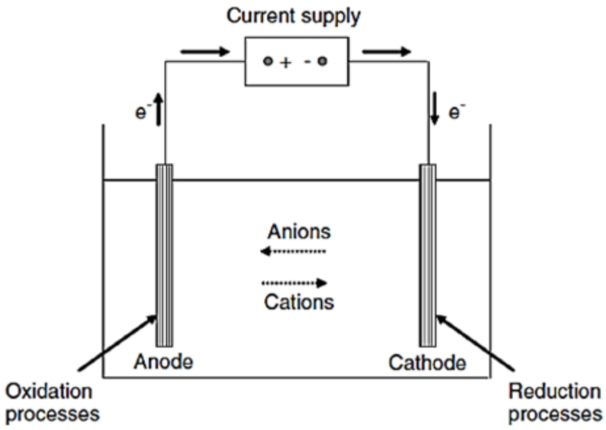


Figure 1.1 – Schematic diagram of an electrochemical reactor.
(Adapted from: Bashir et al., 2014)[6]

Electro-oxidation via BDD electrodes has become very popular due to the chemical and physical properties of the electrode material such as the wide potential window, low background current, chemical and mechanical stability, good resistance to fouling, lack of a surface oxide film, and controllable surface termination.[7]

It is important to mention that even though diamond itself is an extremely hard crystalline form of carbon and it is considered an excellent material for many applications, it needs to be doped with boron in order to improve its electrical conductivity.[8] The most common methods for the synthesis of doped diamond materials are high pressure high temperature (HPHT) growth and chemical vapor deposition (CVD).[9] The majority of electrochemical applications using BDD electrodes make use of the CVD method in the electrode production process.[9] Typical CVD diamond thin-film synthesis involves the activation of a carbon-rich gas mixture, gas phase reactions, the diffusion of diamond-forming gas species onto the substrate surface and the subsequent surface reactions that lead to the formation of a polycrystalline diamond thin film.[10] The boron doping required to produce BDD electrodes is obtained by adding B_2H_6, or $B(OCH_3)$, to the precursor gas mixture, or placing boron powder near the edges of the substrate prior to insertion into the CVD chamber.[8] BDD films are deposited on the surface of support materials to offer the desirable properties of low resistivity, high mechanical strength and inert electrochemical activity.[9] Substrates such as silicon, tungsten, and niobium are the most common support materials.[7] Three categories of BDD are typically distinguished based on the average diamond grain size: (i) ultra-nanocrystalline (UNC; <10 nm), (ii) nanocrystalline (NC; 10 nm – 1 µm) and (iii) microcrystalline (MC; >1 µm).[11] Figure 1.2 shows representative scanning electron microscopy (SEM) images of these three types of BDD film materials.

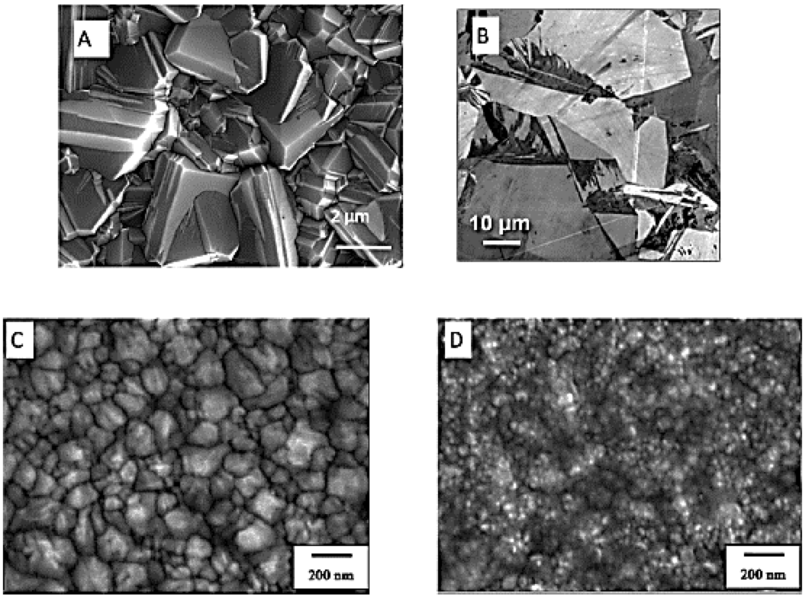


Figure 1.2 - Top-view SEM images of (a) MC BDD; (b) polished “lapped” surface of MC BDD; (c) NC BDD and (d) UNC BDD thin films. (Adapted from: Macpherson, 2015)[11]

The diamond film thickness of commercial BDD electrodes used in EAOPs vary typically between 5 and 15 µm. BDD electrodes are relatively easy to obtain in the current market and they can be found with standard and custom shapes and sizes ranging from single cm^2 up to square m^2. Examples of the customizing possibilities regarding BDD electrodes are presented in Figure 1.3.

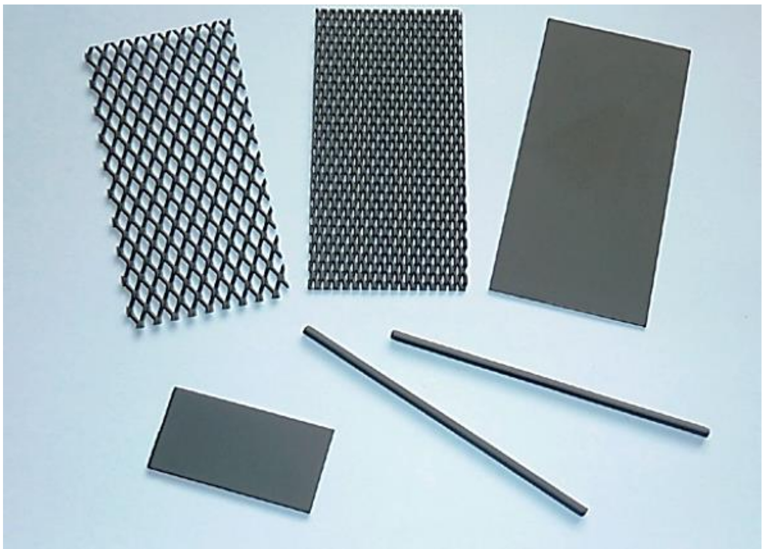


Figure 1.3 - Optical image showing mesh-, plate- and rod-shaped BDD/Nb electrodes from NeoCoat (CH) company. (Taken from https://www.neocoat.ch/en/products/electrodes/bdd-me and accessed on 22.12.2020)

Advanced Diamond Technology (USA), Condias (DE), Element Six (UK), NeoCoat (CH), CSEM (CH) and METAKEM (DE) are important players on the market.[11,12]

2. Introduction

Electrochemical oxidation, particularly the one involving BDD anodes, is becoming more appealing for the treatment of different types of water owing to the efficiency of the electrode material to remove broad range of contaminants.[13,14]

Nevertheless, the **formation of by-products such as perchlorates, chlorates and bromates via use of electrochemical oxidation technology** is raising awareness in the environmental community since these components are often referred to as endocrine disruptive and reprotoxic (CMR) substances.[15,16] Conventional methods that use chemicals like chlorine usually form chlorinated and brominated organic disinfection by-products, e.g. trihalomethanes and haloacetic acids. Furthermore, ozone-based treatments produce well known by-products, namely bromate, nitrosamines (such as N-nitrosodimethylamine or NDMA), aldehydes, ketones, and carboxylic acids. Because of their relevance in drinking water, by-products have been regulated in many countries as primary drinking water contaminants.[15] Risk assessment of these compounds has prompted the U.S. Environmental Protection Agency (EPA) to establish the guideline value of 15 µg/L for perchlorate and the World Health Organization (WHO) to define the values of 70 µg/L for perchlorate, 700 µg/L for chlorate and 10 µg/L for bromate in order to issue a health advisory target for drinking water sources.[17-20]

The formation and control of these compounds during water and wastewater treatment using BDD anodes has been an active research topic in the water and wastewater industry. Therefore, it is crucial to analyze in more depth their formation and possible adverse effects to eradicate them and avoid critical consequences.

Many conventional water treatment plants use a combination of flocculation, coagulation, sedimentation, filtration and disinfection to provide clean water.[21] Next to this most widely applied water treatment technology, conventional treatment processes such as air stripping, adsorption and biological treatment are effective in treating water but have certain disadvantages. A few examples are the shifting and/or concentration of the pollutants, transfer of the contaminants to another medium, causing secondary pollution or being conditioned by narrow range of operating conditions.[22]

Advances in water treatment have led to the development of technologies called advanced oxidation processes (AOPs). These water treatment processes are based on the *in situ* generation of a powerful oxidizing agent, such as •OH .[23] Besides this, AOPs are known for having fast reaction rates and non-selective oxidation, which concedes the simultaneous treatment of multiple contaminants.[24] In this context, EAOPs are considered environmentally friendly, since these treatment techniques are based on the transfer of electrons avoiding any use of chemical reagents.[23] EAOPs can as well generate •OH allowing the degradation and mineralization of a certain range of organic pollutants and effluents such as landfill leachate, pesticides, dyes, perhalogenated organics and pharmaceuticals.[25]

Moreover, EAOPs involving BDD anodes have achieved considerable recognition **owing to the outstanding advantages of the electrode material** such as: high pollutant removal efficiency in wastewater treatment, high efficiencies in the production of oxidants and outstanding features for electroanalysis.[26]

Figure 2.1 presents the increasing number of articles published in the field of "Electrochemical oxidation and BDD", from 1999 to 2021, revealing a steadily growing interest in this technology.

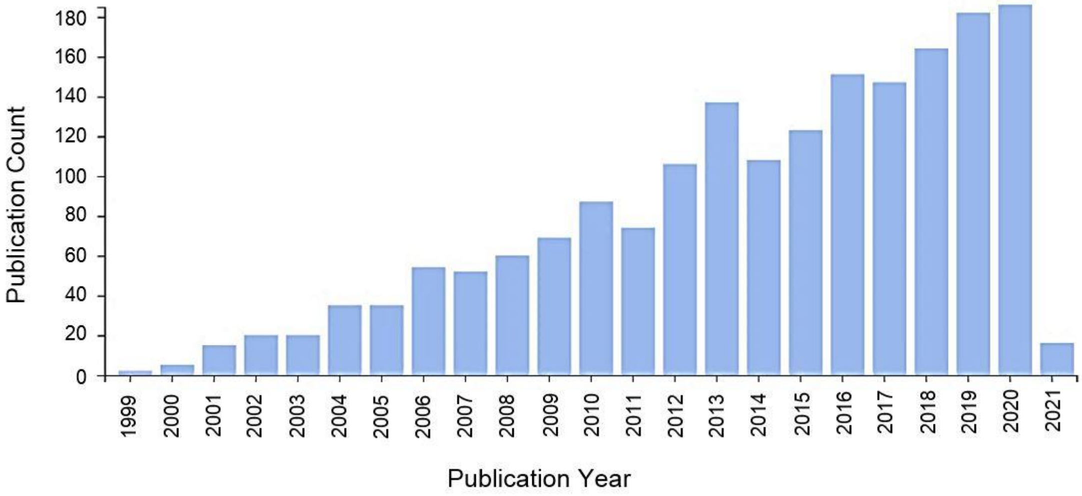


Figure 2.1 – Scientific publications on the topic of BDD and electrochemical oxidation from the period of 1999 to 2021. (Data are based on the results obtained from Web of Science (Clarivate Analytics) using the topic search terms "electrochemical oxidation" AND "BDD"; data accessed on 15.02.2021.)

The selection of the electrode material in EAOPs can compromise the efficiency of the electrochemical oxidation process and affect as well the potential generation of toxic by-products.[16] Even though other anodes such as graphite, Pt, RuO_2, IrO_2, SnO_2, PbO_2 and Ti_4O_7 can be used for the oxidation of contaminants, it has been found that their performance is relatively less when compared to BDD anodes due to less active radical production, higher competitive side reactions, and lower stability and durability.[9]

Table 2.1 presents the different anodic materials and their **oxygen evolution reaction (OER) potentials**. Based on these data, BDD has the highest value of the OER potential. The anodes with high OER potential values promote the complete oxidation of organics to CO_2 and are thus considered to be ideal electrodes for wastewater treatment.

