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Electrochemical oxidation using a boron doped diamond electrode as a water treatment process- removal of residual micropollutants and inactivation of microorganisms

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Abstract

The presence of residual micropollutants in water sources enforce academic and industrial institutions to find, evaluate and introduce new treatment technologies. Advanced oxidations processes (AOPs) are a wide spectrum of treatment options – aimed at generating the highly active hydroxyl radicals ($^{\bullet}$OH) - to eliminate unwanted contaminates in water. Among different AOPs, electrochemical oxidation using boron-doped diamond (BDD) electrodes present an environmentally-friendly technology to remove micropollutants in the effluents of municipal wastewater treatment plants as well as industrial wastewater effluents.

BDD electrode has the ability to generate different oxidant species directly from water. Reactive oxygen species ($^{\bullet}$OH, ozone, hydrogen peroxide and others) and reactive chlorine species (active chlorine, chlorine radicals) are generated simultaneously in real water matric where chloride ions are presence.

In this dissertation, the influence of water matrix and the applied current density on the degradation of different micropollutants were tested. Three chemical substances were investigated, two pharmaceuticals, namely Diclofenac (DCF, nonsteroidal anti-inflammatory drug) and Sulfamethoxazole (SMX, antibiotic) and one industrial micropollutant, Bisphenol A (BPA). Another approach of this work was to assess the disinfection capability of a BDD electrode and define the operational framework (applied current density, the target level of disinfection) that allow such application for non-drinking water usage. Simultaneously to all experiments, the inorganic by-product formation and the specific energy demand were monitored. Among other objectives, the study wanted to define the optimal operational parameters that achieve an acceptable removal level of micropollutant or inactivation of microorganisms and the minimum concentration of inorganic by-products and energy demand.

The results presented in this work provided a relationship between the water matrix and its components and the degradation rate of selected micropollutants. The degradation rates decreased moving from deionized water to wastewater treatment plant effluents due to the complexity of water matrix. For the generated oxidants species, a competitive reactions occurred between the organic and inorganic constituents in the water matrix and target compound or microorganism. Hence, lower dissolved ozone concentrations were measured that resulted in a lower removal efficiency of contaminants. The applied current density is the most important parameter during an electrochemical oxidation using a BDD electrode. It effects the kinetic of

the degradation as well as the formation of inorganic by-products. An applied current density in the range of 100-200 mA cm^{-2} has resulted in an effective removal of micropollutant while mitigating the formation of inorganic by-products.

Finally, an effective 5-6 log inactivation of *Pseudomonas aeruginosa* was achievable and a synergic effect of the reactive oxygen and chlorine species was measurable. High concentrations of disinfection by-products (DBP) (up to 3 mg L^{-1}) were quantified, however it does respect the guidelines limits of non-potable water applications.

The present work has shown a promising potential for BDD electrode as a water treatment option. However, the up-scale approach requests a more reliable experimental set-up based on a continuous flow system. Hence, a realistic comparison between BDD and other treatment options (ozonation, active carbon, etc.) would be possible. Another improvement perspectives would be the enhancing of the hydrodynamic flow inside the reactor and the optimizing of the nano-diamond structure over the electrode.

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Im Namen Gottes, des Gnädigen, des Barmherzigen

Was euch an Wissen zuteil geworden ist, ist gegenüber Gottes Wissen wenig.

(*Quran. Surah:17-Aya:85*)

Sichtbar ist das Unheil an Land und auf dem Meer infolge der üblen Taten, die die Menschen begangen haben.

(Quran. Surah:30-Aya:41)

Contents

1 Chapter One
General Introduction

1.1 Elixirs of Death: Chemicals of Emerging Concerns (CECs) in the environment

In 1968, as the three-man crew of Appollo 8 took the first picture of the earth, rising in the endless dark of space, they were making an image that will write history. The blue Marble – as later known- was fascinating and simple. It is a huge creature made of blue. This Blue is the elixirs of life, it is water. In that image, we were unable to see the man-made pollution, slowly smashing this marble. Indeed, a few number of curious people –living on the blue marble– felt the silent threat. The scream of Rachel Carson, in her book *Silent spring* (1962), lightened the global environmental movement and the debate started.

Since a few decades, the fate of synthetic chemical substances in the environment has emerged as a hot topic (Schwarzenbach et al., 2006). With the increasing attention on the sustainability of our ways of life, new approach on the dimensions of environmental pollutions started and water became the core of the debates. The need for action got a strong attitude and shapes. Climate change, population growth and the needs associated with this explosive growth –world wide– is forcing us to consider each drop as a precious resource that must be used sagely.

Water contamination started to form a field of research in the academia and a huge number of scientific publications induced facts and solutions required to overcome this challenge. Amongst the different contaminants that have been identified, chemicals of emerging concerns (CECs) are of special interest because of their diversity, occurrence, ecotoxicological behaviour and the gaps in regulation. The spectrum of CECs is widely expanding from pharmaceuticals and personal care products (PPCPs) to industrial and agricultural chemicals, including food additives and biocides.

1.1.1 Origin and sources

With the wave of industrialization age, millions of chemical substances were introduced into our life. The numbers of registered chemicals, in the European Union –for instance–, is more than 140,000 and every day, new materials are added to the list (Strempel et al., 2012). During the life cycle of those chemicals, a small amount ended up in the industrial runoff and finally in the water bodies. Furthermore, everyday across the world, billions of people use pharmaceuticals and personal care products which –after serving their purposes in and on our bodies– make its way through the domestic wastewater streams and in best cases found its way into a sewage treatment plant. Urban sewage treatment plants, considered –among others– as major sources of CECs release into the water environment (Michael et al., 2013). Different source points (hotspots) are also responsible, directly or indirectly, for the discharge of these micropollutants into water bodies. Hence, abundant CECs can be found at concentrations of nanogram to microgram in freshwater ecosystem. In particular, Hospitals, industrial and agricultural zones are of high concern because of the high load of such compounds in their liquid discharges (Al Aukidy et al., 2014; Kümmerer, 2001; Pills Report, 2012). The life-cycle of CECs in our environment is illustrated in Figure (1), where several pathways are highlighted.

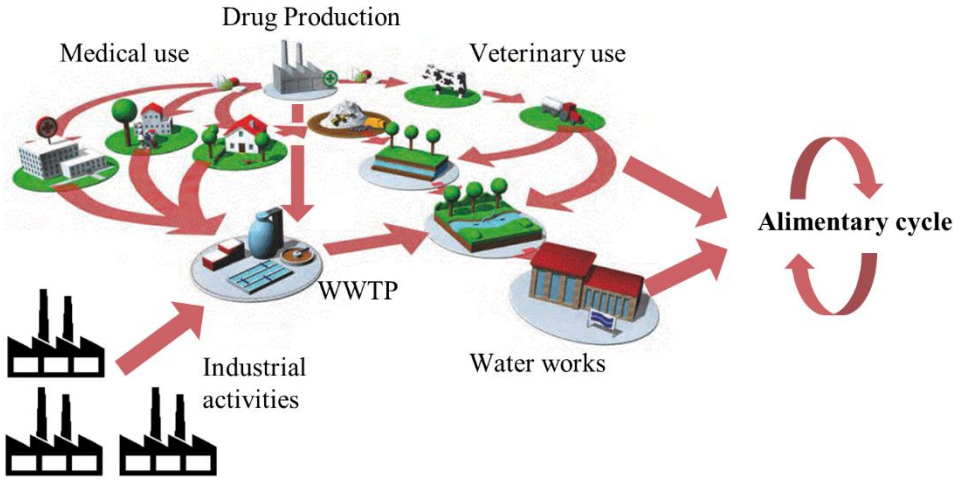

Figure 1- Pathways of input and distribution of CECs in the Environment. (Adapted from Pills Report, 2012)

1.1.2 Fate of CECs in the Environment

There are various sources of CECs in the water environment, however they could be categorized into three main domains viz: (1) domestic wastewater, hospital wastewater and runoff

from gardens, lawns and roadways (2) agricultural runoff, including concentrated animal feeding operations and aquaculture. (3) Industrial wastewater, including manufacturing and finishing discharges. The fate of CECs in the aquatic environment could be evaluated according to the type of water, which include wastewater treatment plants influent and effluents, surface water, ground water and drinking water. In general, a detectable concentration of micropollutants were reported in many studies, covering developed and developing countries. The following discussion will present some literature data about this point.

Different factors that affect the occurrence of micropollutants in water system have been identified. They include variation in climate conditions, physiochemical properties of the substance, water consumption per person per day, local usage and consumer behaviour. Consequently, the highest concentrations of micropollutants have been reported in raw wastewaters (domestic or industrial based), within a spectrum of concentrations that ranged between several hundreds of micrograms per litre and few nanograms per litre. In a recent study, Luo et al., (2014) reviewed many scientific publications, between 2008 and 2014, on the fate of micropollutants in wastewater treatment influents and effluents. Most reported compounds were detected in the concentrations that ranged between 0.1 and 10 µg L^{-1} in the influents. The concentrations detected in the effluents were much lower and the value ranged between 0.001 and 1 µg L^{-1}. A group of compounds –ibuprofen, caffeine, atenolol and nonylphenol– showed relatively higher concentrations in the influents (mean value > 10 µg L^{-1}). A possible reason for the higher concentrations of ibuprofen could be the easy accessibility and the high consumption (Takagi et. al., 2006). Caffeine is a compound present in tea, coffee and many soft drinks that are excessively consumed in our daily life which caused the significant concentrations in the wastewater streams. Steroid hormones and pesticides were detected in lower concentrations (mostly < 1µg L^{-1}). Industrial chemicals such as bisphenol A (BPA) and phthalate derivate were detected in the range of 1 and 10 µg L^{-1} in the influents. After passing the conventional wastewater treatment stages, all these compounds were detected in values lower than 1 µg L^{-1} (Alidina et al., 2014).

Surface waters are normally the receivers of wastewater effluent, after treatment. The residual concentrations of micropollutants attenuate naturally –to varying degree– via such processes as dilution, sorption onto sediment, photolysis and aerobic biodegradation (Pal et al., 2010). The geographical location of the surface water and the population density in this area have a significant effect on the fate of micropollutants in those water bodies (Nakada et al., 2008). The reported concentrations (Luo et. al. (2014), Pal et. al. (2010)) were mostly in the

range of ng L^{-1}. An alarming maximum concentration of ibuprofen (36.8 µg L^{-1}) was detected in Costa Rica (Spongberg et al., 2011). In Germany, Ternes (1998) reported a maximum concentration of 1.2 µg L^{-1} Diclofenac (DCF) in German river receiving sewage effluents. A common benzodiazepine, oxazepam, was reported in the Swedish surface water (River Fyris) in the range of 0.58 µg L^{-1} and in the treated wastewater effluents (0.73 µg L^{-1}) (Brodin et al., 2013). Sulfamethoxazole (SMX) was reported at concentrations less than 100 ng L^{-1} in some European surface waters (Luo et al., 2014). Industrial micropollutants like BPA have also been reported in many surface water sites in Germany, Canada and China, with maximum concentrations of 215, 87 and 881 ng L^{-1}, respectively (Kleywegt et al., 2011; Luo et al., 2014; Peng et al., 2008).

The correlation of the substances found in surface and ground waters is expected in drinking water. The data reviewed by Luo et. al. (2014) showed abundant of micropollutants in drinking water at concentrations below100 ng L^{-1}in different developed countries. However, carbamazepine was reported at concentration exceeding 600 ng L^{-1} in a Canadian study (Kleywegt et al., 2011). In all cases, the measured concentrations in drinking water were lower than the predicated no effect concentration (PENC). Pharmaceuticals traces were also detected in the drinking water of 24 major cities in the USA as shown in a study of 28 sampling stations (Donn et al., 2008).

As previously presented, the fate of micropollutants in water bodies present –without debt– a huge challenge for water and wastewater industries and research that must be considered (Snyder et al., 2003).