Table 2.1 - Most common anodic materials used and their oxygen evolution potential.[27,28]

Electrode Material	Potential for O_2 evolution (V/SHE)
RuO_2	1,4 – 1,7
IrO_2	1,5 – 1,8
Pt	1,6 – 1,9
Graphite	1,7
Ebonex® (Ti_4O_7)	1,7 – 1,8
SnO_2	1,9 – 2,2
PbO_2	1,8 – 2,0
BDD	2,2 – 2,6

According to the literature, there are **three main categories of reactive species that can be electrogenerated at the surface of BDD to oxidize pollutants: reactive oxygen species,**

reactive chlorine species and reactive sulfate species.[13,29-31] The formation and categorization of these reactive species and the generation of oxidants by them will be described in Chapter two.

The BDD-based EAOPs represent an alternative to other water treatment procedures and entail the oxidation of pollutants by chemical reaction with •OH electrogenerated from water discharge at the anode. In the last decade, substantial research articles[15,32-34], reviews[9,12,16,29,35] and books[36,37] have been published that discuss this technology in terms of principles, removal of organic pollutants, removal of micropollutants and application areas.

However, no review articles are available with a specific focus on **by-products formation and their hazardous effects from electrochemical oxidation using BDD electrodes** in the major environmental fields of application of water treatment. Considering that the applicability of electrochemical oxidation via BDD is increasing in many fields, it is important to verify the prejudicial effects of by-products, to perceive them better and address their risk.

This comprehensive review provides the current knowledge on the reactive species formed during electrochemical oxidation with BDD and consequently the by-products formed when using this technology in different fields of application. The toxicity of the by-products is mentioned, with emphasis on the potential hazardous effects for mammalian's health.

Among others, there is an extensive discussion on:

- The reactive species that are electrogenerated during water treatment using BDD, including the formation, mechanisms and the oxidants that are produced (Chapter 3).
- The generation of the by-products and the presence of reactive species during the treatment of landfill leachate, industrial wastewater, disinfection of drinking water and municipal wastewater treatment, and removal of micropollutants (Chapter 4).
- Influencing factors that can be suggested to diminish the negative effects of the by-products (Chapter 5).

Finally, several major conclusions (Chapter 6) as well as future directions of research on the by-products developed at BDD during electrochemical oxidation (Chapter 7) are provided.

3. State of knowledge

Electrochemical water treatment relies on the production of oxidants to mineralize the pollutants encountered in the water. The production of these oxidants also known as reactive species may occur via two mechanisms: direct oxidation or indirect oxidation.[13,38,39]

In **direct electrolysis**, the pollutants are adsorbed on the anode surface and exchange electrons directly with it, without the involvement of other substances besides the electron, as presented in reaction 1:

$$R_{ads} - ze^{-} \rightarrow P_{ads} \qquad (1)$$

where R_{ads} is the adsorbed pollutant on the anode surface and P_{ads} is the oxidized adsorbed pollutant.[39]

In **indirect electrolysis**, on the other hand, the organic pollutants do not exchange electrons directly with the anode surface but rather over the mediation of some reactive species generated at the surface. These species act as intermediaries for electrons shuttling between the electrode and the organic pollutants. To eliminate the organic compounds present in the bulk solution, oxidants like chlorine, hypochlorous acid and hypochlorite or H_2O_2/ozone (O_3) are formed.[13,39,40]

Figure 3.1 presents the mechanisms of electrochemical (direct and indirect) oxidation for removal of organic pollutants.

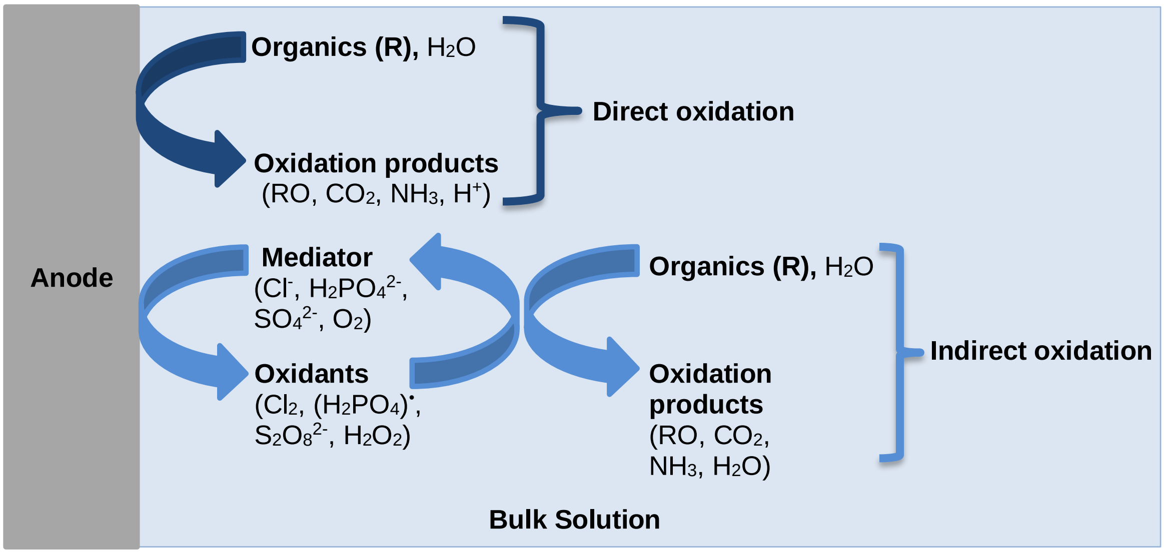


Figure 3.1 - Scheme of electrochemical mechanisms to remove pollutants.
(Adapted from: Sillanpää et al., 2017) [37]

Electrochemical oxidation of organic pollutants can lead to two different pathways: electrochemical conversion or electrochemical incineration (combustion). In electrochemical conversion, the organic substances (*R*) are partially oxidized as presented in reaction 2: [40]

$$R \rightarrow RO + e^{-} \qquad (2)$$

In this case, a following treatment is required to completely mineralize the oxidized substances (*RO*). On the other hand, the principle of electrochemical incineration is that the organic substances (*R*) are fully transformed into carbon dioxide, water and other inorganic constituents as presented in reaction 3: [40]

$$R \rightarrow CO_2 + H_2O + \mathrm{Salts} + e^- \qquad (3)$$

Following, this chapter covers a detailed description of formation of different reactive species and provides a current state of knowledge of the electrogenerated reactive species on the surface of BDD electrodes. In addition, each subchapter gives an overview of the mechanisms of formation of the oxidants originated from the reactive species as well as the by-products known so far originated by them, and their applicability in water treatment.

3.1. Formation of reactive oxygen species (ROS)

Reactive oxygen species are reported as reactive chemical species containing oxygen that present a chemical reactivity due to the oxygen molecule's unpaired electron. ROS are comprehended by species as **•OH, H_2O_2 or O_3** that are formed at the electrode either by water discharge or oxygen reduction.[36] The role of ROS has been underlined by their high disinfecting activity and the ability to oxidize and mineralize organic pollutants such as pharmaceuticals, herbicides and pesticides.[36,41-46]

•OH radicals are the strongest oxidants found in an aqueous solution, with a redox potential of 2.7 V, and can be produced electrochemically by electrolytic discharge of water on the electrode surface (M) as presented in reaction 4. Furthermore, formed •OH act as intermediates for oxygen evolution (reaction 5):[36,47,48]

$$H_2O + M \rightarrow M\,(\bullet OH) + H^+ + e^- \qquad (4)$$

$$M\,(\bullet OH) \rightarrow M + \frac{1}{2}O_2 + H^+ + e^- \qquad (5)$$

H_2O_2 has a redox potential of 1.76 V and its formation can occur either by electrochemical reduction of oxygen on the cathode or by the decomposition of other oxidants such as the ones present in the bulk solution. Therefore, an oxygen gas supply is required to promote the formation of H_2O_2, as presented in reaction 6: [36,49]

$$O_2 + 2H^+ + 2e^- \rightarrow H_2\,O_2 \qquad (6)$$

In the particular case of electrochemical oxidation via BDD anodes, the formation mechanism can be described with the interaction between •OH leading then to the production of H_2O_2, as presented in reactions 7 to 11: [35,50,51]

$$\mathrm{BDD + H_2O \rightarrow BDD(\bullet OH) + H^+ + e^-} \quad (7)$$

$$\mathrm{\bullet OH \leftrightarrow O\bullet + H^+ + e^-} \quad (8)$$

$$\mathrm{2O\bullet \leftrightarrow O_2} \quad (9)$$

$$\mathrm{2\bullet OH \leftrightarrow H_2\,O_2} \quad (10)$$

$$\mathrm{2H_2O \leftrightarrow H_2\,O_2 + 2H^+ + 2e^-} \quad (11)$$

O_3 has a redox potential of 2.08 V and can be generated in solution at an anode, when referring to electrochemical production of O_3. In the production of O_3, formation of adsorbed •OH and adsorbed oxygen are required, as presented in reactions 12-15: [49,52]

$$\mathrm{H_2O \rightarrow \bullet OH_{ads} + H^+ + e^-} \quad (12)$$

$$\mathrm{2\bullet OH \rightarrow O_{2,ads} + 2H^+ + 2e^-} \quad (13)$$

$$\mathrm{\bullet OH_{ads} + O_{2,ads} \rightarrow \bullet HO_{3,ads}} \quad (14)$$

$$\mathrm{\bullet HO_{3,ads} \rightarrow H^+ + O_3 + e^-} \quad (15)$$

Similar to H_2O_2, the formation of O_3 at the BDD anode takes place at the surface of the anode and involves the production of •OH and atomic oxygen, as presented in reactions 16-17. Reaction 18 is the overall reaction for O_3 generation from BDD-based oxidation: [35]

$$\mathrm{\bullet OH \leftrightarrow O\bullet + H^+ + e^-} \quad (16)$$

$$\mathrm{\bullet O + O_2 \rightarrow O_3} \quad (17)$$

$$\mathrm{3H_2O \rightarrow O_3 + 6H^+ + 6e^-} \quad (18)$$

3.2. Formation of reactive sulfate species (RSS)

The presence of sulfate in high concentration in groundwater and surface water is very common since sulfate is highly soluble in water.[53] Therefore, **reactive sulfate species** can be produced from salts that either are present in the effluents or natural waters (groundwater and surface water) or can be added to the solution as an electrolyte (Na_2SO_4 is the most common used) to improve the conductivity of the process.[36,54] The main electrogenerated species concerning RSS are **peroxodisulfate ($S_2O_8^{2-}$)** and **sulfate radicals ($SO_4^{\bullet-}$),** with a redox potential of 2.1 V and 2.5~3.1 V, respectively.[29,36,48] The applicability of RSS can be associated with water and wastewater treatment due to their capability of degrading highly toxic and persistent pollutants (e.g. polychlorinated biphenyls (PCBs), trichloroethene, tertbutylmethylether, chlorinated ethenes, and perfluorinated compounds) and the removal of dyes and cyanide.[36,55-57]

$S_2O_8^{2-}$ can be electrochemically produced from the oxidation of sulfate species, as represented in reactions 19 and 20, and depends on the electrode material chosen for the oxidation of sulfuric acid.[36]

$$2HSO_4^- \rightarrow S_2O_8^{2-} + 2H^+ + 2e^- \quad (19)$$

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \quad (20)$$

The generation of this specie on the BDD surface can be either via direct oxidation, as presented in reactions 19 and 20, or via indirect oxidation, as presented in reactions 21 and 22. The difference between the two possibilities for indirect oxidation lies in the anodic synthesis of •OH in the first process and the presence of sulfate in the water matrix with considerable concentrations in the second case.[35,58]

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

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \quad (22)$$

$SO_4\bullet^-$ can only occur in the presence of HSO_4^- and molecular H_2SO_4 and the reaction with •OH, as represented by reactions 21 and 23, respectively.[36]

$$H_2SO_4 + \bullet OH \rightarrow SO_4^{\bullet-} + H_3O^+ \quad (23)$$

These reactions represent as well the mechanisms of formation of $SO_4\bullet^-$at BDD anodes.[55]

3.3. Formation of reactive chlorine species (RCS)

The development of chlorine in the aquatic environment due to significant concentration of sodium chloride (NaCl) originated from saline wastewater is very common. Industries such as food processing plants, textile, leather, petroleum refineries and chemical (i.e. chlor-alkali industry), produce large quantities of salt-containing wastewater rich in NaCl, among other compounds.[59] The formation of **reactive chlorine species (RCS)** demands presence of Cl^- in order to generate active chlorine, which is produced from the oxidation of chloride ions.[36] NaCl is an example of a frequently used electrolyte with the purpose of active chlorine generation.[60]

Chlorine free radicals ($Cl_2^{\bullet-}$) present an elevated redox potential of 2.0 V.[48] **RCS** are associated with electrochemical chlorination and can be used in fields of water disinfection, treatment of wastewater containing refractory organics and chloride ions, landfill leachates, pharmaceuticals, pesticides and dyes.[36]

The generation of active chlorine can be in the form of **Cl_2**, **ClO^-** or **HClO**, as presented in reactions 24-26, which show the main reactive chlorine species developed.[29,36]

$$2Cl^- \rightarrow Cl_2(aq) + 2e^- \quad (24)$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \quad (25)$$

$$HClO \leftrightarrow H^+ + ClO^- \quad (26)$$

The formation of hypochlorous acid (HClO) and the hypochlorite anion (ClO^-) is described in reactions 24 and 25 but it is important to mention that their development is determined by the pH. For instance, in a pH range of 3-8 the predominant species are HClO, whereas ClO^- is prevailing if pH>8.[29,36]

In the particular case of anodic oxidation by using BDD and in solutions containing considerable concentrations of chloride, chloride-based oxidants can be produced.[35] Among them, dissolved chlorine (Cl_2) is distinguished, that is generated from the competition between the oxidation of chloride at the anode surface and the •OH produced, as presented in reactions 4 and 24. [61]

Additionally, short-lived radical species such as $ClO^\bullet$, $Cl_2^{\bullet-}$ and Cl^- can be formed contributing as an advantage for disinfection processes.[61]

It is relevant to highlight that the direct oxidation of chlorine or hypochlorite species, with high oxidation states in the last case, is considered one of the main drawbacks of electrolysis of water regarding diamond anodes. The reason for this is the formation of hazardous species such as **chlorite** (ClO_2^-), **chlorate** (ClO_3^-) and **perchlorates** (ClO_4^-).[15,26,36,62] The formation of these chlorine species can occur through mediated processes by •OH as presented in reactions 27-30.[26]

$$Cl^- + \bullet OH \rightarrow ClO^- + H^+ + e^- \quad (27)$$

$$ClO^- + \bullet OH \rightarrow ClO_2^- + H^+ + e^- \quad (28)$$

$$ClO_2^- + \bullet OH \rightarrow ClO_3^- + H^+ + e^- \quad (29)$$

$$ClO_3^- + \bullet OH \rightarrow ClO_4^- + H^+ + e^- \quad (30)$$

Figure 3.2 illustrates schematically the main reactive species formed at BDD anodes.

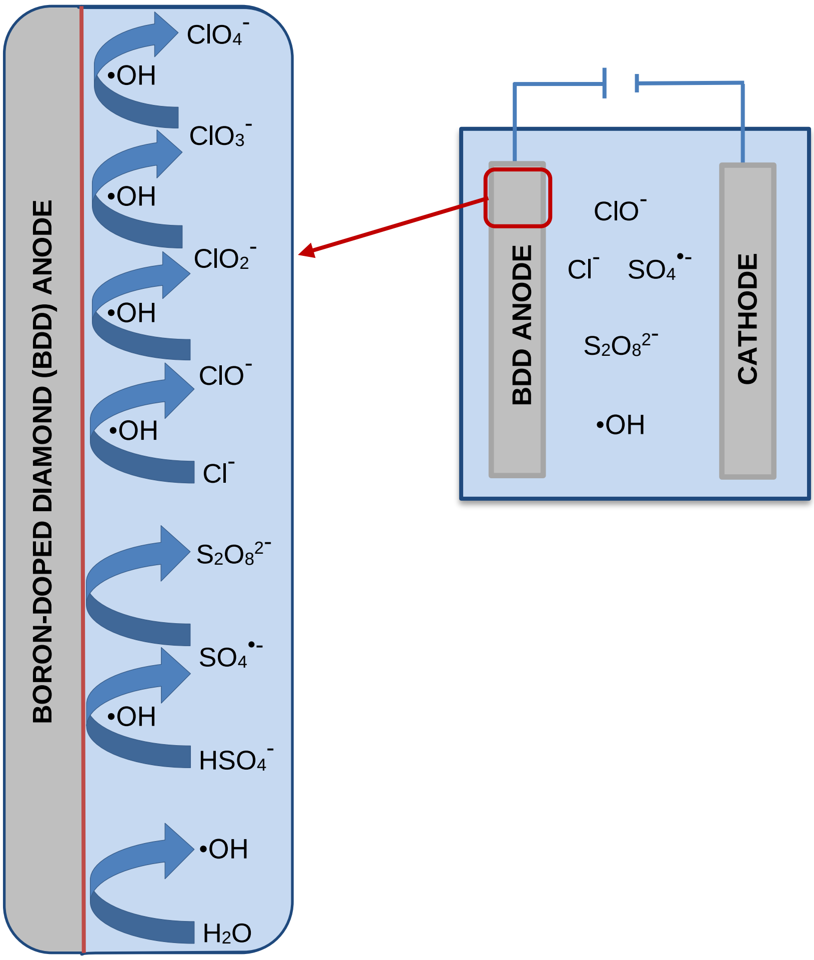


Figure 3.2 - Summary of the main reactive species formed with BDD anodes. (Adapted from: Farhat et al., 2017) [63]

3.4. Formation of other oxidant species

The reactive species mentioned so far can be considered as the most common oxidants in the degradation of pollutants. Nevertheless, species like carbonates and phosphates (commonly found in natural mineral waters and discharged effluents of municipal and industrial plants, respectively), already present in the solution, can act as mediators for the subsequent oxidation of organic pollutants with a redox potential of 1.59 V in the case of carbonate and <2.5 V for phosphates.[36,48,64] These species are electro-generated from the oxidation of common electrolytes such as phosphate (PO_4^{3-}) and hydrogencarbonate (HCO_3^-) yielding peroxodiphosphate ($P_2O_8^{4-}$) and peroxodicarbonate ($C_2O_6^{2-}$), respectively.[64]

Even though $C_2O_6^{2-}$ is considered a weaker oxidant, the main advantages of this oxidant are its biodegradability, non-toxicity and environmental safety. Peroxodicarbonate can be achieved either by the oxidation of carbonate, by the introduction of HCO_3^- as an electrolyte or by the removal of CO_2 from the atmosphere and dissolving it in sodium hydroxide (NaOH), according to reactions 31-34. [36,64]

$$2CO_3{}^{2-} \rightarrow C_2O_6{}^{2-} + 2e^- \qquad (31)$$

$$2HCO_3{}^{-} \rightarrow C_2O_6{}^{2-} + 2H^+ + 2e^- \qquad (32)$$

$$CO_2 + OH^- \rightarrow HCO_3{}^- \qquad (33)$$

$$2HCO_3{}^{-} + 2{\bullet}OH \rightarrow C_2O_6{}^{2-} + 2H_2O \qquad (34)$$

It can be assumed that the reactions for the electro-generation of these oxidants with BDD are the same. For example, the formation of sodium peroxycarbonate $(Na_2C_2O_6{}^{2-})$ was specifically verified during anodic oxidation with BDD electrodes in the presence of sodium carbonate (Na_2CO_3) in the water solution.[65]

Peroxophosphates, in general, can be applied in wastewater treatment.[36] Taking into account the specie of peroxodiphosphate, $P_2O_8{}^{4-}$, can be used as a substitute of persulfate due to its similar properties. Advantage of using phosphate instead of persulfate reflects in easier removal of phosphates from aqueous wastes than sulfates.[36]

$P_2O_8{}^{4-}$ is generated with a first electrochemical reaction that leads to the development of peroxophosphate radicals and afterwards the combination of these radicals produces this anion, as presented in reactions 35 and 36. [62]

$$PO_4{}^{3-} \rightarrow (PO_4^{2-})^{\bullet} + e^- \qquad (35)$$

$$(PO_4^{2-})^{\bullet} + (PO_4^{2-})^{\bullet} \rightarrow P_2O_8{}^{4-} \qquad (36)$$

Additionally, in the presence of phosphate solutions, generated phosphate radicals can react with •OH produced form water oxidation, which leads to the formation of monoperoxophosphoric acid (H_3PO_5), according to reactions 37 and 38. [36,62]

$$H_2PO_4^- \rightarrow (H_2PO_4)^{\bullet} + e^- \qquad (37)$$

$$(H_2PO_4)^{\bullet} + {\bullet}OH \rightarrow H_3PO_5 \qquad (38)$$

In BDD technology, the formation of these species in the bulk solution and the reactions are the same as the ones already mentioned.[35]

4. Main by-products of electrochemical oxidation with BDD technology

In this chapter, the intermediates and by-products in different water matrices are classified, according to the literature, as well as their interaction with the reactive species mentioned in Chapter 3. Concerning the BDD technology and its application in the major fields of water treatment, a selection of scientific literature was made with particular focus on the use of BDD in the treatment of landfill leachate, industrial wastewater, drinking water and municipal wastewater, and the removal of micropollutants, respectively. In the conclusion of each subchapter, a brief toxicity evaluation of identified by-products is provided through a classification of their toxic effects in mammalians. In order to assess the intermediates and by-products from the selected relevant studies, only the papers that provide specific information on these compounds are part of the discussion. Other articles that do not present this information are referenced [66-87], and are not included in the text.

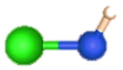
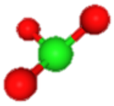
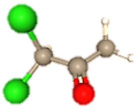
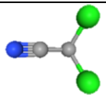
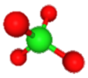
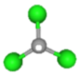
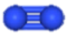
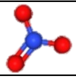
4.1. Municipal landfill leachate treatment

Municipal landfill leachate is a complex wastewater that contains organic compounds, heavy metals, ammonium, chloride, bio-refractory and toxic compounds in high concentrations which can lead to adverse environmental impacts.[69,88] To prevent impacts on the environment and human health, leachate must be collected and treated. Application of AOPs were found effective to reduce the organic content of leachate or could be combined with other processes to produce a treated effluent in accordance with restricted discharge limits. Considering the main contaminants discussed in the treatment of municipal landfill leachate with BDD technology, *Pérez et al.* [88] reported the removal of ammonium using model solutions, which were prepared by dissolving $NH_4H_2PO_4$ in ultrapure water and applying different NaCl concentrations (0-20 g/L), and landfill leachate from a municipal landfill site of Meruelo (Cantabria, Spain). The removal of ammonium was achieved using indirect oxidation where the **reactive chlorine species** took part in the process. In addition, the oxidation by-products obtained during the ammonium removal were detected, in presence of low chloride concentrations (0-2 g/L) and high chloride concentrations (5-20 g/L). When low chloride concentrations were applied, the main ammonium product was found to be **nitrogen gas** whereas 18%-26% was recovered as **nitrate** at the end of the experiments. However, **high levels of chloramines** were also detected as a by-product of the reaction, together with **chlorate** formation and, consequently, **perchlorate**. In the case of high chloride concentrations, ammonium was completely removed and the main oxidation products where the same as in the experiment with low chloride concentration. However, the chloride concentration decreased during the treatment process, and free chloride concentration increased which led to the appearance of chlorate but not perchlorate. *Lacasa et al.* [89] reported and confirmed the same formation of perchlorate when using BDD electrolysis under low concentration of chlorides.