1.1.3 Environmental impact on human and other organisms

In the complex macroscopic ecosystem, human and organisms are exposed to a mixture of CECs. In the simplest case, just one isolated substance would affect the organisms. The functionality of many micropollutants –mainly PPCP and biocides– is designed to perform a concrete purpose in the target organism. The presence of those biological active substances in water bodies could have some effects on humans but those effects are still unknown. However, many evidences have shown that the interactions between CECs in the ecosystem and organisms – even at low concentrations – have negative impact. Brodin et al., (2013) reported that benzodiazepine anxiolytic drug (oxazepam) at environmental relevant concentrations (1.8 µg

L^{-1}), increased activity, reduced sociality and increased feeding rate of the wild European perch (*Perca fluviatilis*). The feminization of male fish is also an old topic related to the presence of endocrine-disturbing chemicals (EDCs) in water. A clear evidence from UK rivers, contaminated with treated wastewater effluents, where wild roach (*Rutilus rutilu*) have shown intersex indications (male fish with developing eggs in their testes) in all 17ß-estradiol (E_2) concentrations categories (<1 ng L^{-1} , 1-10 ng L^{-1} and > 10 ng L^{-1}) (Jobling et al., 2005).The same intersex problems have been reported in Canada (Bahamonde et al., 2015; Tetreault et al., 2011). The chronical toxicity effect of 17α-ethynylesthradiol (EE2) (synthetic estrogen used in birth-control pills) at a very low concentrations (5-6 ng L^{-1}) over a period of 3 years led to the collapse of fathead minnow population (*Pimephales promelas*) (Kidd et al., 2007). The same problem was reported by Brozinski el. al.(2013) as they detected three pharmaceuticals – naproxen, DCF and ibuprofen– in the bile of bream (*Abramis brama*) and roach (*Rutilus rutilus*). Even though the concentrations of the found micropollutants in the bile were in the range of ng L^{-1} (The worst case was 48 ng L^{-1} DCF in roach bile), it is an indication that treated wastewater discharges in surface water are the main resources of micropollutants in water bodies. The negative impact of micropollutants is not just related to a single organisms living in water environment but also to a group of population. In (2004), Oaks. et al. provided evidence that the residues of veterinary DCF present in the livestock carcasses were responsible for the dramatic decline (34-95%) in the population of the oriental white-backed vulture (*Gyps bengalensis*). After almost 8 years, the same phenomena was observed outside Asia where the carcass of Eurasian griffon vulture (*Gyps fulvus*) was found in Spain. The analyses of tissues have shown elevated flunixin (a nonsteroidal anti-inflammatory drug NSAID, the same group of DCF) (Zorrilla et al., 2014).

A new dimension of threats to human health is the spreading of antibiotic resistance bacteria in the ecosystem. Antibiotic residues have been identified as the main factor that increase resistance against antibiotics in some microorganisms through a gene selective mechanisms (Davison, 1999). Domestic and industrial discharges –loaded with antibiotics residues– increased antibiotic resistance in faecal bacteria located downstream of the discharge (Sidrach-Cardona et al., 2014).

The complexity and the diversity of CECs and their fate in the environment lead to the fact of exposing a mixture of substances, where each might be in an extremely low concentrations. A synergetic or additive effect could be expected with a very high negative impact. A mixture

of five estrogenic chemical –at concentrations of one-fifth of the median effective concentration (EC_{50}) of each chemical– has shown the potential to act additively and have a harmful effect on the male fathead minnows (Brian et al., 2005). This additive effect is not exclusive to estrogenic compound but it has also been recently reported for pesticides (Tang et al., 2014).

1.2 Removal of CECs from contaminated water: the available options

During the 20th century, wastewater treatment plants were designed and developed to achieve mainly two purposes. First, improving the hygienic conditions of the residential areas and second, reduce the organic loads discharged in the environments and removing nutrients such as nitrogen and phosphorus.

So far, conventional wastewater treatment plants have shown limited elimination rate of a wide range of micropollutants, thus action plans need to be developed on the strategies of eliminating these genre of pollutants from the aqueous streams. The tertiary treatment step considers the application of an advanced treatment systems to achieve a sufficient removal of micropollutants and a level of disinfection before discharge in surface water or reuse in the water cycle. In order to achieve this goal, different advanced treatment processes have been evaluated in the last few years. Depending on the mechanisms of treatment, the tertiary methods have been categorized, mainly into two groups (1) chemical oxidation including a spectrum of advanced oxidation processes (e.g. ozonation, Fenton reaction and UV/H_2O_2) (2) physical treatment, including membrane technologies and activated carbon adsorption. The later treatment option, however, have been found to be insufficient in removing polar organic compounds (Snyder et al., 2003) and has no disinfection potential in water.

During the last decade, the advanced oxidation processes (AOPs) gain more and more attention among water specialist in academia and the industry. These processes are based on the generation of highly reactive radical intermediate, especially the hydroxyl radical (Glaze et al., 1987). Hydroxyl radicals are among the most powerful oxidants known with a reaction rate constants in the range of 10^9 M^{-1} s^{-1} (Hoigne, 1997). The unselective characteristic of the hydroxyl radical induces a very large number of possible reactions with organic and non-organic species present in the reaction environment.

The spectrum of AOPs is very wide and can be categorized in two main group: Heterogeneous and Homogeneous processes. These include single and multiple combinations of oxidants that have been developed to eliminate organic pollutants, e.g.O_3, O_3/H_2O_2, H_2O_2/UV, UV/O_3, UV/TiO_2, Fe^{+2}/H_2O_2 and Fe^{+2}/H_2O_2+hυ (Fenton and photo-Fenton reactions). The oxidation reactions of contaminants by means of AOPs would –theoretically– end up in complete mineralization, however, the presence of oxidant scavengers will affect this approach. The scavenger species – organic and inorganic– will consume hydroxyl radicals, competing with organic pollutants for radical reactions. The practical application of AOPs is faced with the presence of such scavenger species in water that extends the treatment time and ending up in an economically less efficient process (Andreozzi, 1999). A new trend in the application of AOPs is the combination with a conventional–biological – step, as pre or post-treatment process, aimed at producing more biodegradable and less toxic intermediate products (Ganzenko et al., 2014).

In recent years, the electrochemical based AOPs –known as EAOPs–have gained more attention due to several advantages over normal AOPs (Martínez-Huitle and Ferro, 2006; Sirés et al., 2014; Sirés and Brillas, 2012). The EAOPs do not use any chemicals during the process. Besides, the operation under mild and versatile conditions, the high energy efficiency and the easy handling are – among other – advantages that distinguish the application of EAOPs (Sirés et al., 2014). The EAOPs can be classified into two groups: (1) Anodic oxidation (AO), where, at the anode surface, *in situ* OH radicals are generated. (2) Electro-Fenton (EF), via *in situ* electrocatalytically generated Fenton's reagent, including different coupling with other photo-, sono- or physio-chemical treatment methods (Oturan and Aaron, 2014). The present study focused more on the AO, using boron doped diamond electrode. The anode material is a crucial element in an AO. Originally, the AO process was conducted with high O_2 evolution overpotential anodes (Brillas and Martínez-Huitle, 2011), such as Pt, Graphite, PbO_2, doped SnO_2, IrO_2 or dimensionally stable (DSA) anodes. An essential feature of the anode material is to inhibit the generation of oxygen molecule and impose the formation of significant amount of oxidising agent such as hydroxyl radicals (Comninellis et al., 2008). The previously reported electrode materials are not stable against the reactive species formed on its surface and an erosion of the material would be possible (Barrera-Díaz et al., 2014). The boron-doped diamond (BDD) electrode, however, shows an outstanding specification for electrochemical oxidation processes promoting it as a very promising anode material.

1.3 Boron doped diamond (BDD) electrode

Among the different anode materials, boron-doped diamond electrode has shown a unique features which allows the application in different fields. Since the 1980s, different studies have been carried out to examine the utilization of BDD electrode for environmental applications (Fujishima, 2005). Thus, BDD electrode has drawn more attention as a convenient process for the *in situ* generation of different oxidant species and for the possession of operational advantages over other AOPs (Fryda et al., 2003; Kraft et al., 2003; Tröster et al., 2004).

1.3.1 Electrochemical properties and applications of BDD

Normal intrinsic diamond is an insulator (band-gap = 5.45 eV) and not suitable for use as an electrode material (Comninellis and Chen, 2010). However, by doping it with certain elements (phosphorous, nitrogen, or boron), electrical conductivity property is achieved. In most cases, boron is used as a dopant, resulting in a p-type semiconductor (Kraft, 2007). Because of the low activation energy of boron atoms (0.37 eV), they act as an acceptor (positive charges or holes) in the structure of boron-doped diamond. Increasing the concentration of boron atoms in the structure would affect the conductivity behaviour of the electrode thus, a typical boron concentration in diamond is around 10^{19}-10^{21} atoms cm^{-3} (Ferro, 2002; Kraft, 2007).

The most striking electrochemical feature of the doped diamond is the very high overpotential for both oxygen and hydrogen evolution. Comparing a BDD electrode with other common electrode materials (e.g. platinum, iridium dioxide), a much higher overpotential of diamond electrode for oxygen and hydrogen evolution is obvious Fig. (3). The wide potential window from -1.25 V to + 2.8 V vs. standard hydrogen electrode (SHE) enables the generation of strong oxidants such as ozone and hydroxyl radicals, with small amount of side reactions for oxygen evolution (Tröster et al., 2002). Another feature of boron-doped diamond is its corrosion stability with inert surfaces and low adsorption capability for atomic hydrogen or oxygen (Fryda et al., 2003; Fujishima, 2005). These features give the BDD electrode a promising future in many environmental applications, as well as chemical (analytical and synthetic) and industrial fields.

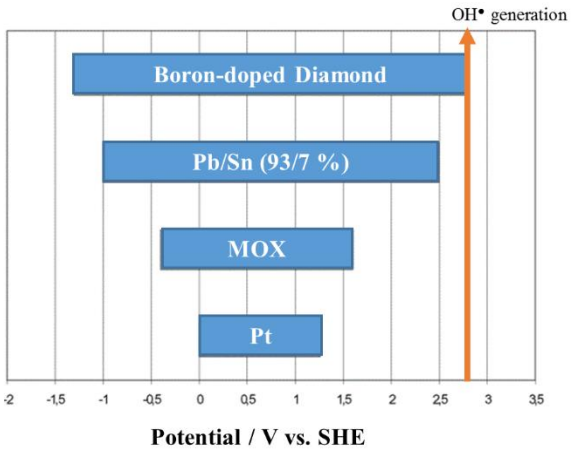

Figure 2. Overvoltage values before water decomposition for BDD electrode compared to common materials. The width of the bars represent the potential region for water stability in electrochemical applications- (adapted from Tröster et.al 2002).

1.3.2 Oxidants formation on BDD

Different forms of reactive oxygen species, such as hydroxyl radicals ($HO^{\bullet}$), hydrogen peroxide (H_2O_2), and ozone (O_3), could be generated, *in-situ* via water oxidation on BDD electrodes. In aqueous solutions, the main reaction on BDD electrode is the formation of hydroxyl radicals which is the primary product (eq.1.1 (Michaud et al., 2003)).

$$H_2O \rightarrow HO^{\bullet} + H^+ + e^- \quad (1.1)$$

Bergmann (2010) also reported the formation of hydroxyl radicals from hydroxide ions on the BDD surface (eq. 1.2)

$$OH^- \rightarrow HO^{\bullet} + e^- \quad (1.2)$$

After the formation of the hydroxyl radicals, and because of the extremely reactive properties of those radicals, the occurrence of other reactions follow. Hydrogen peroxide is generated by the reaction of two hydroxyl radicals, with each other or with water (eq. 1.3) (Bergmann, 2010; Marselli et al., 2003; Michaud et al., 2003).

$$2HO^{\bullet} \rightarrow H_2O_2 \quad (1.3)$$

This then diffuses in the solution as shown in (1.4) or is oxidized to oxygen as in (1.5)

$$(H_2O_2)_{electrode} \rightarrow (H_2O_2)_{solution} \quad (1.4)$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \quad (1.5)$$

A further reaction of hydroxyl radicals is the oxidation to atomic oxygen (1.6), then formation of ozone by reaction with dioxygen (1.7) or evolution of oxygen gas (1.8)

$$HO^{\bullet} \rightarrow O^{\bullet} + H^{+} + e^{-} \quad (1.6)$$

$$O^{\bullet} + O_2 \rightarrow O_3 \quad (1.7)$$

$$2O^{\bullet} \rightarrow O_2 \quad (1.8)$$

The equations 1.4 through 1.8 were also reported in previous studies (Arihara et al., 2006; Bergmann, 2010; Marselli et al., 2003; Michaud et al., 2003).

On the cathode, where proton (hydrogen ions) are reduced to form hydrogen gas (eq. 1.9)

$$2H^{+} + 2\,e^{-} \rightarrow H_2 \quad (1.9)$$

Beside reactive oxygen species (e.g. $HO^{\bullet}$, O_3, H_2O_2, $O^{\bullet}$), other oxidants species could be formed. In real water matrix, an abundance of inorganic anions such as chloride (Cl^{-}), sulfate (SO_4^{-2}) are present, and those ions could be oxidized on the BDD electrode to form new oxidants in the matrix such as chlorine species Cl_2, HClO and ClO^{-} (Martínez-Huitle and Brillas, 2009) or peroxodisulfate $S_2O_8^{-2}$ (Michaud et al., 2003).