Anglada et al. [90] used a landfill leachate from an intermunicipal sanitary landfill site (DEDISA) of Chania, West Crete (Greece), and electrochemically treated it using a BDD anode. Their study addressed the issue of formation of both chlorinated organic compounds and nitrate ions due to presence of organic matter and ammonia and/or organic nitrogen electro-oxidation in the presence of chloride ions. **Chloroform, dichloroacetonitrile, 1,2-dichloroethane and 1,1-dichloroacetone** were the main chlorinated organic compounds formed as a result of organic matter oxidation. The chlorinated organic by-products formation was explained as a consequence of the interaction between organic compounds and **reactive chlorine species**, such as active chlorine or chlorine radicals. In addition, the levels of chlorinated organic compounds were assessed with an eco-toxicity experiment, before and after electro-oxidation of landfill leachate. It was found that, even though chlorinated volatile organic compounds were formed, the electro-oxidation process diminished the toxicity.

In conclusion, it can be asserted that the use of electrochemical oxidation via BDD electrodes for the treatment of landfill leachate, in general, translates in the formation of **nitrogenized** and **chlorinated compounds**, as presented in Table 4.1 along with their respective toxicity. Further assessment is still needed due to the reported development of chlorinated volatile organic compounds that could possess high and acute toxicity and carcinogenicity.

Table 4.1 - Principal by-products formed with BDD on the treatment of landfill leachate. (The 3D structures were obtained via PubChem and accessed on 20.01.2021)

Classification	Oxidation by-products	3D Chemical structure	Mammalians toxicity	Potential contributors	References
Chlorinated compounds	Chloramines		Weakly mutagenic	RCS	[88,91]
	Chlorate		Endocrine disruptive		[17,88]
	1,1-Dichloroacetone		Hepatotoxic		[90,92,93]
	1,2-Dichloroethane		Possibly carcinogenic		[90,94]
	Dichloroacetonitrile		-		[90]
	Perchlorate		Endocrine disruptive		[18,88,89]
THMs	Chloroform		Possibly carcinogenic	RCS	[90,95,96]
Nitrogenized compounds	Nitrogen		-	RCS	[88]
	Nitrate		Hematotoxic		[88,97,98]

4.2. Industrial wastewater treatment

The definition of industrial wastewater is very complex and wide-ranging due to the different types of industries and various applied treatments that result in a distinctive composition and characterization of the effluent.[99] However, industries such as cement mills, sugar and thermal power plants, distilleries, fertilizers, mining industry, tanneries, and manufacturers of petroleum/petrochemicals, integrated iron and steel, pulp and high-quality paper, pharmaceuticals, dyes, dye intermediates, textiles and pesticides, among others, can be considered the major polluting industries.[100] The following subchapters describe and discuss the wastewater and its contaminants that result from several of the main industries, the role of BDD technology, and the identification of intermediates/by-products.

4.2.1. Paper mill industry

Paper mill industry effluent is characterized by high levels of total organic carbon (TOC) and chemical oxygen demand (COD), color, potentially toxic chlorinated compounds, tannins, resin acids, suspended solids, heavy metals and sulphur compounds along with lignins and derivatives of lignin.[101] *Klidi et al*. [101] reported the results of electrochemical oxidation of real paper mill wastewater derived from Halfa industries (Tunisia) by galvanostatic electrolysis using BDD anodes and Ti-Ru-Sn ternary oxide anodes. To promote the degradation of this effluent and to study the removal of ammonium ions, NaCl was introduced in the wastewater to generate reactive chlorine species and to support the indirect oxidation. The presence of high concentration of electrogenerated **•OH** with the use of BDD anodes led to the oxidation of **hypochlorite to chlorate and further to perchlorate**. Additionally, ammonium ions removal by the BDD anodes reached 47% after 3h of electrolysis which can be explained by the interaction with electrogenerated •OH that can oxidize both organic compounds and ammonium.

4.2.2. Textile/dye industry

The effluents discharged from textile factories can be defined as highly polluted and very alkaline or acidic wastewaters with a mixture of dyes, metals and other pollutants (e.g. chlorine and alkaline compounds).[102,103] However, when it comes to studies of electrochemical oxidation applied to this type of wastewater with BDD, the majority of papers found explore the degradation of dyes. In terms of colorants, there are synthetic dyes and natural dyes. Considering synthetic dyes, their classification relies on the chemical structure and the mode of application, and some examples are azo, anthraquinone, sulphur, phthalocyanine and triarylmethane.[104] This type of wastewater is generally identified by a strong color, large numbers of suspended solids, broadly fluctuating pH, high COD, and biological toxicity.[105]

Solano et al. [106] investigated anodic oxidation of real effluent discharged by Brazilian textile industry using a BDD anode and introducing Na_2SO_4 or NaCl salts with the objective of verifying the applicability of this treatment and in situ generation of the strong oxidant species, such as peroxodisulfates or active chlorine. The effluent sample was mainly composed of remazol red BR (RRB), novacron blue C-D (NB), amylum and different additives. During the oxidation of real textile effluent using Na_2SO_4, the following by-products, presented in Figure 4.1, were detected: **aromatic compounds** (benzoic acid, hydroquinone, phenol, benzoquinones) and **aliphatic acids** (acetic, propionic, oxalic and butyric acids).

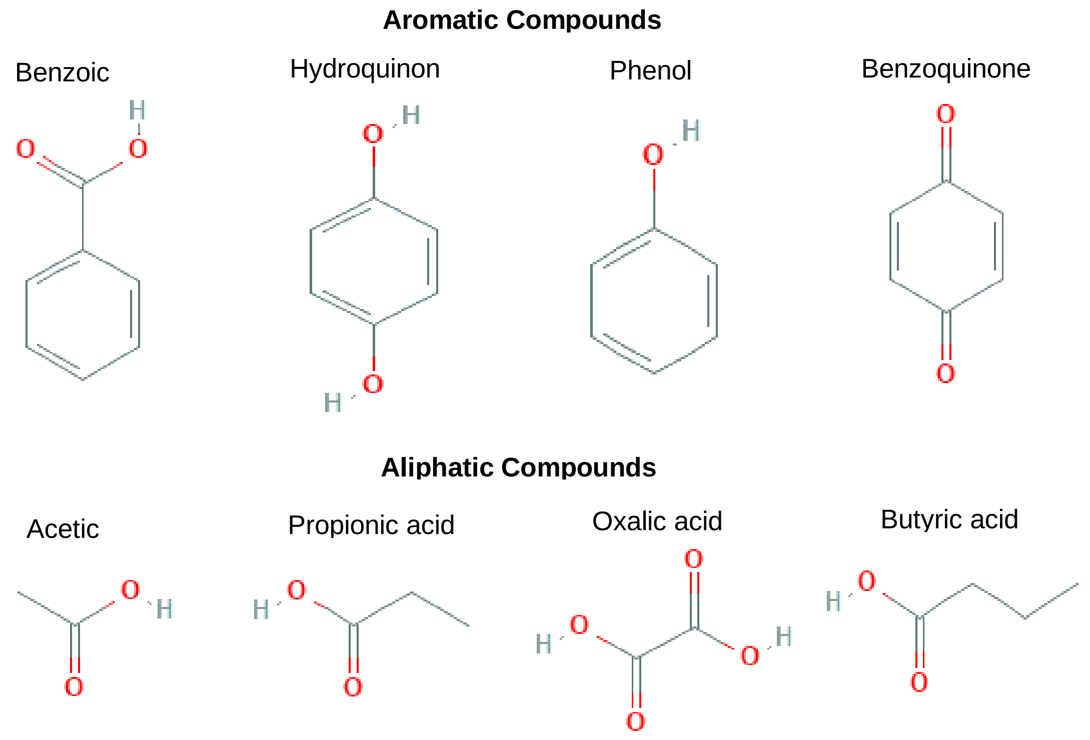


Figure 4.1 - Chemical structures of the aromatic and aliphatic by-products generated during the electrochemical oxidation of real textile effluent using Na_2SO_4.[106] (The structures were obtained from PubChem and accessed on 20.01.2021)

According to the authors [106], these by-products occur due to the assumed presence of sulfate ions on the surface of the BDD anode with the following development of peroxodisulfates in the bulk solution. This allows the degradation of organic matter, dissolved in real textile effluent, with the interaction between ROS and RSS (i.e., peroxodisulfate), leading up to quasi-complete degradation (CO_2, carboxylic acids and water). On the other hand, in the presence of chloride, intermediates such as phenol, chlorobenzene, 2-hydroxy benzoic acid, 1,4-dihydroxy benzene and chloroform were detected and their development was justified, in this study, by the interaction between chloro-oxidant species at the site of the azo bond and the terminal N,N-dimethyl chain.

Pacheco et al. [107] identified oxalic acid, hydroquinone and maleic acid as intermediate products, when using Na_2SO_4 as an electrolyte, at the end of the degradation of model solutions with the following aromatic amines: 3-amino-4-hydroxy-5-nitrobenzenesulfonic acid, 5-amino-2-methoxybenzenesulfonic acid, 2,4-dihydroxyaniline hydrochloride and benzene-1,4-diamine.

Considering the degradation of dyes with BDD anodes, *Costa et al.* [105] investigated the use of electrochemical oxidation of acid black 210 dye (AB-210) with different electrolytes (i.e., chloride and phosphate) and under different pH conditions. Their results showed the formation of **absorbable organic halogens (AOX)** during the AB-210 electro-oxidation in chloride electrolyte. On the other hand, phosphate electrolyte achieved the degradation of the dye without the development of organochlorine compounds. In another study, *Migliorini et al.* [108] assessed the degradation of the reactive orange 16 dye (RO16) with BDD electrodes. Two different BDD/Ti electrodes were used, and namely comprising relatively lower and higher doped BDD by applying different acceptor concentrations of boron during the CVD growth process (i.e.,$4{,}0\times10^{21}$ and $8{,}0\times10^{21}$ boron atoms cm^{-3}). The anodes were analyzed in terms of efficiency for the electrochemical degradation of a simulated wastewater containing RO16. Aromatic compounds were detected as the intermediates with both electrodes, yet their proper classification was not provided which compromised the assessment of their toxicity. The higher doped BDD electrode (i.e., $8{,}0\times10^{21}$ boron atoms cm^{-3}) proved to be more efficient for the degradation of RO16. Furthermore, it was assumed that reactive oxygen species, particularly •OH radicals, contributed to the degradation of the dye and the formation of the intermediary compounds.

In a similar study, *Vasconcelos et al.* [109] investigated the degradation of Reactive Black 5 (RB5) with relatively different acceptor concentrations of boron (i.e., $3{,}0\times10^{20}$ and $6{,}0\times10^{20}$ boron atoms cm^{-3}), for the BDD/Ti anodes. In this study, the relatively high-doped BDD (i.e., $6{,}0\times10^{20}$ boron atoms cm^{-3}) performed best, by way of the formation of aliphatic compounds during the degradation of RB5. The rupture of the azo dye molecule led to the formation of naphthol and quinone/anthraquinone tautomer, phthalic anhydride, benzoic acid, phenol, hydroquinone, and catechol, allowing at the end the development of aliphatic acids. It was shown that the electro-oxidation with BDD/Ti electrodes is a promising method for the removal of RB5 dye from water due to their capability of breaking the aromatic groups to form aliphatic compounds, such as oxalic acid, that are less toxic and readily converted into CO_2. In terms of assessing the main oxidants that contributed to the development of these compounds, K_2SO_4 was used as an electrolyte in the aqueous solution, however, the intervention of •OH for the breaking of the azo dye was also described.

4.2.3. Saline industrial wastewater

Saline industrial wastewater can originate from many industries (e.g. chemical industry, food processing plants, textile industry, leather industry and petroleum refineries) and is characterized by a water matrix that, among others, is rich in salts, phenols and polycyclic aromatic hydrocarbons.[59] *Anglada et al.* [110] used BDD anodes and electro-oxidation to treat a wide variety of saline industrial effluents. However, relatively high concentrations of **trihalomethanes** (i.e. chloroform, bromoform, dibromochloromethane and bromodichloromethane) were identified and, in all cases, **chloroform** was the main by-product. Their formation was assumed to be caused by the high concentrations of **chloride ions** (14 333 – 36 283 mg/L) already present in the effluents. Additionally, the formation of **nitrogen gas** and **nitrate ions** is assumed to be caused by the participation of **chlorine species** in the electro-oxidation.

4.2.4. Tannery industry

Tannery industrial wastewater is designated as a side stream of the process of leather fabrication from rawhides and animal skins, which uses high amounts of water and chemicals that are afterwards discharged into the environment with high concentrations of pollutants (i.e. sulfide, chromium and heavy metals) and toxic gases.[111,112] Moreover, this wastewater is characterized as highly alkaline and saline and it contains a lot of organic matter and suspended solids, with high levels of biological oxygen demand (BOD) and COD, deep in color, and high concentrations of ammonia, sulfur and nitrogen.[113]

Lu et al. [111] studied the use of electrochemical oxidation by using different anodes (Ti/RuO_2, Ti/IrO_2 and Ti/BDD) for the treatment of tannery wastewater after biological pretreatment with an activated sludge process. In general, Ti/BDD presented good efficiency in each of the parameters, such as removal of color, COD, TOC, and total nitrogen (TN). However, during the process chloroform generation was reported. With increasing electrolysis time, the concentration of the **generated $CHCl_3^-$** was low (below 0.2 µg/L). In terms of assessing the main contributors to chloroform production, it was assumed that indirect oxidation involving reactive chlorine species took place in the process. Besides this, the direct oxidation via **•OH** was the main contributor to the removal of the pollutants.

4.2.5. Olive oil mill industry

The demand of olive oil is rapidly increasing worldwide and, as a consequence, environmental pollution caused by olive mill wastes (OMW) is constituting a serious challenge for the handling and disposal of OMW. This wastewater contains high amounts of organic materials, odor, coloring, oily shine and increasing oxygen demand.[114] Therefore, *Flores et al*.[115] assessed the degradation of 4-hydroxyphenylacetic acid, one of the most common phenolic compounds detected in this type of effluent, by anodic oxidation with hydrogen peroxide (AO-H_2O_2) using a BDD/air-diffusion tank reactor and Na_2SO_4 as an electrolyte. 4-Hydroxybenzenemethanol and 4-hydroxybenzaldehyde were detected as the two primary **aromatic by-products and one final aliphatic carboxylic acid** (i.e. acetic acid) was also identified. The two primary aromatic by-products result from the initial attack of **•OH** formed at BDD that further leads to the decarboxylation with hydroxylation of 4-hydroxyphenylacetic acid to produce the diol 4-hydroxybenzenemethanol, which is finally oxidized to 4-hydroxybenzaldehyde. The final treated solution contained a large proportion of **unidentified products and recalcitrant by-products** that are even more difficultly oxidized by BDD (•OH) than final aliphatic carboxylic acids.

4.2.6. Conclusions

The by-products identified in industrial wastewater treatment when applying BDD technology were chlorinated species, aromatic species and aliphatic species. To elucidate the reader, Table 4.2 presents a summary of the major by-products discovered in these industries, their toxicity and the identification of the potential contributor reactive species.

Table 4.2 - Principal by-products formed in the treatment of industrial wastewater using BDD technology.

Classification	Oxidation by-products	Mammalians toxicity	Type of industry	Potential contributors	References
Chlorinated compounds	Perchlorate	Endocrine disruptive	Paper mill	•OH	[18,101]
	THMs	Possible carcinogenic and Weakly mutagenic	Saline and Tannery	RCS and •OH	[110,111, 116]
Hydrocarbons	Aliphatic compounds	-	Textile/Dyes	ROS and peroxodisulfate	[106]
	Aromatic compounds	-	Olive mill	•OH	[115]

4.3. Drinking water and Municipal wastewater treatment

Microbial load exists in natural water coming from surface or groundwater sources and, therefore, disinfection is a crucial water treatment method as it ensures that water is free of pathogenic micro-organisms causing waterborne diseases.[117] Municipal wastewater not only poses a risk for human health but also for aquatic environment, due to the presence of contaminants like nitrogen and phosphate, trace elements (i.e. iron and manganese), dissolved salts, particularly NaCl, and bicarbonates.[118] Therefore, the adequate treatment to this type of wastewater is required to prevent the discharge of these pollutants.

The following subchapters describe the main contaminants discussed in the disinfection of drinking water and municipal wastewater treatment, with respect to BDD technology and the identification of intermediates/by-products.

4.3.1. Drinking water disinfection

Considering that water is a natural resource required for human survival, it is important to address the removal of microbes from drinking water with quality and safe methods. For this reason, disinfection has been widely used as it ensures that water is free of pathogenic micro-organisms.[117] *Bergmann et al*. [51] performed electrochemical water disinfection in non-divided cells with systems containing sulfate, chloride, chlorite, chlorate and nitrate ions, with the purpose of studying the formation of inorganic by-products in the presence of these ions. When the electrolyzing water contained sulfate and carbonate as sodium salts, the formation of the by-product H_2O_2 was verified due to the anodic production of •OH radicals. This formation is possible due to the absence of active chlorine and ClO_2 which would lead to its decomposition. During electrolysis of sodium chloride solution, the formation of by-products such as chlorine dioxide and chlorate was determined, which indicates the oxidation activity by •OH. In the system containing nitrate, the electrolysis led to the formation of nitrite and ammonium ions due to the probable participation of •OH. Consequently, in the presence of varied chloride concentration in water containing nitrate, the formation of chloramines was also observed due to chloride oxidation that generates chlorine species that could react with ammonia.

The formation of another by-product, namely **perchlorate**, was observed by *Bergmann et al*. [119] when operated in single chloride, hypochlorite, chlorite and chlorate solutions. During the process all chlorite, hypochlorite and chlorate were completely converted to perchlorate and it was noticed that hypochlorite seemed to react faster than chlorite and was also able to form ClO_2 during the process. Chloride species exhibited an exponential growth of perchlorate formation, due to better adsorption/reactivity of chloride ions on the BDD anode surface that got converted to chlorate. Although it was not the objective of the study, according to the authors, ozone and **•OH** might have participated in the formation of this by-product.

Additionally, when electrolyzing treated drinking water supplied by the regional Koethen waterworks (MIDEWA, Germany) in both studies [51,119], all chloride ions present in the water reacted to perchlorate, meaning that all intermediates were converted to higher oxidized species and finally perchlorate. In both artificial and regional drinking water, it was observed that a high concentration of chloride results in a lower perchlorate formation.[119,120] However, it is relevant to mention that the values measured for perchlorate in regional drinking water were still critically high (approximately 200 µg/L).[119] Consequently, generation of perchlorate by-product was assumed to be under **•OH** radical participation.

According to *Bergmann et al*. [121], BDD was found to be associated with the highest **halogenate** (i.e., bromide and chloride) and **perhalogenate** (i.e., perbromate and perchlorate) formation potential. Therefore, the occurrence of perhalogenates in water electrolysis, performing experiments in synthetic waters using BDD, was studied. When analyzing the electrolysis of a synthetic drinking water system containing chloride, perchlorate formation was observed, as expected from the previous studies.[51,119,120] This formation is dependent on the reaction potential of other species able to react with oxidants and other species generated at the anode, such as **•OH** and **•O radicals**, O_3 , chlorine radicals, active chlorine, chlorite and chlorine dioxide. Besides, it is important to notice that by conducting the electrolysis over a longer time, all chloride is finally converted to perchlorate. While the active chlorine formation is a limiting process, chlorite and chlorine dioxide are also probable intermediates, which are difficult to detect due to their high reactivity.

Regarding the synthetic drinking water system containing bromide, it was verified that all bromide was converted to active bromine, bromate and perbromate.[121] Active bromine is an important intermediate and precursor of bromate and perbromate, and perbromate is predominantly formed from bromate. As result, the by-products identified at the end of the experiment were **bromate** and **perbromate**. *Bergmann et al*. [122] determined that nearly all bromide in the synthetic water was converted to bromate toward the end of the electrolysis, which indicates the formation of other products, since it was not a complete conversion. The formation of bromine was verified only temporarily, but bromite was not obtained. Considering the formation of **perbromate**, its concentration grew steadily and at a slow rate. Given the above, it was assumed that the participation of **•OH and •O radicals** in the bromate formation is the most logic conclusion and that a higher bromide concentration can promote a faster generation. Alternatively, in an experiment using only bromate solution as the electrolyte, bromide formation was identified, along with an extremely slow perbromate formation, and both bromate and bromide reached a steady state-like concentration with time.[122] When only the bromide solution (at the same starting concentration) was electrolyzed, more **perbromate** formation was observed. Therefore, according to the results obtained, perbromate formation is faster in bromide electrolysis. Besides the mechanism of converting bromate to perbromate, it can be assumed that other mechanistic steps might have taken place, probably involving bromine and bromite, which are not intermediates in bromate electrolysis.[122]

Finally, when comparing perhalogenate formation in electrolysis of a synthetic drinking water system containing both chloride and bromide (halogenate form), starting from a similar molar concentration, it was possible to conclude that the risk of perbromate generation in synthetic drinking water is relatively low, whereas the perchlorate formation appears to be easier on BDD anodes.[121]

4.3.2. Municipal Wastewater

Municipal wastewater is the most abundant type of wastewater and it is characterized by low organic strength and high particulate organic matter content.[123] The treatment of wastewater is essential for the protection of downstream users from health risks and for protecting nature from nutrient pollution in surface waters.[124] *Bagastyo et al.* [125] investigated the performance of electrochemical oxidation using BDD electrodes for the treatment of reverse osmosis concentrate (ROC) from secondary-treated wastewater effluents. The untreated ROC contained Br^-, Cl^- and I^- ions. The depletion of chloride ions led to the formation of by-products, such as free available chlorine (**FAC**, i.e., Cl_2, HClO and ClO^-) and chloramines, which were probably generated by the participation of **•OH radicals**. Regarding the formation of halogenated by-products, namely **adsorbable organic halogen (AOX),** it was verified the generation of **adsorbable organic chlorine (AOCl), bromine (AOBr) and iodine (AOI)** during the electrochemical oxidation of ROC. It was noticed that above 80% of AOX formed (in mM) corresponds to AOCl, which is consistent with the very high Cl^- concentration in ROC. Additionally, at the end of the experiments, residual FAC was still measured. Accordingly, the available Br^- and I^- ions were also converted to halogenated by-products, particularly AOBr (i.e., HOBr/OBr^-) and AOI (i.e. HOI/OI^-), due to the probable participation of •OH radicals, similar to the chlorine species. To summarize, from the three AOXs mentioned above, only the AOCl and AOBr remained at the end of the experiments. In order to study the formation of individual halogenated organic by-products during electrochemical oxidation, the two commonly measured by-product classes, namely total trihalomethanes (THMs) and total haloacetic acids (HAAs), were analyzed.[125] As result, the following compounds of the two classes were identified, as presented in Figure 4.2.