In summary, BDD electrode in aqueous solution has the capability to generate, *in-situ*, a mix of reactive oxygen species and other oxidants which undergo the direct and indirect degradation of organic pollutants or inactivate microorganisms in contaminated water.

1.3.3 Application of BDD for CECs elimination

The use of BDD electrode for the degradation of wide range of CECs have been shown in several studies and reviewed in a recent publication (Oturan and Aaron, 2014). The operational parameters varied among all studies, however the efficiency of the degradation process is always affected by the applied current densities and the initial concentration of the micropollutants. A common outcome of all studies was the total removal of pollutants and high mineralization efficiencies. Another significant observation is that very few studies were conducted in urban or industrial wastewater treatment effluents. Table 1 gives some details on selected number of studies of BDD application for micropollutants removal in different water matrices-

Table 1: selected –recently published (2012-2015) - researches of EAOP using BDD electrode for degradation / mineralization of CECs in different water matrices

Pollutant	Matrix	Experimental conditions	Results summary	Reference
Diclofenac (DCF)	Bidistilled water	Batch reactor; $[Na_2SO_4]$=0.1 M, $[DCF]_0$= 300 mg L^{-1}, reaction volume :100 mL ; Electrode BDD/Nb: 6 cm^2; current density: 42 mA cm^{-2}; room temperature	DCF reduction of 99.8% within 600 min of electrolysis. Disappearance of the solutions' toxicity after 5-8 h of electrolysis for a solution of 10 mg L^{-1} and an applied current density of 8 mA cm^{-2}	(Vedenyapina et al., 2013)
	Deionized water	Batch reactor; 64 cm^2 BDD/Ti; $[DCF]_0$=150 mg L^{-1}; $[NaClO_4]$=0.5 M; PH=6.5; current densities=10, 15 and 20 mA cm^{-2};	Higher DCF decay was achieved at a current density of 15 mA cm^{-2}. Higher current density lead to oxygen evolution and less efficiency. A fluid velocity (u) between $41.1 \leq u \leq 58.4$ cm s^{-1} has no effect on the DCF degradation.	(Coria et al., 2014)
Ibuprofen	Deionized water	Batch reactor; Reaction volume: 200 mL; 25 cm^2 BDD/Nb anode. 20 ± 2°C ; $[IBU]_0$= 0.2 mM and 0.05 , 0.1 mM; $[Na_2SO_4]$=0.05 M or [NaCl] = 0.1 M; PH=3; current densities= 2, 4, 8, 12, 20 mA cm^{-2}	A pseudo-first-order kinetic for IBU degradation. The apparent rate constant increase with applied current and independent on the initial concentration. NaCl as a supported electrolyte is performing better than Na2SO4. An almost complete mineralisation of IBU in 480 min of electrolysis	(Ambuludi et al., 2013)

Table 1 (continued)

Pollutant	Matrix	Experimental conditions	Results summary	Reference
Sulfamethoxazole (SMX)	Synthetic wastewater	Batch reactor; $[SMX]_0$=0.1-100 mg L^{-1}; 78 cm^2 BDD anode; reaction volume=500 mL; flow rate=21.4 L h^{-1}; $[Na_2SO_4]$=5000 mg L^{-1}; current densities= 15-100 mA cm^{-2}; 25°C	A reduction of the SMX concentration below 0.1 mg L^{-1} was achievable. The degradation rates increased with an increase of the applied current densities. TOC measurement refer to reduction but not completely mineralisation after 350 min of electrolysis	(Martín de Vidales et al., 2012)
	Wastewater solution	Batch reactor; reaction volume= 500mL; $[SMX]_0$= 250 mg L^{-1};$[Na_2SO_4]$=0.1 mol L^{-1}; 36 cm^2 BDD/Nb anode; current densities= 7.2, 21.7 and 36 mA cm^{-2}; flow rate=1.5, 3.5 and 5 L min-^{1}; 25°C	The best obtained conditions for SMX degradation were 36 mA cm^{-2}, pH=5 and flow rate 5 L min^{-1}.Increasing the flow rate accelerate the degradation kinetic. Current efficiency increased with when applied lower current density. Different TPs were identified.	(de Amorim et al., 2013)
Sulfonamides	Deionized water / secondary WWTP effluent	Batch reactor; reaction volume=100 mL; For deionized water matrix $[Na_2SO_4]_0$=6.1 g L^{-1}; [each SNs]$_0$=10, 50, 100 and 200 mg L^{-1};different temperature values 25-60°C; different PH=2.0-7.4;current densities= 0.05, 2, 5, 10 and 15 mA cm^{-2}.10 cm^2 BDD/Si anode	Higher degradation rate were achieved at higher current density but the current efficiency decreased. Higher temperature accelerates the degradation process. Higher degradation grade in WWTP effluent compared with deionized water with supporting electrolyte.	(Fabiańska et al., 2014)

Table 1 (continued)

Pollutant	Matrix	Experimental conditions	Results summary	Reference
Sulfamethazine	Deionized water	Batch reactor as divided and undivided cell; 3 cm^2 BDD anode; reaction volume=100 mL ;[sulfamethazine]$_0$= 193-1930 mg L^{-1}; [Na_2SO_4]=0.5 mol L^{-1}; PH= 2.0-6.0; current densities=33.3 – 150 mA cm^{-2}; 35 °C	Divided cell showed better degradation ability. Almost total mineralisation was achieved for 193 mg L^{-1} initial concentration and 0.5 mol L^{-1} Na_2SO_4 at current densities ≥66.6 mA cm^{-2}.	(El-Ghenymy et al., 2013)
Dipyrone (Sodium metamizole)	Deionized water	Flow-by reactor with 50 L h^{-1} and 300 L h^{-1}; 16.6 cm^2 BDD/Ti anode; reaction volume=2 L; [Na_2SO_4]=0.1 mol L^{-1} and [K_2SO_4]=0.1 mol L^{-1}; [Dipyrone]$_0$=100 mg L^{-1}; applied potential = 0.5 -5.5 V.	Better removal of dipyrone at higher flow rate and higher applied potential. The highest TOC removal was achieved at an applied potential of 5.0 V and a flow rate of 300 L h^{-1} and reached 95.2% after 8 h reaction.	(Reis et al., 2013)
Omeprazole	Deionized water	Batch reactor; reaction volume = 100 mL; 3 cm^2 BDD/Si anode; Carbon-PTFE air-diffusion electrode as a cathode where H_2O_2 could be generated; [omeprazole]$_0$= 16.9 (or) 169 mg L^{-1}; 0.146 M NaH_2PO_4 + 0.025 M H_3PO_4; current densities= 33.3 - 150 mA cm^{-2}; 35 °C	BDD anode was able to partially mineralize omeprazole (78%) at 100 mA cm^{-2} after 360 min of reaction (18 Ah L^{-1}). Enhancement of degradation rate was performed when increasing the applied current density and the initial concentration. Different intermediate were identified.	(Cavalcanti et al., 2013)

Table 1 (continued)

Pollutant	Matrix	Experimental conditions	Results summary	Reference
Cyanazine	Deionized water	Batch reactor; reaction volume=100 mL; [Na_2SO_4]= 0.05 mol L^{-1}; PH=3; 3 cm^2 BDD/Si anode; Carbon-PTFE O_2-diffusion electrode as a cathode where H_2O_2 could be generated; [cyanazine]$_0$= 55, 110, 145 mg L^{-1}; current densities=33.3 – 150 mA cm^{-2}; 35 °C	The mineralization rate increased with increasing current density. 69% TOC removal was achieved at 150 mA cm^{-2} and 110 mg L^{-1} initial concentration. Better TOC removal was achievable using Electro-Fenton or Photoelectro-Fenton.	(Borràs et al., 2013)
Imazapyr	Deionized water	Batch reactor; reaction volume= 450 mL; [K_2SO_4]= 0.1 mol L^{-1} ; 4.15 cm^2 BDD/Ti anode; [imazapyr]$_0$=4.6-100mg L^{-1}; current densities=10, 50, 100, 150 mA cm^{-2};PH=6.8	BDD can successfully applied to treat imazapyr contaminated aqueous solutions; An optimum condition for a completely degradation was 50 mA cm^{-2} and PH=3 and 45°C. Higher initial concentrations require higher current charge to be completely degraded.	(Souza et al., 2014)
2,6-dichlorobenzamide (BAM)	Deionized water	Batch reactor; reaction volume=1.0 (or) 0.5 L; [BAM]$_0$=100 mg L^{-1}; [NaCl]=0.10 M; 10 cm^2 BDD/Nb anode.	After 400 min of treatment, almost 90% removal was achieved More transformation products were formed due to the presence of chloride ions. Two degradation pathways were identified.	(Madsen et al., 2015)

Table 1 (continued)

Pollutant	Matrix	Experimental conditions	Results summary	Reference
Tetracycline	Real secondary WWTP effluent	Batch reactor; reaction volume=100 mL; $[Tetracycline]_0$=25, 50 and 100 mg L^{-1}; $[Na_2SO_4]$=0.1 M; 1 cm^2 BDD/Nb anode; current density= 50, 100 and 200 mA cm^{-2}	90% degradation was achieved after 30 min reaction applying 200 mA cm^{-2}. The differences between 100 and 200 mA cm^{-2} were not significant. The degradation efficiency increased with increasing current density and temperature but noticeably decreased with increasing the initial concentration. 75% TOC removal and ca. 100% tetracycline degradation were achieved in WWTP within 150 min of reaction.	(Chen et al., 2014)
Abamectin-Acaricide	Deionized water	Batch reactor; reaction volume=75 mL; $[Abamectin]_0$= 10 mg L^{-1}; $[COD]_0$=2340 mg L^{-1}; [NaCl]= 2 g L^{-1}; other supporting electrolyte were tested; 1 cm^2 BDD anode; current densities= 15-80 mA cm^{-2}	Around 88% of COD removal was achieved applying 60 mA cm^{-2} and 2 g L^{-1} of NaCl. Higher current densities lead to higher degradation level. Higher electrolyte concentration decrease the COD removal. 98% removal of initial Abamectin concentration was achieved after 2.5 h and 80 mA cm^{-2}.	(Errami et al., 2014)
Methyl Parathion (MP)	Deionized water	Batch reactor (H-type cell); reaction volume= 250 mL; 40 cm^2 BDD anode; $[MP]_0$=100 ppm; $[Na_2SO_4]$=0.04M and $[NaHSO_4]$=0.05 M; current densities:0.25, 0.625, 1.25, 2.5 and 5 mA cm^{-2}; PH=2.0	Applying 5 mA cm^{-2}, and after one hour of reaction, the initial concentration of MP was decreased from 100 to 10 ppm. Two hours were needed to reach 0 ppm at 5 mA cm^{-2}, where three hours were needed to reach the 0 ppm applying 0.625 mA cm^{-2}.	(Campos-González et al., 2014)

Table 1 (continued)

Pollutant	Matrix	Experimental conditions	Results summary	Reference
Methyl Parathion (MP)	Deionized water	Batch reactor; reaction volume=350 mL; 4.15 cm^2 BDD/Ti anode; $[MP]_0$=60 mg L^{-1}; $[H_2SO_4]$=0.1 M; 25°C; current densities= 5, 10, 25, 50 and 100 mA cm^{-2};	80% MP degradation was achievable applying 100 mA cm^{-2} after three hours of reaction. Just 20% removal of MP when applying 5 and 10 mA cm^{-2}.	(Alves et al., 2013)
Profenofos	Deionized water	Batch reactor; reaction volume= 2L; $[Profenofos]_0$= 400mg L^{-1};$[H_2SO_4]$=0.1 mol L^{-1} and $[K_2SO_4]$= 0.1 mol L^{-1}: 16.6 cm^2 BDD/Ti anode; current densities= 10 to 200 mA cm^{-2}.	The morphological character of the BDD surface has an effect on the degradation efficiency. Small grain diamond structure electrode operating at a flow rate of 300 L h^{-1} and 200 mA cm^{-2} has achieved a removal of 96.5 % of Profenofos after 2 hours of operation. This was 70% when using a big grain of diamond on the surface of electrode. A TOC removal of 87% was possible.	(Cordeiro et al., 2013)
Bisphenol A (BPA)	Deionized water	Batch reactor; reaction volume= 400mL; $[BPA]_0$= 150mg L^{-1};$[H_2SO_4]$=0.1 mol L^{-1}; 18 cm^2 BDD/Nb anode; current densities= 6.5, 15 and 30 mA cm^{-2}; flow rate=1.5, 4.0 and 7.0 L min^{-1}; 25 and 40°C	Abatement of COD was affected by flow rate, temperature and current density; current efficiency was higher after hydrodynamic optimization of the reactor. The best conditions in term of current efficiency were the highest flow rate and the lowest current density	(Pereira et al., 2012)

1.3.4 Inactivation of microorganisms using BDD

Beside the removal of CECs, disinfection can be obtained by BDD application. Conventional disinfection technologies such as chlorination or ozonation have different drawbacks that limit their application in some cases. The chemicals used in such technologies require high safety specifications to be considered, thus enhancing the operation costs. Furthermore, the formation of disinfection by-products (DBPs), during chlorination or ozonation and the loss of disinfection efficiency, through the presence of organic matter, are crucial when considering those technologies (Li and Ni, 2012; Sedlak and von Gunten, 2011). The applicability of physical disinfection processes such as UV irradiation, membrane separation and thermal disinfection is associated with high cost and maintenance efforts and does not fulfil the requirements for primary and residual water disinfection (Martínez-Huitle and Brillas, 2008; Schmalz et al., 2009).