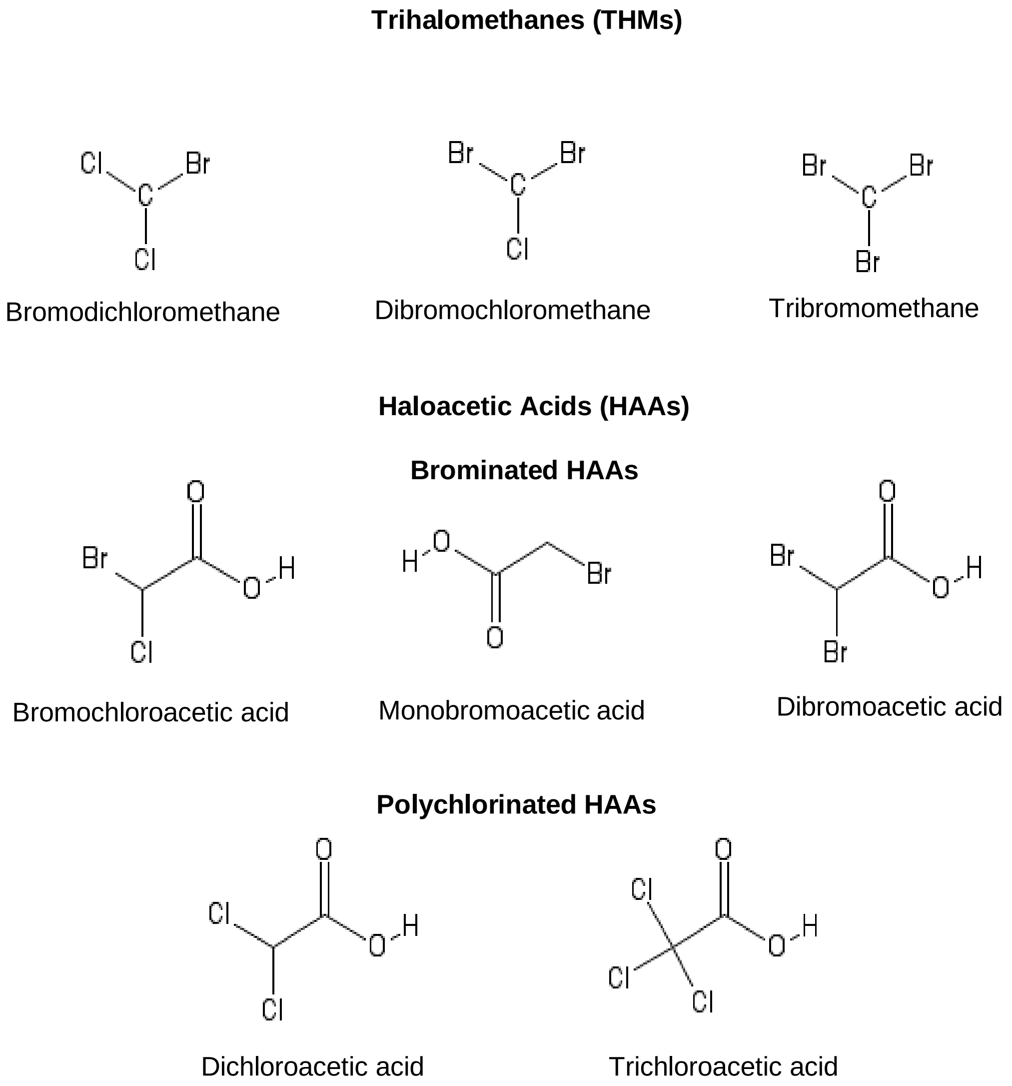


Figure 4.2 – Chemical structures of the halogenated organic by-products generated during the electrochemical oxidation of the reverse osmosis concentrate.[125] (The structures were obtained from PubChem and accessed on 20.01.2021)

Considering **THMs**, trichloromethane (TCM) was the dominant species (above 70% on a molar basis), followed by bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM).[125] Moreover, **polychlorinated HAAs** (i.e. dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA)) were prominent among the HAAs measured in this study. On the other hand, **brominated HAAs** (i.e. bromochloroacetic acid (BCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA)) were detected at lower concentrations. Finally, it is important to notice that both halogenated organic by-products classes were not completely degraded and the potential contributors were assumed to be mainly reactive chlorine species and •OH radicals.

Garcia-Segura et al. [126] assessed the electrogeneration of chloramines in different water matrices containing NH_4Cl, urea and synthetic urine using BDD anodes, with sodium perchlorate monohydrate and NaCl as supporting electrolytes. While the predominant species observed in all experiments were **monochloramines** (NH_2Cl), the generation of dichloramine ($NHCl_2$) and trichloramine (NCl_3) was also verified due to the formation of **chlorine active species** (i.e., Cl_2, $HClO/ClO^-$, Cl_2O and ClO_2). Even though the participation of **•OH radicals** and oxygen evolution is also assumed, it was determined that the presence of ammonia in the solution is essential for the formation of chloramines. As a result, lower concentrations of chloramines were observed in the urea solution and synthetic urine matrix compared with the NH_4Cl solutions.

Zöllig et al. [127] studied the electro-oxidation of human urine using BDD anodes in order to analyze the formation of chlorate, perchlorate and organic chlorination by-products (OCBPs). Concerning the oxidation of chloride from the urine, the dominant by-products formed were chlorate and perchlorate, while all chloride was oxidized at the end of the experiments. The OCBPs generated were **dichloromethane, trichloromethane, tetrachloromethane and 1,2-dichloroethane** and, after analyzing the results, it was verified that tetrachloromethane was built from dichloromethane or trichloromethane through successive chlorination. Nevertheless, the elimination of dichloromethane and trichloromethane may have resulted from further oxidation, to a small extent by chlorination to tetrachloromethane, or by complete mineralization to CO_2, which was indicated by the smaller production of OCBPs. As to 1,2-dichloroethane, no information regarding its preservation at the end of the experiments was provided. Additionally, the formation of an **unknown fraction of AOX**, which were assumed to be either chloramines or longer chained or untargeted OCBPs that could not be detected with the method used (i.e., GC-MS). As described in the paper, the formation of the by-products mentioned were promoted by the participation of **•OH radicals** and the presence of **active chlorine**.

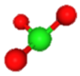
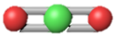
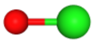
Concerning the electrochemical treatment of authentic latrine wastewater, *Jasper et al.* [128] evaluated the formation of by-products using BDD anodes. They observed the formation of inorganic by-products, such as **nitrate, chlorate and perchlorate**, but only nitrate and perchlorate remained at the end of the experiment. The generation of nitrate was promoted by the presence of ammonium in the wastewater. Moreover, it was assumed that the participation of **•OH radicals**, the presence of **chloride** and the oxidation of hypochlorous acid at the anode contributed to the appearance of chlorate and perchlorate. When analyzing organic by-products like **THMs** (e.g., chloroform, bromodichloromethane and bromoform), chloroform was the predominant product formed, but it did not remain till the end of the experiment. Other organic by-products, such as chlorinated haloacetic acids (e.g., monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA)) were also detected. Although DCAA dominated the production of haloacetic acids and even lasted until the end of the experiment, the three haloacetic acids were further oxidized.

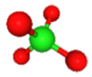
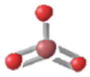
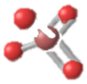
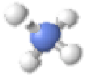
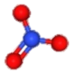
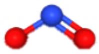
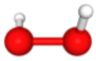
In another study on the treatment of municipal wastewater, *Cano et al.* [129] investigated the disinfection capability of the electrolysis using BDD, in a very wide range of current densities (1.3-130 A/m^2), to determine the optimum operation condition for attaining the water disinfection without generating non-desired or even hazardous disinfection by-products. It is important to notice that chlorine salt was not added to the treated wastewater used in this experiment. At the lowest current density of 1.3 A/m^2, the by-products formed were hypochlorite, monochloramine, dichloramine and trichloramines. Accordingly, it is assumed that the main contributors to their formation are •OH radicals and the presence of chlorine and ammonia. On the other hand, when the current density was increased, the formation of chlorate was determined, along with the by-products mentioned before in lower concentrations.

4.3.3. Conclusions

Most of the aqueous solutions studies analyzed dealing with BDD technology for the disinfection of drinking water and wastewater reported the formation of **halogenated by-products** (i.e., chlorate, perchlorate, bromate and perbromate). Additionally, in the wastewater treatment, chlorination by-products, such as **chloramines** (due to the frequent appearance of ammonia in this water matrix), **trihalomethanes and haloacetic acids** were also identified. Table 4.3 presents a summary of the major by-products discovered in these fields, their toxicity and the identification of the potential contributor reactive species.

Table 4.3 - Principal by-products formed with BDD on the disinfection of drinking water and wastewater. (The 3D structures were obtained via PubChem and Chemdoodle and accessed on 20.01.2021)

Classification	Oxidation by-products	3D Chemical structure	Mammalians toxicity	Water matrix	Potential contributors	References
Chlorinated compounds	AOCl	NA*	-	WW	•OH	[125]
	Chlorate		Endocrine disruptive	DW, SW and WW	ROS and RCS	[17,51,120, 127,129]
	Chloramines	NA*	Weakly mutagenic	SW and WW	•OH and RCS	[51,91,125, 126,129,130]
	Chlorine dioxide		Neurotoxic and Respiratory toxic	SW	•OH	[51,118, 131, 132]
	FAC	NA*	-	WW	•OH	[125]
	Hypochlorite		-	WW	•OH and RCS	[129]

Classification	Oxidation by-products	3D Chemical structure	Mammalians toxicity	Water matrix	Potential contributors	References
Chlorinated compounds	Perchlorate		Endocrine disruptive	DW, SW and WW	ROS and RCS	[18,51,119-121, 127, 128]
Brominated compounds	AOBr	NA*	-	WW	•OH	[125]
	Bromate		Mutagenic and Possibly carcinogenic	SW	ROS	[121,122,133, 134]
	Perbromate		-	SW	ROS	[121, 122]
Nitrogenized compounds	Ammonium		-	SW	•OH	[51]
	Nitrate		Hematoxic	WW	NI	[97,98,128]
	Nitrite		Hematoxic	SW	•OH	[51,97,98]
Other compounds	HAAs	NA*	Oxidative stress and Possibly carcinogenic	WW	RCS and •OH	[125,135]
	Hydrogen Peroxide		-	SW	•OH	[51]
	THMs	NA*	Possible Carcinogenic and Weakly mutagenic	WW	RCS and •OH	[116,125,127]

Abbreviations: DW, drinking water; NA*, not applicable; NI, not identified; SW, synthetic water; WW, wastewater. *These by-products were categorized to synthetize the table, and for that reason, the 3D molecular structure was not presented.

4.4. Removal of micropollutants from water

Micropollutants (MPs) can be defined as anthropogenic compounds that are detected in the aqueous environment, in concentrations ranging from µg/L to ng/L, and are constituted by various compounds, such as pesticides, pharmaceuticals, cosmetics, flame retardants, perfumes, waterproofing agents, plasticizers and insulating foams.[136] The following subchapters describe the main MPs removed using BDD technology, and the identification of intermediates/by-products

4.4.1. Pharmaceuticals

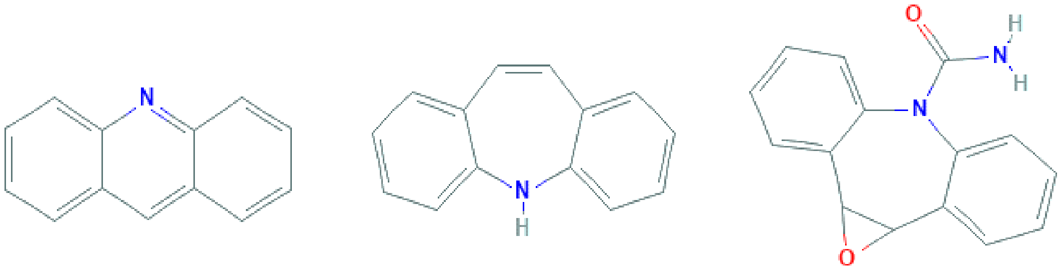
Worldwide, pharmaceutical products such as analgesics, anti-inflammatory drugs, antibiotics, lipid regulators, beta-blockers and X-rays contrast media have emerged, being used in human and animal for health treatment, to improve life quality and to increase life expectancy.[137] However, these compounds can reach water streams and become a threat to public and animal health.

Frontistis et al. [138] studied the electrochemical degradation of pharmaceutical compounds using BDD and focused on the degradation of ethyl paraben (EP). The major transformation by-products encountered during the experiment were identified. The degradation experiments were carried out using secondary treated wastewater and pure water with the use of $HClO_4$, Na_2SO_4 and NaCl as supporting electrolytes. In the presence of Na_2SO_4, the by-products detected during the electrochemical oxidation of EP were marked as monohydroxylated derivatives of this compound. The formation of these derivatives was assumed due to •OH participation in the presence of this electrolyte, and the ROS as the main contributor to the electrochemical oxidation of EP.