BDD electrode offers an environmentally friendly, economically and operationally competitive technology, which is applicable in a wide range of microbiologically contaminated water. Reactive oxygen species (ROS), such as hydroxyl radicals, ozone, singlet oxygen and hydrogen peroxide, are formed during the operation in water on the surface of the electrode and in the bulk solution leading to a high efficiency during the oxidation process. In the presence of ions, such as chloride, sulfate and bicarbonate, free chlorine, peroxodisulphate and other weak oxidants can be produced during the electrolysis, which are known to be powerful disinfectants (Pérez et al., 2010; Polcaro et al., 2009).

1.3.5 By-products formation

A drawback of electrochemical oxidation using BDD electrodes is the formation of organic and inorganic by-products (or disinfection by-products (DBPs)) (Bergmann. et al., 2011; Bergmann and Rollin, 2007; Haaken et al., 2012). In a real case, where the contaminated water contains chloride and bromide ions, such by-products formation would be unavoidable. The highly reactive oxidant species, formed during the electrolysis process – mainly hydroxyl radicals and ozone – are able to oxidize halogenated ions present in water (Deborde and von Gunten, 2008; von Gunten and Pinkernell, 2000). Among the generated inorganic by-products, bromate, chlorate and perchlorate are of great concern because of their negative impact and

possible carcinogenic effect on human health (Bergmann et al., 2010; 2011). Hydroxyl radicals (Standard oxidation potential E° = 2.80 V vs. SHE at 298.15 K) are capable to oxidize chloride ions (eq. 1.11) and forming hypochlorous acid ($ClOH^-$) (eq. 1.12) (von Gunten, 2003), which in further oxidation steps would form chlorate (ClO_3^-) and perchlorate (ClO_4^-) (Palmas et al., 2007)

$$Cl^- \rightarrow Cl^{\bullet} + e^- \; (E^{\emptyset} = -2.59\, V\ vs.SHE) \text{ (Isse et al., 2011)} \quad (1.11)$$

$$Cl^- + HO^{\bullet} \leftrightarrow ClOH^- \quad (1.12)$$

However, chloride is not oxidized by ozone (E° = 2.08 V vs. SHE at 298.15 K) but bromide can be oxidized by both ozone and hydroxyl radicals (eq.1.13-1.15) (von Gunten, 2003).

$$Br^- \rightarrow Br^{\bullet} + e^- \; (E^{\emptyset} = -2.04\, V\ vs.SHE) \text{ (Isse et al., 2011)} \quad (1.13)$$

$$Br^- + HO^{\bullet} \rightarrow BrOH^- \quad (1.14)$$

$$Br^- + O_3 \rightarrow BrOOO^- \rightarrow OBr^- + O_2\ (or)\ Br^{\bullet} + O_3^{\bullet -} \quad (1.15)$$

The bromide species formed through the previous reactions could be further oxidized to form bromate (BrO_3^-) and perbromate (BrO_4^-).

Moreover, the reaction of halogen species with organic molecules found in water will promote the formation of the harmful adsorbable organically bound halogens (AOX) and the trihalomethanes (THMs). Those species were measured and reported elsewhere (Heim et al., 2014; Ureña de Vivanco, M., 2013).

1.4 Research Objectives

Within a framework of electrochemical advanced oxidation process (EAOP), using BDD electrode, the overall aim of this dissertation is to investigate the applicability of the BDD electrode as an EAOP for water and wastewater treatment. This overarching goal is divided into three main objectives including (i) electrochemical oxidation of three selected micropollutants, namely, DCF, SMX and BPA in different water matrices (ii) inactivation of *Pseudomonas aeruginosa* as representative of microorganisms in contaminated water using BDD (iii)

simultaneously to the previous two objectives, assessing the formation of inorganic by-products and the specific energy demand during the process. Details on the objectives and the related hypotheses are provided in the following sections

1.4.1 Task 1: Influence of the water matrices on the DCF degradation

Research Questions: How can the water compositions affect the electrochemical degradation of DCF using BDD electrode? Is it possible to apply a serial coupling of RP and HILIC LC-MS for the identification of transformation products (TPs) and what are the results obtained? How can a suspected screening of TPs be conducted with respect of the physical-chemical properties of the suspected TPs?

Hypotheses: The differences in water composition will affect the degradation process of DCF using BDD electrode. Both inorganic and organic substances in water matrix consume the reactive oxygen species which result in a slower degradation process. DCF and some of its TPs can be detected using RP-HILIC LC-MS serial coupling as a new analytical method.

Objectives:

- Electrochemical degradation of DCF in three water matrices. The water matrices are pure water, synthetic water simulating a hard drinking water and the effluent of WWTP as a real water matrix. The influence of water composition on the degradation process will be assessed.
- Prepare a list of known TPs of DCF degradation by means of AOPs. The list contains analytical information such as accurate mass (m/z), Log*D* and molecular formula.
- Based on the information of the TPs list, develop a procedure for the identification of the suspected TPs. The relationship of retention time, log*D* and the TPs mass should be integrated in this approach to show the effect of the serial coupling of RP-HILIC LC-MS method.

1.4.2 Task 2: Influence of the applied current densities on the degradation of SMX in wastewater effluent.

Research Questions: What is the effect of applied current densities on the electrochemical degradation of SMX using BDD electrode? In a real WWTP effluent, is it possible to achieve

a total removal of SMX? How do the detected TPs develop during the process? What is the specific energy demand associated with the process and how can it be assessed?

Hypotheses: BDD electrode will be able to degrade SMX in real WWTP effluent and different known TPs would be detectable applying the RP-HILIC LC-MS approach. One of the main operational parameters during EAOPs using BDD electrode is the applied current density. An increase in its value will lead to an acceleration in the degradation process. However, this acceleration is associated with an increase in the energy demand.

Objectives:

- Electrochemical degradation of SMX in WWTP effluent applying two different current densities, namely 208 and 333 mA cm^{-2}.
- A suspected screening approach as described in task 1 would be applied to identify known TPs. Compare the development of the TPs during the two experiments.
- Estimate the specific energy demand of the process.

1.4.3 Task 3: Degradation of BPA in different water matrices and applying different current densities.

Research Questions: What are the effects of the water matrix and applied current densities on the electrochemical degradation of BPA? Based on the identified TPs, can the water matrix affect the degradation pathway of BPA? In a WWTP effluent, how do the formation of inorganic by-products develop? What are the possibilities to control the energy demand and the formation of inorganic by-products during the process?

Hypotheses: In an electrochemical degradation process applying BDD electrode, the components of water matrix has a limited effect on the degradation pathway of the BPA. The degradation of BPA in WWTP effluent will lead to the removal of the parent compound but not to full mineralization. Under those conditions, high concentrations of inorganic by-products will be formed.

Objectives:

- Electrochemical degradation of BPA is studied in four different water matrixes and two different current densities. The water matrices are deionized water, synthetic water with and without dissolved organic compound and WWTP effluent. The current densities are 125 and 208 mA cm^{-2}.
- A suspected screening approach as described in task 1 will be executed to identify the known TPs in the treated deionized water and WWTP effluent. Construct a degradation pathway based on the identified TPs and assessing any differences in the pathway due to the water matric.
- Quantify the inorganic by-products (chlorate and perchlorate) and estimate the specific energy demand of the process and discuss those value from an applicability perspective.

1.4.4 Task 4: Electrochemical disinfection using BDD electrode

Research Questions: What is the influence of chloride ion concentration on the disinfection performance of a BDD electrode? How does the disinfection performance interact with the applied current density during the process? How to optimize the relation between the disinfection level, the formation of disinfection by-products (DBP) and the energy demand of the process?

Hypotheses: The electrochemical disinfection using BDD electrode achieves high disinfection level of *Pseudomonas aeruginosa* (*P. aeruginosa*) in a water matrix contains chloride ions. A synergetic effect of *in-situ* ozone and the free chlorine generated during the process will result in an effective bactericidal impact. At lower current densities, the DBP formation, the energy demand and the disinfection level could be integrated in an achievable approach.

Objectives:

- Electrochemical disinfection of *P. aeruginosa* in deionized water at two – relatively low – current densities (42 and 167 mA cm^{-2}) to show the efficiency of disinfection.
- Compare the disinfection performance of the BDD electrode in different water matrices. Beside deionized water, two synthetic waters with different chloride ion concentrations are considered.

- Follow the concentration of the dissolved ozone and free chlorine during the experiment.
- Quantify the DBP (chlorate and perchlorate) and monitor the energy demand during the process.
- Connect the desired disinfection level with the energy consumption and the concentration of DBP to simulate an applicable scenario.

1.5 Organisation of Dissertation

The dissertation is organized into seven chapters. Chapter 1 provides an introduction, including background of the CECs problematic in the environment and available technologies to remove CECs. The EAOP using a BDD electrode was described. The applicability of BDD electrode for CECs removal and for disinfection was presented. A literature review of some of the recent scientific works done in this field was summarized. The drawback of the BDD electrode regarding the formation of inorganic by-products was referred to in this chapter. Moreover, the objective of the dissertation, tasks and hypothesises were introduced. Chapter 2 describes the experimental setup and summarizes the applied parameters in the following tasks. Chapter 3 includes the results of the research. Task 1 was published in Journal of Separation Science in August, 2013 and is presented as point 3.1. Task 2 was published in the international Journal of Environmental Pollution and Solutions in October, 2013 and is presented as point 3.2. Task 3 has been submitted to Chemosphere and is presented as point 3.3. Task 4 was published in Chemosphere in November, 2014 and is presented a point 3.4. The last Chapter, 4, presents the research conclusions and an Outlook for the future work.

2 Chapter Two
Materials and Methods

2.1 Experimental setup

All experiments were performed using a conductive diamond electrode system (Figure 4). (CONDIAS GmbH, Itzehoe, Germany). The system consisted of a feed container (1), holding the contaminated water, before it was circulated through the reaction cell (4) by means of a centrifugal pump (2) (NPY-2051, Speck Pumpen, Hilpoltstein, Germany), at the pre-determined constant flow rate. The electrical power was provided by a laboratory power supply (5) (EA-PS 3032-10B Heiden Power-Germany). Two sensors (3) placed on the hoses connecting the different parts were placed to measure the temperature, pressure and flow rate. Three reaction cells (4) where used. The first reactor (Glass reactor (Esau & Hueber)/ 92 cm^3) was a double chamber cell with a cylindrical cross section (Ureña de Vivanco, M. et al., 2013). The second reactor was CONDIAPURE® (CONDIAS GmbH, Germany) and has a volume of 45 cm^3 and a cylindrical cross section. The third reactor was a modified generation of the second one (CONDIAPURE-SHORTY ®) within a 19 cm^3 volume and a rectangle cross section. Figure 5 showed the detailed geometric scheme of the three used reactor cells.