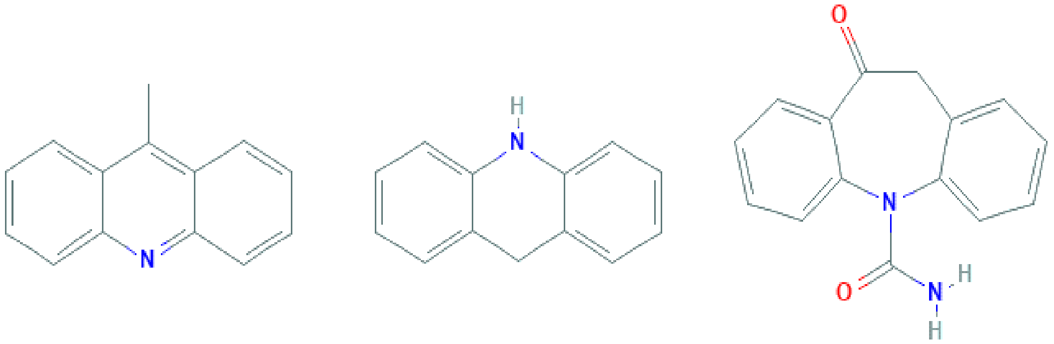
El-Ghenymy et al. [139] identified aromatic intermediates, carboxylic acids and the conversion of the initial N of sulfamethazine to ions of NH_4^+ and NO_3^- in the electrochemical incineration of the antimicrobial sulfamethazine ($C_{12}H_{14}N_4O_2S$) in Na_2SO_4 electrolyte. They proposed a reaction pathway where **•OH radicals** were also considered to be the main oxidants involved, allowing to assume that the intermediates detected could be caused by this species.

In the presence of NaCl, the identified by-products were mentioned to be formed with the intervention of •OH and chlorine radicals and can be generally categorized as: **chlorinated EP, chlorinated and non-chlorinated dimers, chlorinated and non-chlorinated trimers, dealkylated and hydroxylated EP, and chlorinated hydroxyl benzoquinone as later stage product**.[138] Even though $HClO_4$ was also used as an electrolyte in this study, any associated by-products were not mentioned. In terms of toxicity, this article only raises concern for the presence of organochlorinated by-products in the treated sample.

García-Espinoza et al. [140] investigated the effect of electrocatalytically generated active chlorine on carbamazepine degradation using Nb/BDD or Ti/IrO_2 anodes in the presence of NaCl. Six organic compounds (i.e. acridine, iminostilbene, 10,11-epoxycarbamazepine, 9-methylacridine, 9,10-dihydroacridine and oxcarbamazepine), presented in Figure 4.3, were identified as by-products. The generation of these compounds was assumed to be due to the intervention of reactive chlorine species, in particular •Cl. The authors also proposed a degradation pathway for carbamazepine and discussed the acute toxicity, permitting to say that the presence of remnant active chlorine is the main factor responsible for the increase of toxicity.



Acridine Iminostilbene 10,11-Epoxycarbamazepine



9-Methylacridine 9,10-Dihydroacridine Oxcarbamazepine

Figure 4.3 – Chemical structures of the aromatic by-products formed from the degradation of carbamazepine.[140] (The structures were obtained from PubChem and accessed on 20.01.2021)

Mordačíková et al. [141] reported the participation of active chlorine species for the identified chlorinated by-products during the oxidation process of four pharmaceuticals (carbamazepine, diclofenac, trimethoprim, and venlafaxine) with BDD electrodes in wastewater. *Garcia-Segura et al.* [148] reported the presence of **$\mathbf{ClO^-}$, $\mathbf{ClO_3^-}$ and $\mathbf{ClO_4^-}$ ions, chloramines and organochlorinated** by-products, as well as the electrogeneration of organochloride and organobromide derivatives, in the anodic oxidation of a secondary wastewater effluent with 21 pharmaceuticals introduced synthetically (i.e. sulfadiazone, trimethoprim, ranitidine, norfloxacin, lincomycin, gemfibrozil, acetaminophen, tramadol, metoprolol, diclofenac, carbamazepine, enrofloxacin, venlafaxine, citalopram, roxithromycin, sertraline, hydrochlorothiazide, ibuprofen, diatrizoate, phenytoin and iopromide). Considering the specific case of the pharmaceutical diclofenac, *Heim et al.* [142] investigated the removal of this target compound in different water matrices (deionized water, drinking water and wastewater effluents spiked with diclofenac) and also identified the presence of chlorinated by-products (**chlorate and perchlorate**) in deionized water. However, three structures with two aromatic rings (derived from hydroxylation or decarboxylation of the original compound diclofenac), 2,5-dihydroxybenzaldehyde (identified in deionized and drinking water, but not in the wastewater effluent), mixture of maleic acid and fumaric acid, and oxalic acid were also detected as transformation products. Chlorate, **perchlorate, bromate and perbromate** development (formed in drinking water and wastewater effluent) was also found. It is relevant to mention that the drinking water and wastewater effluent already had the introduction of chloride and bromide, in the beginning of the experiment, and for that reason their presence was assumed to contribute to the development of the inorganic by-products. Other transformation products were assumed to be produced due to the reactions involving oxidants, such as **•OH and O_3**. In another research, performed by *Amorim et al.* [143], the simultaneous electrochemical removal of two antibiotics (sulfamethoxazole – SMX and trimethoprim – TMP) with Na_2CO_3 as a supporting electrolyte was the main objective. Six aromatic (i.e. azepine, 4-aminothiophenol, benzenesulfonamide, sulfanilamide, 1,2,4,5-tetramethoxybenzene and benzoquinone) and three aliphatic organic intermediates (their classification was only mentioned as isomers compounds) were properly identified and an oxidation pathway of the simultaneous SMX and TMP electrochemical degradation was proposed. Once more, it was assumed that **reactive oxygen species** played an important role in the development of the intermediates.

According to *Feng et al.* [144], the presence of the aromatic intermediates formed from pharmaceutical residues can have significant influence on the increase/decrease of the solution toxicity.

4.4.2. Pesticides

Pesticides are used widely in agriculture to protect crops from e.g. pathogens, fungi, insects and weeds.[145] These substances can be classified as insecticides, fungicides, herbicides, garden chemicals, household disinfectants and rodenticides.[146] They contain one or more active substances that can enter in surface waters by drift or agriculture runoff, or leach into groundwater with the overall consequence of risking the safety of ecosystems and human health.[145] Therefore, *Bu et al.* [147] studied the degradation of herbicide atrazine, using BDD anode to activate persulfate (PS) and Na_2SO_4 as an electrolyte. They discovered two primary de-alkylation products of atrazine, namely deethyl-atrazine and deisopropyl-atrazine in the BDD/PS system. On the other hand, 70% of atrazine was transferred to secondary by-products or other primary by-products via other reactions, including olefination, alkyl chain oxidation, deamination, dechlorination, and hydroxylation. The ecotoxicity assessment indicated that the identified by-products were less harmful than atrazine. The formation of these products and by-products was assumed as a result of the interaction of oxidants, such as **ROS (•OH) and RSS (SO_4•-)**. In another study, *Garcia-Segura et al.* [148] reported the presence of **ClO^-, ClO_3^- and ClO_4^- ions, chloramines and organochlorinated by-products** in the degradation of atrazine, among others pesticides also introduced in the effluent of a secondary municipal wastewater. Furthermore, they revealed the electrogeneration of organochloride and organobromide derivatives, which were accumulated during the treatment at low µM level. The explanation for the generation of these compounds could be due to the presence of chloride and bromide in the secondary effluent and the reactions between **reactive chlorine species (chloride ion), bromide ion and •OH**. *Madsen et al.* [149,150] conducted two research pathways for the case of the electrochemical oxidation of the herbicide 2,6-dichlorobenzamide, i.e. one in chloride medium and the other in the presence of sodium sulfate. Regarding these two experiments, the degradation intermediates were detected and, even though they were not properly identified, the authors claimed that these compounds could be unidentified carboxylic acids. In chloride medium, the initial oxidation was most likely due to active chlorine (hypochlorous acid/hypochlorite), permitting to say that **reactive chlorine species** contributed somehow to the intermediates formation. In sodium sulfate medium, the involvement of **•OH and RSS** could be a possible explanation for the development of the degradation intermediates.

4.4.3. Other compounds

Even though pharmaceuticals and pesticides are frequently encountered in the aqueous environment and the discussion of their intermediates and by-products is very important, other contaminants such as plastics, phenolic, nitrophenol and biomedical compounds constitute a problem as well.

Yining et al. [151] studied the electrochemical degradation of dimethyl phthalate, an additive mostly used in plastic manufacture and also in the production of cosmetics, lubricants, carpeting, decorative cloths and other products. They used BDD anodes and Na_2SO_4 as a supporting electrolyte. They identified **aromatic and aliphatic compounds** as by-products, where most of them were alcohols and organic acids, and also proposed a reaction sequence for the electrochemical oxidation of the starting contaminant. The main contributors for the degradation of dimethyl phthalate and consequently the development of intermediates and by-products were assumed to be **•OH** and possibly oxidants such as **H_2O_2** and **oxygen**. *Li et al.* [152] reported the influencing factors and the chlorinated by-products formation in the electrochemical oxidation of bisphenol A, a plastic monomer and plasticizer. The identified degradation intermediates were mentioned to be mainly chlorinated bisphenol A compounds and chlorinated phenols. However, due to the operating factors, the toxicity assessed with the bacteria V. fischeri decreased, regardless the presence of chlorinated by-products (e.g. chloroform, perchlorate and active chlorine) being suggested. Lastly, a degradation pathway and the contribution of **•OH and active chlorine** in the generation of these chlorinated by-products was presented.

Panizza et al. [153] studied the electrochemical oxidation of phenolic compounds, with BDD anode and $HClO_4$ as the electrolyte. Gallic acid, a phenolic-type compound that can be found in numerous food processing wastewaters, such as those from wine distilleries, olive oil factories, boiling cork process, as well as in other industrial synthetic effluents was used as a model compound. Aliphatic acids were mentioned to be the intermediates, whereas •OH radicals were designated to lead to their development. *Li and Ni* [154] also mentioned the presence of •OH in their study on resorcinol, a white crystalline phenolic compound present mainly in the adhesives of rubber products, wood additives, manufacture of chemicals, explosive primers, antioxidants, flame retardants, UV stabilizers, dyes, agricultural chemicals, fungicidal creams and lotions, meta-amino phenols, hair dyes, and pharmaceuticals.[155] In their experiment, a model water containing NaCl electrolyte in the presence of this phenolic compound was used with a BDD anode, and the by-products were analyzed. The study results revealed the formation of **chloroform, chlorate and perchlorate**, mainly due to the reaction with •OH. Chloroform and chlorate generation was also suspected to be related with the concentration of free available chlorine. However, both chloroform and chlorate were completely mineralized in the BDD electrochemical system by •OH, leaving perchlorate as the only stable remaining by-product at the end of the experiment.

Zhang et al. [156] and *Cañizares et al.* [157] investigated two nitrophenolic compounds, called p-nitrophenol and 4-nitrophenol, respectively. Nitrophenol compounds are widely used in manufacturing industries of synthetic dye materials, pharmaceutical compounds, pesticides, leather treatment processes and military applications and, for that reason, their presence is common in industrial and agricultural wastewaters.

In the study by *Zhang et al.* [156] BDD and Pt anodes were used and two electrolytes were employed, i.e. NaCl and $NaNO_3$. $NaNO_3$ electrolyte was widely discussed regarding pH and current density effects but no intermediates or by-products were reported. However, in the case of NaCl, an intermediate 5-chloro-2,4-hydroxyl-phenol was found. Besides this, a possible degradation pathway was described in H_3PO_4 media where the main intermediates with BDD as anode were hydroquinone and p-aminophenol, while intermediates containing a benzene ring were accumulated with Pt as anode. These results were explained by the participation of •OH and chloride based oxidant species.[156] Contrarily, in the research of the electrochemical degradation of 4-nitrophenol [157], Na_2SO_4 was used as an electrolyte and the identification of the intermediates was performed. Hydroquinone, phenol, p-aminophenol, maleic acid and oxalic acid were designated as the main intermediates and the final products were carbon dioxide and ammonium. Additionally, a degradation pathway was proposed by the research group and •OH and reactive sulfate species were presumed to take part in the degradation and intermediates formation.[157]

Zhang et al. [158] studied the electrochemical degradation of ethidium bromide, a DNA intercalating pollutant, commonly disposed by biomedical laboratories, with the use of Na_2SO_4, Na_2CO_3, $NaNO_3$, and NaCl as supporting electrolytes. Even though NaCl was the optimal electrolyte in terms of performance of pollutant removal, it led to the formation of hazardous chlorinated species. Furthermore, in the presence of Na_2SO_4 electrolyte, **ammonium and nitrite ions** were detected as by-products and their development was suspected to be due to the participation of **•OH and probably reactive sulfate species**.