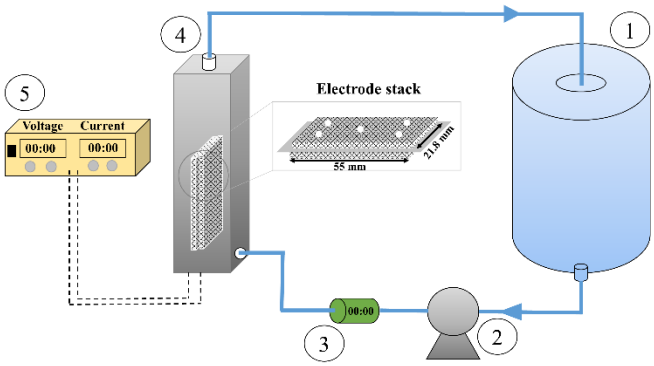

Figure 3- Flow schematic of the BDD system. (1) Feed container (2) pump (3) sensors (4) reactor cell (5) power supply

The electrode stack consisted of two BDD cathodes and two BDD anodes on a niobium substrate (CONDIAS GmbH, Germany), with an overall effective anode area of 24 cm^2 (For

the DCF experiments, an electrode stack of one cathode and one anode was used with an overall anode area of 12 cm²). A nafion cation exchange membrane was placed in direct contact to each cathode and anode in order to receive a gap-free sandwich structure. This enhanced the current density locally and therefore promoted ozone formation and enabled the operation of the electrode at low electrical conductivities (Kraft et al., 2006b, 2006a). The system was operated in a recirculation mode so that flow rate could be adjusted between 0.5 and 10 L min^{-1}. The applied current could be regulated between 0 and 10.0 A. All experiments were conducted at room temperature (25 ± 2 °C) and slightly alkaline pH value (8.5 ± 0.5). Different current densities were applied, depending on the goal of the experiments. A summary of the applied parameters for all the experiments conducted is shown in Table 3.

Kraft et al. (2006b) has shown that the best current efficiency (20-24%) for ozone generation should be located in the range of 50 and 175 mA cm^{-2} and that after this range, the efficiency decreased owing to an increase in ozone decay in the water. Previous studies (Heim et al., 2011; Ureña de Vivanco, et al., 2013) have shown that efficient ozone production, applying the same BDD electrode at lower current densities than 42 mA cm^{-2} is not sufficient. This could be due to the confinement of generated hydroxyl radicals to the electrode surface. Consequently, the lowest applied current density in the recent studies (42 mA cm^{-2}) was chosen, with respect to the possibility of efficient ozone production as well as a minimum energy consumption during the process. The other applied current densities (167, 208, 291 and 333 mA cm^{-2}) were selected to assure a sufficient ozone generation and simultaneously a worst-case scenario for DBPs formation. All experiments were carried out in duplicate and showed a good reproducibility. The mean values of the results of the replicated experiments are presented. Samples were collected directly before the feed container (Fig.4 (1)) after a period of 0, 1, 2, 3, 5, 7.5, 10, 15, 20, 30 and 60 minutes. The oxidation reaction in the sample was stopped by adding 20 µL of 10 mM Na_2SO_3 solution after sampling, and then filtered through 0.22 µm PVDF Pleomax filters before the chromatographic analysis

2.2 Chemicals and water matrices

Phosphoric acid (85%), 5,5-indigodisulphonic acid sodium salt (indigo carmine), sodium hydroxide (NaOH), sodium thiosulfate ($Na_2S_2O_3$), sodium sulfite (Na_2SO_3), calcium chloride ($CaCl_2$), potassium bromide (KBr), potassium iodide (KI), magnesium sulphate heptahydrate ($MgSO_4 \cdot 8H_2O$), sodium hydrogen carbonate ($NaHCO_3$) and sodium nitrate ($NaNO_3$), as well

as ethylenediamine monohydrate and bovine serum albumin (BSA) were purchased from Merck (Germany). Native humic acid (30-40% soil extract) was purchased from Carl Roth (Karlsruhe, Germany). All chemicals were of analytical grade. DCF and BPA were purchased from Sigma–Aldrich Chemie (Steinheim, Germany). SMX was purchased from Sigma Aldrich (St. Louis Missouri, USA). Acetonitrile HiPerSolv Chromanorm was purchased from BDH (Poole, UK). Water LC-MS Chromasolv was bought from Fluka (Buchs, Switzerland). Ammonium acetate was purchased from Sigma-Aldrich (Seelze, Germany). Fumaric acid, oxalic acid, metha- and para-hydroxybenzoic acids were obtained from Sigma (Deisenhofen, Germany), maleic acid from SERVA (Heidelberg, Germany). All chemicals were of analytical-reagent grade. The solutions were prepared using deionized water ultra-pure water (Milli-Q, 18.2 MΩ cm).

Experiments were carried out in three water matrices: MilliQ water (deionizer "Milli-Q Plus 185", electrical conductivity of 0.055 µS cm at 20°C, pH 5.5), a real effluent of the municipal WWTP, Garching, Germany, collected after the secondary sedimentation stage and before the UV irradiation step. Different synthetic water matrices were prepared as stated in the different sections of the thesis. In order to ensure the clarity of the experimental method, the details of the compositions of the different synthetic waters are presented in the materials and methods section.

2.3 Methods

All analytical methods (chemical and biological) applied during the study are presented in the related tasks.

Table 2 a summary of the applied parameters during the experiments

	P.aeruginosa Disinfection	Bisphenol A degradation	Sulfamethoxazole degradation	Diclofenac degradation
Treated volume [L]	10	3	3	3
Reactor (Name /volume)	CONDIAPURE ® /45 cm³	CONDIAPURE-SHORTY ® /19 cm³	Glass reactor / 92 cm³	Glass reactor / 92 cm³
Electrode area [cm²]	24	24	12	12
Applied current densities [mA cm^{-2}]	42; 167	125; 208	208; 333	291
Temperature [°C]	25 ± 1	25 ± 2	20 ± 1	20 ± 1
Initial concentration	10^7-10^8 CFU mL^{-1}	43.8 µM	5.5 µM	50 µM

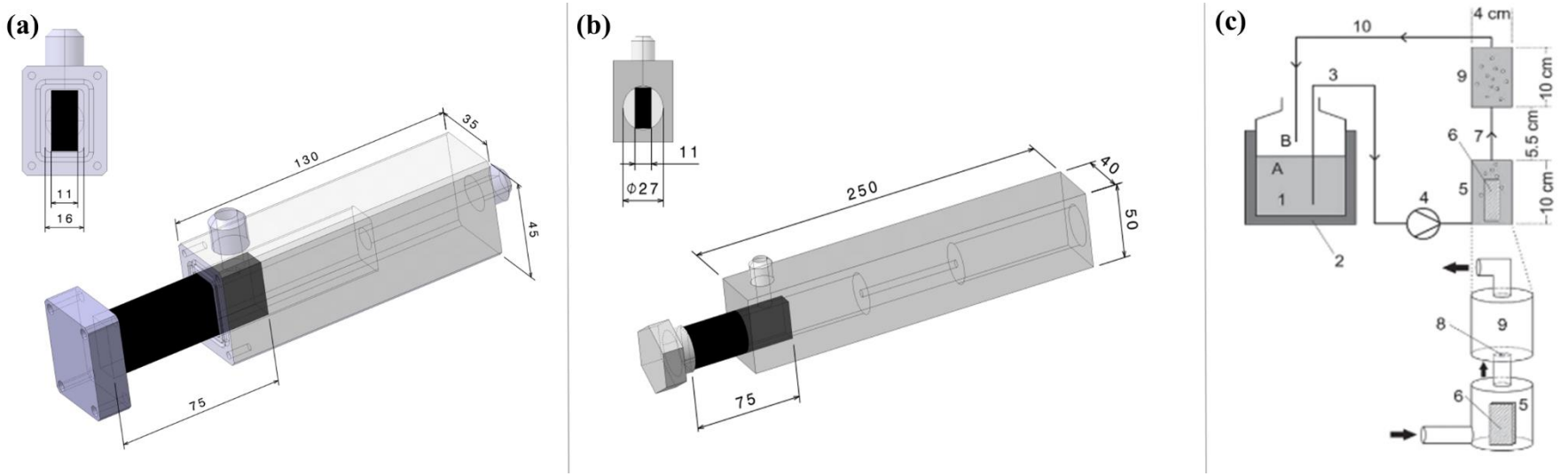

Figure 4- Schemes of the employed reactor cells (a) CONDIAPURE SHORTY® (b) CONDIAPURE ® (c) Glass reactor

3 Chapter Three
Results and Discussion

3.1 Serial coupling of RP and zwitterionic hydrophilic interaction LC–MS: Suspects screening of diclofenac transformation products by oxidation with a boron-doped diamond electrode

DCF is a widely used anti-inflammatory drug that is barely eliminated during conventional wastewater treatment plant (Soufan et al., 2012). It has been detected in many effluents of wastewater treatment plants, surface and groundwater, as well as in drinking water. Even though DCF is present at low concentrations, there is some evidence of its negative effects on the environment as presented in point 1.1.3.

In order to investigate the effect of water matrix on the degradation process of DCF, the electrochemical oxidation of DCF using a BDD electrode was investigated in different water matrices (deionized water matrix, synthetic water matrix (hard water) and real secondary effluent of WWTP). One goal of this section was the analytical approach of applying the serial coupling of reverse phase and zwitterionic hydrophilic interaction LC-MS for the identification of both polar and unipolar transformation products of DCF degradation.

The results showed in this section are referring to an effect of the water matrix as reaction media on the degradation behaviour of DCF. The competitive reactions between the reactive oxygen species (mainly hydroxyl radicals and ozone) and the organic and inorganic matter in the different matrices have led to a variability in the degradation progress. The analytical approach was successfully implemented and have shown an easy, reliable and flexible screening features that allows the separation of polar and nonpolar TPs in a single injection.

The results of this section are presented with permission from Rajab, M., Greco, G., Heim, C., Helmreich, B., Letzel, T., 2013a. Serial coupling of RP and zwitterionic hydrophilic interaction LC-MS: suspects screening of DCF transformation products by oxidation with a boron-doped diamond electrode. J. Sep. Sci. 36, 3011–3018. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Co-authors contributed through valuable insight into overall direction of the research and experimental planning; experimental execution, data analysing, review published data were performed by Mohamad Rajab.

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Research Article

Serial coupling of RP and zwitterionic hydrophilic interaction LC–MS: Suspects screening of diclofenac transformation products by oxidation with a boron-doped diamond electrode

The presence of pollutants and their transformation products (TPs) in the water system is a big concern because of possible adverse effects on the aquatic environment. Their identification is still a challenge that requires the combination of different chromatographic techniques. In the current research, serial coupling of RPLC and zwitterionic hydrophilic interaction LC with TOF-MS was investigated as a single separation technique for the screening of suspected TPs from electrochemical oxidation of diclofenac using a boron-doped diamond electrode. Diclofenac oxidation was performed in three water matrices in order to study its transformation in different chemical contexts. 47 TPs resulting from similar oxidation methods were selected from the literature. As in most cases standards were not available, an identification procedure based on accurate mass data and chromatographic behavior was proposed. According to this procedure, 11 suspected TPs, previously analyzed by LC, GC, or ion chromatography, were detected in a single injection. The method was proved to be reliable and versatile and it could be efficiently employed as a comprehensive analytical tool for the simultaneous analysis of compounds in a wide polarity range.

Keywords: Advanced oxidation process / Hydrophilic interaction liquid chromatography / RP LC / Serial coupling / Suspects screening
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1 Introduction

The presence and the fate of pharmaceuticals in the aquatic environment is a topic of growing interest, since pharmaceutical drugs and their transformation products (TPs) have been identified as a class of new emerging environmental contaminants [1]. Pharmaceuticals are widely employed for the treatment of human and animal diseases. After administration, they are in part excreted and classical wastewater (WW) treatment processes are in some cases ineffective, so that many drugs can reach the aquatic environment [2–4]. Although, in general, no acute toxic effects can be detected, pharmaceutical compounds are considered to cause damage to aquatic organisms after long-term exposure [5]. Moreover, in combination with other drugs present in the water, the toxicity is considerably increased [6, 7]. Thus, it is regarded as necessary to remove pharmaceuticals before they enter the environment [8].

In recent years, increasing efforts have been spent in the development of more effective methods for the elimination of persistent pollutants in WW. At the same time, the study of their TPs is considered of primary importance, as they may represent a risk even higher than the parent compounds [9]. In this context, analytical chemists are receiving more and more requests to provide reliable tools for the screening of pharmaceutical TPs. LC coupled to MS is the most used technique for TP analysis, as confirmed by the vast literature available [1, 10, 11].