4.4.4. Conclusions

In general, it can be asserted that the use of electrochemical oxidation with BDD for the treatment of water with MPs translates in the formation of nitrogen, chlorinated and aromatic species. Table 4.4 summarizes the major by-products discovered in the removal of the MPs and the identification of the potential contributor reactive species.

Table 4.4 - Principal by-products formed with BDD on the removal of MPs.

Classification	Oxidation by-products	Type of MPs	Potential contributors	References
Chlorinated compounds	Chlorate	Phenolic and Pharmaceutical	RCS and ROS	[142,153]
	Organochlorinated compounds	Pharmaceutical and Pesticide	RCS and •OH	[148]
	Others**	Pharmaceutical	RCS	[141]
	Perchlorate	Pharmaceutical, Phenolic and Plastic monomer	RCS and •OH	[142,152,153]
Derivatives of MPs	Chlorinated and non-chlorinated derivatives	Pharmaceutical	•OH and RCS	[138]
	Monohydroxylated derivatives	Pharmaceutical	•OH	[138]
Hydrocarbons	Aliphatic compounds	Pharmaceutical and Plastic additive	RCS and ROS	[142,151]
	Aromatic compounds	Pharmaceutical and Plastic additive	RCS and ROS	[140,142,151]
Nitrogenized compounds	Ammonium	Nitrophenolic and DNA intercalating pollutant	•OH and RSS	[157,158]
	Nitrite	DNA intercalating pollutant	•OH and RSS	[158]
THMs	Chloroform	Plastic monomer and Phenolic	•OH and RCS	[152,153]

Abbreviations: NA*, not applicable; *These by-products were categorized to synthetize the table, and for that reason, the 3D molecular structure was not presented; ** Chlorinated by-products that weren't characterized

In terms of toxicity, the effects on mammalians health (i.e., rats and humans) were provided when available. Therefore, endocrine disruptors (i.e. chlorate and perchlorate)) [17,18], hematotoxicity (i.e. nitrite) [97,98] and possible carcinogenic (i.e. chloroform) [95,96] were the main health risks mentioned. Even though this factor is reported in the studies to decrease with this technology, further assessment is still needed due to the presence of the reminiscent active chlorine.

5. Influence of process conditions to minimize by-product formation

The findings from Chapter 4 show that the variety and quantity of intermediates and by-products formed depend largely on the composition of the solution/water matrix. An optimization of the process conditions when using BDD electrodes can potentially contribute to the mitigation of by-products. For this reason, a good understanding of the complex relationship between this electrode technology, process conditions and reactive species is extremely important to determine the main factors that influence the by-products formation (Figure 5.1).

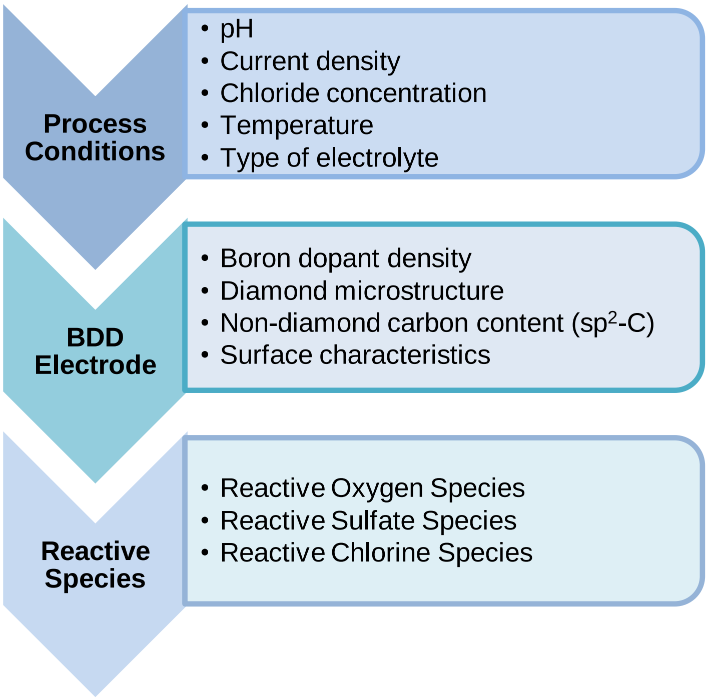


Figure 5.1 - Main factors that influence the by-products formation in EOAPs with BDD technology.

The electrogeneration of by-products is influenced by experimental factors, such as pH, current density, chloride concentration, temperature and type of electrolyte. For example, *Li and Ni* [154] reported that in the presence of a basic and neutral condition (pH 10 and 7), the production of disinfection by-products (i.e. chloroform, chlorate and perchlorate) in NaCl electrolyte increased when comparing to an **acidic condition** (pH 4). For this reason, the acidic condition is presumed to be more favorable for this technology. Similar to this, *Sánchez-Carretero et al.* [34] described that not only a basic pH favored the production of perchlorate, but also high current density. According to their study, the generation of perchlorate increased with current densities superior to 300 Am^{-2} and higher applied charges (i.e., 60 Ah dm^{-3}). *Bergmann et al.* [119,120] observed the same increase of perchlorate production when operating at high current densities, and added that when working with a range of 50-250 ppm of chloride concentration, this compound formation was enhanced by lower chloride concentration. Operating with **relatively high chloride concentrations** allowed to attain the desired disinfection level and to maintain the formation of undesired by-products (i.e., perchlorate) at a minimum level.

Bergmann et al. [122] identified that the bromate and perbromate formation was influenced by varying the current density, in the range of 50-200 A/m^2 for bromate, and 200-700 A/m^2 for perbromate. It was observed that the higher current densities enhance the formation of these compounds. Based on the literature presented, **lowering of the current densities** can mitigate the production of halogenated and perhalogenated by-products. When applying low temperatures (5 ºC), the formation of perbromate increased compared to standard room conditions (20 ºC). Therefore, the use of BDD technology in the electrolysis of aqueous systems containing bromide is advised without the need of active cooling.

The use of **supporting electrolytes** to enhance the conductivity of a solution and to provide the electrogeneration of strong oxidant species is very common in EAOPs. However, the nature of the electrolyte can highly influence the production of toxic by-products.[4] *Ganiyu and Martínez-Huitle*[29] identified a study[125], in their review, that assessed the generation of total THMs and HAAs using BDD anodes and three common electrolytes (i.e. Na_2SO_4, NaCl and $NaNO_3$). The authors concluded that these disinfection by-products presented higher values with NaCl (9.08 µM / 62.48 µM), followed by Na_2SO_4 (1.90 µM / 13.62 µM) and $NaNO_3$ (0.23 µM /1.12 µM) for total THMs and HAAs, respectively. Since $NaNO_3$ generated lower concentrations of by-products, it could be a suitable candidate to substitute NaCl or Na_2SO_4, but further assessment is needed.

The formation of reactive species is important for the feasibility of EAOPs. In addition, the **BDD anode material** itself determines the efficiency of reactive species formation. Depending on how the BDD has been grown, the resulting material properties can vary significantly among different electrodes. Previous studies have outlined the interplay between boron dopant density, non-diamond carbon content (sp^2 carbon) and grain morphology, among others, and the electrode performance in various applications.[29,11] According to *Ganiyu and Martínez-Huitle,*[29] the abundance of reactive species such as free •OH and reactive chlorine species is directly related to increasing the diamond composition (i.e. higher sp^3/sp^2 ratio). On the other hand, reactive sulfate species, in particular persulfate, were mentioned to be favored by increasing the graphitic, or non-diamond carbon, composition (i.e., lower sp^3/sp^2 ratio).[29]

Overall, providing the optimal conditions for electrochemical oxidation with BDD is not easy since this system is complex and presents various potential interactions between material, operating and water matrix parameters. Considering that halogenated and perhalogenated compounds were frequently identified in the studies presented in Chapter 4, table 5.1 summarizes the recommended operating conditions, according to the literature, to minimize their formation with this technology.

Table 5.1 - Recommended process conditions to minimize halogenated and perhalogenated compounds formation with BDD anodes.

Compound	Parameter	Process conditions	References
Chlorate and Perchlorate	pH	Working with acidic pH is advised.	[154]
	Current density	Low current densities.	[34,119,120]
	Chloride concentration	Operate with high chloride concentrations.	[119,120,159, 160]
	Electrolyte	The use of $NaNO_3$ supporting electrolyte as potential substitute to NaCl or Na_2SO_4.	[29,125]
Perbromate and Bromate	Current density	Low current densities.	[122]
	Temperature	No active cooling is needed.	

6. Conclusions

This review paper summarizes the current state of knowledge of the by-products electrogenerated by using BDD anodes in the different fields of water treatment. The major conclusions drawn are the following:

- The presence of reactive species plays an important role in the oxidation of the pollutants found in municipal landfill leachate, industrial wastewater, drinking water and municipal wastewater. Chlorine ions and hydroxyl radicals were mostly identified in the degradation of the contaminants.
- The formation of by-products is enhanced through the interaction between the pollutants and reactive species. The most common contributors for the generation of by-products are reactive oxygen and chlorine species due to their higher oxidation potential.
- The development of chlorinated by-products is dominant in all the areas, presumably due to the presence of chloride ions in the solution/water matrix. Other identified by-products are derivative species of the initial compounds, nitrogen species, aromatic and aliphatic compounds.
- The few toxicological studies available showed that the use of BDD technology lowers the initial toxicity of the solution. However, in terms of toxicity effects, there was a considerable number of by-products classified as possibly carcinogenic, endocrine disruptive and mutagenic.
- Operating conditions, such as current density, supporting electrolyte, pH, chloride concentration and temperature have an impact on the production of halogenated and perhalogenated by-products. The formation of chlorate and perchlorate can be reduced when applying an acidic pH, low current densities, high chloride concentrations and supporting electrolytes like $NaNO_3$. Avoiding the cooling and working with low current densities allows to diminish bromate and perbromate development.
- The BDD anode material itself can also affect the generation of reactive species and probably by-products. Relatively high diamond (sp^3 C) and graphitic (sp^2 C) content, for example, can favor the development of reactive chlorine species and reactive sulfate species.

7. Future perspectives

Electrochemical oxidation involving BDD anodes is becoming increasingly notorious for water treatment with demonstrated potential to remove a broad range of contaminants. However, a more comprehensive investigation of the by-products generated is required for the safe and beneficial use of this treatment technology. For instance, future studies, involving this technology and the oxidation of pollutants, should perform an in-depth analysis of by-products formation employing chemical analysis using HPLC or GC-MS. Further research is needed to assess the impact of different process conditions and BDD material characteristics on the by-product formation. This is essential since BDD has a high overpotential towards OER, meaning that it easily produces •OH, which interacts with the ions present in the bulk solution and, in certain conditions, may contribute to the undesired generation of hazardous species. For this reason, future studies on BDD-based EAOPs could be conducted with different supporting electrolytes and applying BDD electrodes with systematically varied material properties, including boron dopant density, non-diamond carbon content, grain morphology and surface finish.

Another aspect to consider in the future research is toxicity. This factor should be assessed and discussed more frequently since, in some cases, the formed by-products can have a higher toxicity than the initial compound and, consequently, be more harmful. Future studies should thus include a more frequent eco-toxicity assessment of the samples (e.g., with bacteria or embryo fish) to provide an accurate analysis of the possible adverse effects posed by the by-products generated with BDD in the respective field of water treatment.

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