The number and the chemical nature of TPs generated by treatment of a pharmaceutical are largely dependent on the degradation method employed. Recently, advanced oxidation processes (AOPs) have come into focus as effective

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Abbreviations: **AOP**, advanced oxidation process; **BDD**, boron-doped diamond; **DCF**, diclofenac; **EIC**, extracted ion chromatogram; **HILIC**, hydrophilic interaction liquid chromatography; **IC**, ion-exclusion chromatography; **TP**, transformation product; **WW**, wastewater; **WWTP**, wastewater treatment plant; **ZIC-HILIC**, zwitterionic HILIC

and environmentally friendly technologies to degrade persistent pollutants [12–14]. They are characterized by the *in situ* formation of highly reactive oxidative species, aiming at mineralization of the treated compounds [12]. TPs produced by AOPs are in general smaller and more polar than the parent drugs, and in most cases reference standards are not available. These aspects have implied the necessity to combine the information acquired by LC, GC, or ion-exclusion chromatography (IC) in order to obtain a comprehensive view of the TPs generated [15–17]. Even though the data collected using these three different analytical setups have led to important results, such an approach is extremely time and resource consuming, and thus cannot be applied for routine analyses on a large amount of samples.

A more efficient alternative, still poorly investigated, can be the hyphenation of hydrophilic interaction liquid chromatography (HILIC) with RPLC coupled with high-accuracy MS, such as TOF-MS. This technique is a powerful tool for comprehensive and simultaneous analysis of compounds in a wide range of polarity. Among the different possibilities to combine HILIC to RPLC, serial coupling is an easy setting, which does not require the use of specific interfaces, such as valve-switching systems used in 2D chromatography. To the best of our knowledge, only three serial RPLC–HILIC coupled methods have been described in the literature so far, and just two of them have been applied to real matrices [18–20]. Serial RPLC–HILIC coupled methods are emerging as a reliable technique, with a great potential to find application in several fields for the analysis of complex samples by a single injection [19, 20]. However, more investigations are required to establish the versatility of such methods.

Owing to the broadening of the elution window, these methods may minimize the number of false negatives in suspects and unknown screening approaches when reference standards are not available during method development [10]. Moreover, as reference standards cannot be later used for confirmation, the retention behavior can be used as an independent parameter with which to support accurate MS data for compound identification [20].

The aim of this study is to evaluate the feasibility and convenience of the serial coupling of RPLC and zwitterionic HILIC (ZIC-HILIC) with TOF-MS detection as a single-injection screening method for the analysis of suspect TPs produced by AOPs. We selected diclofenac (2-(2,6-dichlorophenylamino)phenyl acetic acid, DCF) as a model pharmaceutical. DCF is a widely used anti-inflammatory drug that is barely eliminated during conventional WW treatments [21] and it can be detected in many effluents of wastewater treatment plants (WWTP), surface and groundwater, as well as in drinking water. Even though DCF is present at low concentrations, there is some evidence of its negative effects on the aquatic environment [6, 22–24].

A boron-doped diamond (BDD) electrode was chosen for the AOP method for the degradation of DCF.

BDD electrodes have already been successfully applied for the removal of a variety of organic pollutants [12–14], as well as DCF, from water and WW [6, 16, 25]. As the removal efficiency and the formation of TPs depend on the composition of the water matrix [12], the DCF oxidation reaction was carried out in pure water, synthetic water simulating a hard drinking water, and the effluent of a WWTP as a real water matrix.

2 Materials and methods

2.1 Chemicals

Sodium hydroxide, sodium sulfite, calcium chloride, potassium bromide, potassium iodide, magnesium sulfate heptahydrate, sodium hydrogen carbonate, and sodium nitrate were purchased from Merck (Darmstadt, Germany). DCF was purchased from Sigma-Aldrich Chemie (Steinheim, Germany). Acetonitrile HiPerSolv Chromanorm was purchased from BDH (Poole, UK). Water LC-MS Chromasolv was bought from Fluka (Buchs, Switzerland). Ammonium acetate was purchased from Sigma-Aldrich (Seelze, Germany). Fumaric acid, oxalic acid, *meta*- and *para*-hydroxybenzoic acids were obtained from Sigma (Deisenhofen, Germany), and maleic acid from SERVA (Heidelberg, Germany). All chemicals were of analytical reagent grade.

2.2 Water matrices

Experiments were carried out in three water matrices: MilliQ water (deionizer "Milli-Q Plus 185," conductivity 0.055 μS/cm at 20°C, pH 5.5), synthetic hard drinking water (hard water) and an actual WW collected from the effluent of the municipal WWTP Garching, Germany, after secondary sedimentation and before the UV irradiation step. The hard water contained 250 mg/L chloride (NaCl), 1.0 mg/L bromide (KBr), 0.1 mg/L iodide (KI), 50 mg/L nitrate ($NaNO_3$), and 200 mg/L sulfate (Na_2SO_4) in MilliQ water, with a total hardness of 0.9 mmol/L at pH 8.9. The WWTP effluent contained 180 ± 10 mg/L chloride (bromide was below the LOD of 0.5 mg/L) and 12 mg/L dissolved organic carbon at pH 8.0 and a conductivity of 1170 μS/cm. The pH was controlled based on Standard Method 4500-H^+ [26]. Chemical analysis of dissolved organic carbon was performed with an Elementar High TOC II-Analyzer according to Standard Method 5310 after filtration through a 0.45 μm polypropylene membrane filter. Chloride and bromide concentrations were analyzed by ion chromatography with a DIONEX ICS-1000 device according to Standard Method 4110.

2.3 DCF oxidation experiments

Experiments were conducted with a CONDIAPURE® test system (CONDIAS, Itzehoe, Germany) using a DIACHEM®

electrode stack (CONDIAS) integrated into an optically accessible glass reactor (Esau & Hueber, Schrobenhausen, Germany) (Supporting Information Fig. S1). A detailed description of the reactor unit is given elsewhere [27, 28]. In situ oxidation was performed with a single anode/cathode pair and a surface of 24 × 50 mm^2 per electrode. The applied current was 3.5 A. A total of 3 L of DCF solution was prepared in a glass vessel (20 ± 1°C), which was connected to the operation unit with an inlet and outlet tube. The reaction solution was circulated through the glass reactor by a centrifugal pump (PY-2071, Speck Pumpen, Hilpoltstein, Germany) at a flow rate of 4 L/min.

A total of 3 L of each water matrix spiked with 50 μM DCF was treated for 60 min and the samples (2 mL each) were collected directly from the glass vessel after 0, 1, 2, 3, 5, 7.5, 10, 15, 20, 30, and 60 min. The oxidation reaction in the sample was stopped by adding 20 μL of 10 mM Na_2SO_3 solution after sampling, and then filtered through 0.22-μm PVDF Pleomax filters before the chromatographic analysis.

2.4 Chromatographic analysis

The chromatographic analysis is based on a method recently described [20]. Two Agilent HPLC systems series 1260 Infinity (Waldbronn, Germany) consisting of a binary pump, an on-line degasser, and a mixing chamber were used. The column temperature was maintained at 20°C. The system was coupled with an Agilent TOF-MS system series 6230 equipped with a Jet Stream ESI interface (Agilent Technologies, Santa Clara, CA, USA). For the first separation a Poroshell 120 EC-C_{18} (50.0 × 3.0 mm, 2.7 μm) (Agilent Technologies) was used and the second separation was performed with a ZIC®-HILIC column (150 × 2.1 mm, 5 μm, 200 Å; Merck Sequant, Umeå, Sweden). The two columns were coupled in series through a T-piece with mixing frit (Upchurch Scientific, Oak Harbor, WA, USA). The third port of the T-piece was connected to the second binary pump. The RPLC mobile phase was a mixture of ammonium acetate 10 mM/acetonitrile (90:10, v/v; solvent A) and ammonium acetate 10 mM/acetonitrile (10:90, v/v; solvent B) using the following gradient program: 0–7 min, isocratic 0% (B), flow rate 0.05 mL/min; 7–12 min, linear gradient 0–50% (B), flow rate 0.05 mL/min; 12–13 min isocratic 50% (B), flow rate from 0.05 to 0.1 mL/min; 13–22 min, linear gradient 50–100% (B), flow rate 0.1 mL/min; 22–37 min, isocratic 100% (B), flow rate 0.1 mL/min. The HILIC mobile phase was a composition of acetonitrile (solvent C) and water (solvent D) and the solvent from the RP column. To the RPLC mobile phase run-out, the following HILIC gradient at a flow rate of 0.4 mL/min was added through the T-piece: 0–6 min, isocratic 0% (D); 6–13 min, linear gradient 0–40% (D); 13–37 min, isocratic 40% (D). The injection volume was 10 μL. The Jet Stream ESI source was used in negative mode with the conditions described elsewhere [20]. The HPLC systems, the ESI interface, and the MS detector were controlled and data were acquired and processed by MassHunter software (Agilent Technologies, Waldbronn, Germany).

2.5 Data analysis

LC–MS data were processed using the extracted ion chromatogram (EIC) technique in which the chromatogram is defined by its accurate mass within 10 ppm mass tolerance. The accurate mass data of the TPs were processed through the "Generate Formulas" algorithm, which provided a list of possible molecular formulas. The algorithm comprises functionalities such as elemental type and range, electron configuration, and comparison of the theoretical with the measured exact mass, isotope abundance, isotope spacing. The agreement with these conditions is expressed by a score value. The logarithm of distribution coefficient (log*D*) was calculated at pH 7.0 with MarvinSketch 5.12.4 software.

3. Results and discussion

3.1 Selection of suspected DCF TPs by oxidation with a BDD electrode

BDD electrodes generate hydroxyl radicals directly from water due to the very high overpotential for oxygen and hydrogen evolution on its surface. Through further reactions, other reactive oxygen species could be formed, such as ozone and hydrogen peroxide [29]. However, the generation of oxidants can be extended to include nonoxygen reactive species, such as Cl_2, when operating in a solution that contains the respective ions [29, 30].

Thus, dependent on the water composition, the range of oxidant species that can be produced by the BDD electrode is very large and comprises species generated by many other AOPs, such as ozonation, photo-Fenton, UV-H_2O_2, photodegradation, and also chlorination, in case of chloride-containing water.

DCF degradation by AOP techniques is the subject of several papers [6, 15–17, 21, 23, 25, 31, 32], which describe the formed TPs. Through a deep literature search, 47 DCF TPs—produced by various AOPs—were selected in order to cover a vast range of structural differences in the number of carbon atoms, aromatic rings, and polar groups. Supporting Information Table S1 shows DCF and the 47 selected TPs, with their molecular formulae, proposed structure, exact mass, degradation method with which they were produced, method of analysis, and relative references.

The degradation of DCF by BDD electrode oxidation was studied at the concentration of 50 μM in three different water matrices: MilliQ water, a synthetic hard water containing a specific amount of electrolytes, and a real WW collected from the effluent of a local WWTP.

Oxidation mixtures were periodically injected on a serial RPLC–ZIC-HILIC–ESI(−)-TOF-MS system. Some suspected DCF TPs were small organic acid compounds, and ZIC-HILIC columns are already reported to retain similar

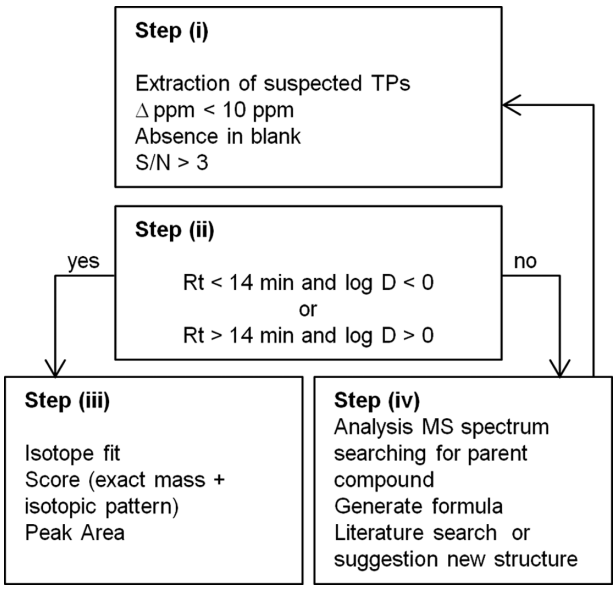

Figure 1. Procedure for the identification of suspected DCF TPs.

molecules [33]. ESI-MS detection was performed in negative mode, because of the presence of carboxyl and phenolic functionalities for several TPs. The selected TPs were used to investigate the DCF oxidation mixtures with the suspects screening approach as further described [10].

3.2 Degradation of DCF

DCF was identified by the EIC technique on the basis of the accurate mass of its $[M–H]^-$ ion at m/z 294.0094 within 2 ppm mass tolerance. DCF was eluted at 25.05 min (RSD% 0.2, $n = 25$). DCF was effectively removed from all the water matrices (Supporting Information Fig. S2). However, the time required to complete the degradation differed among the three solutions. DCF removal in MilliQ water was completed in 15 min, in hard water in 20 min, whereas 30 min were necessary to obtain the total elimination in WWTP effluent. In order to also achieve a complete degradation of the eventual TPs, the reaction was prolonged up to 30 min in MilliQ water, and up to 60 min in hard water and WW. The variability in the degradation progress among the water matrices can be explained through competitive reactions with the organic and inorganic matter at high concentrations in hard water and WW [8, 27]. These substances can affect the availability of oxidative species, leading to a less effective DCF degradation. Furthermore, the presence of radical scavengers, such as carbonate in hard water and WW effluent, may reduce the amounts of hydroxyl radicals [34].

3.3 Screening procedure

LC–MS data of the DCF oxidation mixtures and the blanks of the water matrices were examined according to the procedure

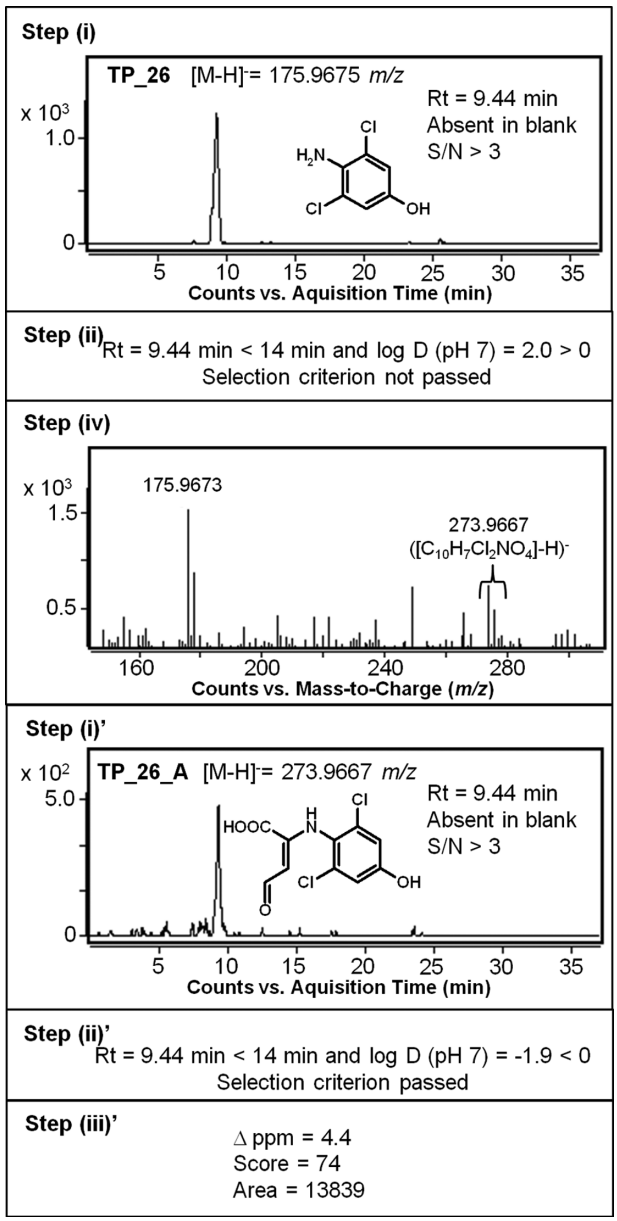

Figure 2. Application of the identification procedure for the screening of TP_26 in MilliQ water after 10 min reaction time.

schematized in Fig. 1. The single steps of the procedure are explained in detail below.

Step (i). The exact masses of all possible TPs from the list of suspects were extracted within 10 ppm mass tolerance. S/Ns and retention times for the observed peaks were noted. All the peaks present also in the blank and/or with S/N < 3 were discarded.

Step (ii). The RPLC–ZIC-HILIC chromatogram can be divided in two regions: the first one until 14 min corresponds to the window were the HILIC-retained compounds are eluted, whereas compounds eluted later are the

RPLC-retained ones (for more details, see Ref. [20]). Both HILIC and RPLC separation methods are in part based on partitioning. Therefore, the logarithm of distribution coefficient (log*D*), as a descriptor of the molecular hydrophilicity, can be related to the chromatographic behavior, with an approach already successfully used [35, 36]. TPs are in general not commercially available, so that the identification procedure has to rely on the calculated log*D* value at pH 7.0 in water. According to the definition of log*D*, hydrophilic molecules have negative log*D* values, whereas more hydrophobic compounds display positive values. Based on these considerations, molecules with negative log*D* values were expected to be HILIC-retained and to elute before 14 min. Therefore, the criterion according to which retention time < 14 min and log*D* value < 0 (HILIC-retained compounds) or retention time $>$ 14 min and log*D* value > 0 (RPLC-retained compounds) was selected.

Step (iii). The MS spectrum of all the peaks that passed step (ii) was consulted for confirmation of isotopic pattern. This is particularly important in the case of DCF and its TPs, which have a distinctive isotopic pattern due to the presence of Cl atoms. Finally, score values, which consider mass deviation and isotopic pattern fit [37], and area values were listed for each peak.

Step (iv). All the peaks that did not pass the selection criterion described in the step (ii) were further processed to evaluate if they correspond to in-source fragments. The relative MS spectra were inspected for potential parent compounds. The molecular formula was proposed with the help of a "Generate Formulas" algorithm, which takes into account both exact mass and isotopic pattern fits. A literature search for DCF TPs corresponding to these data was performed. In the absence of a positive match, a new molecular structure was suggested on the basis of the available data. Subsequently, the new proposed TP was subject to steps (i–iii), checking that the retention time was the same as that of the in-source fragment.

3.4 Screening of suspected DCF TPs

The procedure described above was applied and discussed in detail for the screening of TP_26 in MilliQ water at 10 min oxidation reaction time. TP_26 can correspond to two dichlorohydroxyanilines differing in the position of the hydroxyl group (in Fig. 2 only one is represented). The EIC for $[M–H]^-$ at 175.9675 m/z gave a peak at 9.44 min in the HILIC region with $S/N > 3$, absent in the blank (Fig. 2, step (i)). The log*D* (pH 7) values of the two possible structures were 2.0 and 2.7, accounting for hydrophobic molecules. This was in disagreement with the retention behavior (Fig. 2, step (ii)). Therefore, the presence of a parent compound signal, with mass higher than TP_26 and isotopic pattern fitting for two Cl atoms, was investigated in the MS spectrum. For the signal at 273.9667 m/z, which responded to these characteristics, the formula $C_{10}H_7Cl_2NO_4$ was generated. As no DCF TP with the same formula was found in the literature, a new structure was suggested that comprised a four-carbon chain attached to dichlorohydroxyaniline. The chain can be the result of the oxidative degradation of the DCF nonchlorinated ring (Fig. 2, step (iv)). The formation of similar DCF TPs has been recently described as products of permanganate oxidation [37]. The EIC for $[M–H]^-$ at 273.9667 m/z gave a peak at 9.44 min, confirming that TP_26 was actually an in-source fragment (Fig. 2, step (i)′). The negative log*D* (pH 7) value of –1.9 was in agreement with the retention behavior (step (ii)′). The label TP_26_A was assigned to this new TP. Finally, the mass difference and score value were listed (step (iii)′). The peak area was processed for describing the compound evolution over time.

This procedure was applied to all suspected TPs. Besides TP_26_A, the following TPs from the list were found in experiments performed in MilliQ water (Table 1 and Fig. 3): TP_4, TP_6, TP_8, TP_15, TP_27, TP_34, TP_41, and TP_46. Inspection of the respective MS spectra did not present any possible parent compound.

Table 1. Accurate mass measurements of the (tentatively) identified suspected TPs in MilliQ water (M), hard water (H), and wastewater (WW) at 10 min oxidation reaction time

Transformation Product	R_t (min)	RSD (%)	Matrix	Log*D* (pH 7.0)	Molecular formula	Exp mass (m/z)	Calc mass (m/z)	ppm error	Score
TP_1	25.83	0.07 ($n = 8$)	WW	1.6	$C_{14}H_{10}NO_2Cl_3$	327.9721	327.9704	− 5.1	98
TP_4	24.09	0.19 ($n = 27$)	M, H, WW	0.8	$C_{14}H_{11}NO_3Cl_2$	310.0047	310.0043	− 1.3	97
TP_6	22.22	0.33 ($n = 15$)	M, WW	3.3	$C_{12}H_9NO_4Cl_2$	299.9863	299.9836	− 9.1	75
TP_7	24.71	0.14 ($n = 19$)	H, WW	4.5	$C_{13}H_{10}NOCl_3$	299.9769	299.9755	− 4.6	93
TP_8	23.72	0.18 ($n = 28$)	M, H, WW	5.0	$C_{13}H_9NO_3Cl_2$	295.9901	295.9887	− 4.9	90
TP_12	23.52	0.04 ($n = 9$)	H	3.6	$C_{13}H_{11}NO_2Cl_2$	282.0089	282.0094	1.8	79
TP_15	23.18	0.21 ($n = 29$)	M, H, WW	2.3	$C_{13}H_9NO_2Cl_2$	279.9942	279.9938	− 1.6	94
TP_16	11.57	1.93 ($n = 9$)	H	3.8	$C_{13}H_7NO_2Cl_2$	277.9784	277.9781	− 1.1	84
TP_26_A	9.44	1.82 ($n = 25$)	M, H, WW	− 1.9	$C_{10}H_7Cl_2NO_4$	273.9667	273.9679	4.4	74
TP_27	8.44	0.68 ($n = 11$)	M, H	− 2.4	$C_8H_8O_4$	167.0361	167.0350	− 6.8	82
TP_34	7.72	0.82 ($n = 19$)	M, H	− 1.3/−1.8	$C_7H_6O_3$	137,0251	137.0244	− 5.0	71
TP_41	5.41	1.68 ($n = 26$)	M, H, WW	− 6.1	$C_4H_4O_4$	115.0044	115.0037	− 6.3	68
TP_46	13.63	1.22 ($n = 21$)	M, H, WW	− 8.7	$C_2H_2O_4$	88.9884	88.9880	− 4.3	65

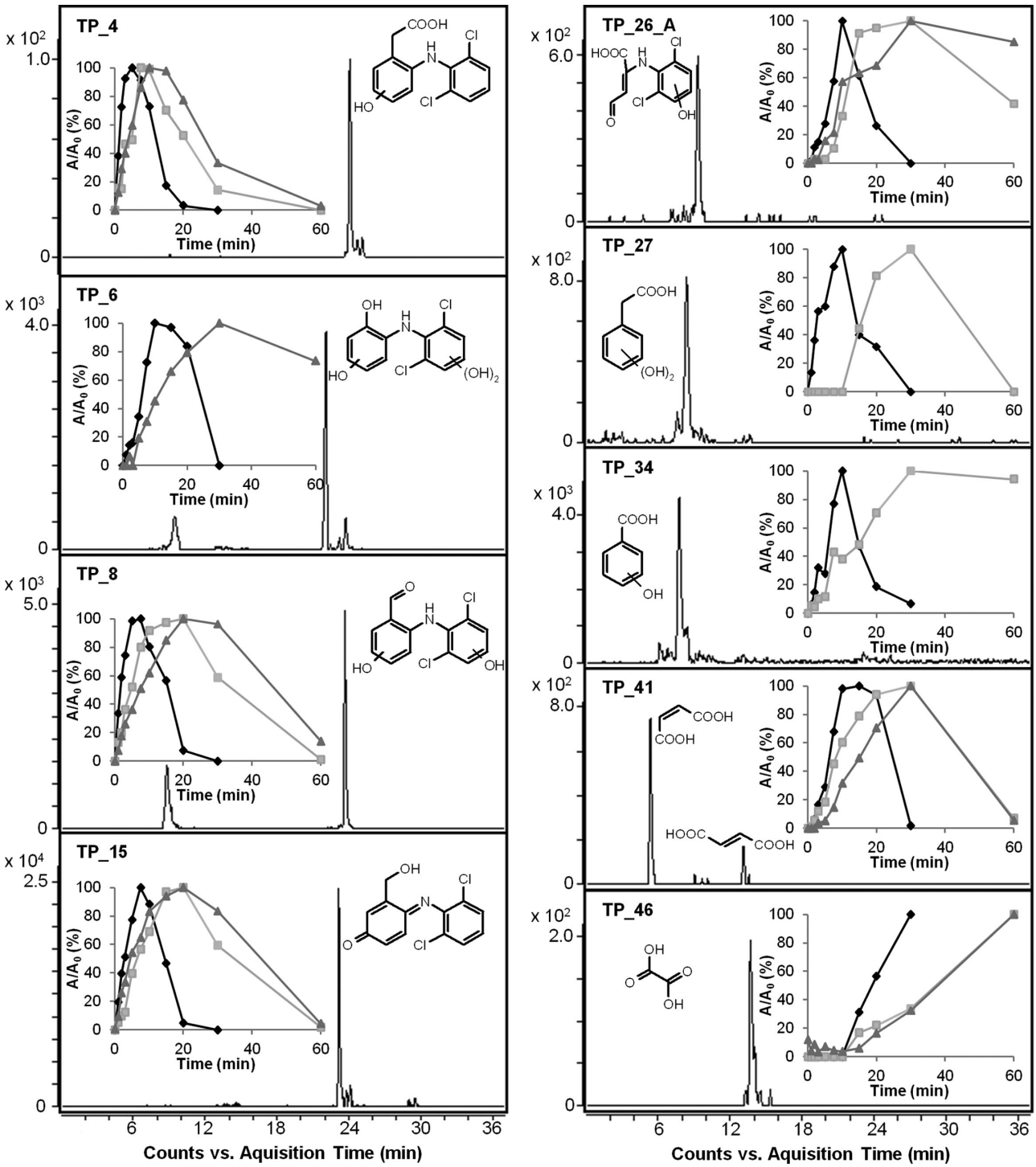

Figure 3. EICs relative to TPs found in MilliQ water. (Inset) Evolution over time in MilliQ water (black), hard water (light gray), and WWTP effluent (dark gray) estimated by the areas (A/A_0) of the relative extracted ion peak.

A first analysis of MS spectra relative to the minor peaks in the HILIC region observed for TP_6 and TP_8 suggested that they can be isomers or in-source fragments of polar open-ring structures. Their study will be topic of future investigations. The higher mass deviation for TP_6 may be the result of the presence of unresolved interferences in mass spectral data, as observed by shifts in the measured mass of the analyte peak over the time when the ratio of analyte/interference varied. The EIC relative to TP_41 revealed to two distinct peaks, which were identified as maleic (5.41 min) and fumaric acid (12.65 min) by injection of solutions spiked with pure standards. In accordance with the negative value of log *D*,

both compounds were HILIC-retained. The poor retention observed for maleic acid may be ascribed to an intramolecular hydrogen bond, which prevents possible interactions with the stationary phase [38, 39]. Similarly, it was possible to identify TP_46 as oxalic acid. The EIC for the molecular ion of TP_34 revealed a peak at 7.72 min, which was in disagreement with its log*D* value of 1.7. However, from the analysis of the MS spectrum, no parent compound was identified. *m*- and *p*-hydroxybenzoic acids are structural isomers of TP_34, but more hydrophilic due to the presence of a carboxyl group. Indeed, their log*D* values are −1.3 and −1.8, respectively. The peak at 7.72 min was identified as hydroxybenzoic acid by injection of the relevant spiked solutions, but it was not possible to distinguish between the two isomers. In Fig. 3, the EICs for TPs in MilliQ water are reported, along with their molecular structures and time evolution for the main peak in the matrices where they were found. Other chromatographic and mass data are presented in Table 1. All the TPs showed slower formation and degradation rates in hard water and WW in comparison with MilliQ water. In some cases they were still present at the end of the treatment. As previously discussed for DCF, also the TP oxidation rates may be influenced by a reduced amount of oxidative species available in hard water and WW [8, 27, 34].

Four additional TPs were detected exclusively in hard water and/or WW, indicating a role of ionic species, such as chloride, in their formation pathway. TP_1 corresponds to chloro-DCF and it was detected only in the experiments performed in the WW effluent. TP_7 and TP_12 were found in hard water and WW experiments, but they were absent in MilliQ water. These TPs were previously reported in a study about the water chlorination of DCF [21]. The formation of constitutional isomers different in the position of OH and Cl group may account for the several peaks observed in the EICs.

Lastly, EIC relative to TP_16 gave a peak at 11.57 min present only in the hard water experiments that did not fit with the log*D* value (3.8). However, inspection of the MS spectrum did not reveal any possible parent compound. Also in this case, as discussed for TP_26_A, an open ring in an advanced state of oxidation may be hypothesized, but it was not possible to suggest a convincing molecular structure. The EICs relative to TPs found exclusively in hard water and/or WW are reported in Fig. 4.

Overall, several DCF TPs were detected with a single injection. By comparison with the literature, analysis of compounds TP_1 to TP_15 was performed by RPLC, TP_ 27, and TP_34 were analyzed by GC, whereas TP_41 and TP_46 were examined by IC.

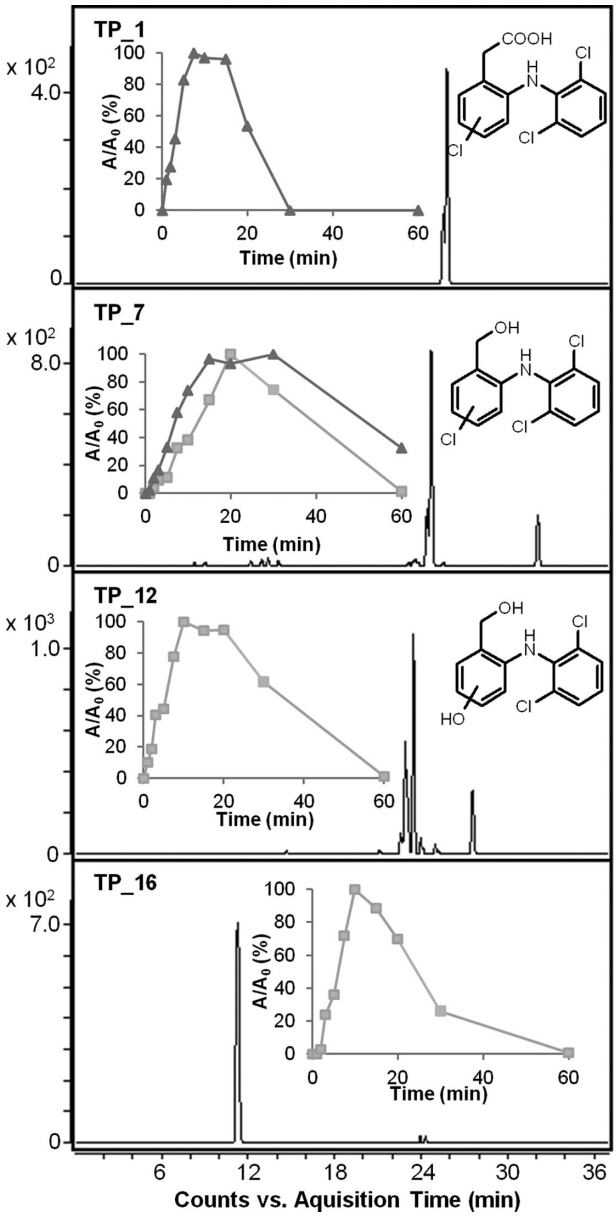

Figure 4. EICs relative to TPs found exclusively in hard water or WWTP effluent. (Inset) Evolution over time in hard water (light gray), and WWTP effluent (dark gray) estimated by the areas (A/A_0) of the relative extracted ion peak.

4 Concluding remarks

The serial coupling of RPLC and ZIC-HILIC was applied for a comprehensive investigation of different suspected TPs from DCF oxidation using a BDD electrode. Accurate mass detection and the qualitative relationship of the retention times with the logarithm of the distribution coefficient, log*D*, of the suspected TPs were the key steps in the identification procedure. The repeatability of the retention times was comparable to that achieved in our previous study about serial RPLC–HILIC coupling. The broadening of the elution window realized with this method allowed the separation in a single injection of TPs, which were previously analyzed by a combination of LC, GC, or IC. On these bases, serial RPLC–HILIC coupled methods operating in gradient mode appear as easy, reliable, and versatile screening tools for comprehensive data collection.

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5 References

[1] Agüera, A., Bueno, M. J. M., Fernández-Alba, A. R., *Environ. Sci. Pollut. Res.* 2013, *20*, 3496–3515.

[2] Bound, J. P., Voulvoulis, V., *Chemosphere* 2004, *56*, 1143–1155.

[3] Pedrouzo, M., Revert, S., Borrull, F., Pocurull, E., Marc, R. M., *J. Sep. Sci.* 2007, *30*, 297–303.

[4] Khetan, S. K., Collins, T. J., *Chem. Rev.* 2007, *107*, 2319–2364.

[5] Fent, K., Weston, A. A., Caminada, D., *Aquat. Toxicol.* 2006, *76*, 122–159.

[6] Zhao, X., Hou, Y., Liu, H., Qiang, Z., Qu, J., *Electrochim. Acta* 2009, *54*, 4172–4179.

[7] Rodríguez-Alvarez, T., Rodil, R., Quintana, J. B., Triñanes, S., Cela, R., *Water Res.* 2013, *47*, 3220–3230.

[8] Wert, E. C., Gonzales, S., Dong, M. M., Rosario-Ortiz, F. L., *Water Res.* 2011, *45*, 5191–5199.

[9] Fatta-Kassinos, D., Vasquez, M. I., Kümmerer, K., *Chemosphere* 2011, *85*, 693–709.

[10] Krauss, M., Singer, H., Hollender, J., *Anal. Bioanal. Chem.* 2010, *397*, 943–951.

[11] Petrovic, M., Farré, M., Lopez de Alda, M., Perez, S., Postigo, C., Köck, M., Radjenovic, J., Gros, M., Barcelo, D., *J. Chromatogr. A* 2010, *1217*, 4004–4017.

[12] Menapace, H. M., Diaz, N., Weiss, S., *J. Environ. Sci. Health A* 2008, *43*, 1–8.

[13] Frontistis, Z., Brebou, C., Venieri, D., Mantzavinos, D., Katsaounis, A., *J. Chem. Technol. Biotechnol.* 2011, *86*, 1233–1236.

[14] Martínez-Huitle, C. A., Quiroz Alfaro, M. A., *J. Environ. Eng. Manag.* 2008, *18*, 155–172.

[15] Pérez-Estrada, L. A., Malato, S., Gernjak, W., Agüera, A., Thurman, E. M., Ferrer, I., Fernández-Alba, A. R., *Environ. Sci. Technol.* 2005, *39*, 8300–8306.

[16] Brillas, E., Garcia-Segura, S., Skoumal, M., Arias, C., *Chemosphere* 2010, *79*, 605–612.

[17] Calza, P., Medana, C., Baiocchi, C., Pelizzetti, E., *Curr. Anal. Chem.* 2005, *1*, 267–287.

[18] Louw, S., Pereira, A. S., Lynen, F., Hanna-Brown, M., Sandra, P., *J. Chromatogr. A* 2008, *1208*, 90–94.

[19] Falasca, S., Petruzziello, F., Kretz, R., Rainer, G., Zhang, X., *J. Chromatogr. A* 2012, *1241*, 46–51.

[20] Greco, G., Grosse, S., Letzel, T., *J. Sep. Sci.* 2013, *36*, 1379–1388.

[21] Soufan, M., Deborde, M., Legube, B., *Water Res.* 2012, *46*, 3377–3386.

[22] Letzel, M., Metzner, G., Letzel, T., *Environ. Int.* 2009, *35*, 363–368.

[23] Sein, M. M., Zedda, M., Tuerk, J., Schmidt, T. C., Golloch, A., von Sonntag, C., *Environ. Sci. Technol.* 2008, *42*, 6656–6662.

[24] Stülten, D., Zühlke, S., Lamshöft, M., Spiteller, M., *Sci. Total Environ.* 2008, *405*, 310–316.

[25] Faber, H., Melles, D., Brauckmann, C., Wehe, C. A., Wentker, K., Karst, U., *Anal. Bioanal Chem.* 2012, *403*, 345–354.

[26] Eaton, A. D., Clesceri, L. S., Rice, E. W., Greenberg, A. E., Franson, M. A. H., *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC 2005.

[27] Heim, C., Ureña de Vivanco, M., Rajab, M., Glas, K., Horn, H., Helmreich, B., Letzel, T., *Brew Sci.* 2011, *64*, 83–88.

[28] Ureña de Vivanco, M., Rajab, M., Heim, C., Helmreich, B., Letzel, T., *Chem. Eng. Technol.* 2013, *36*, 355–361.

[29] Michaud, P. A., Panizza, A., Ouattara, L., Diaco, T., Foti, G., Comninellis, C., *J. Appl. Electrochem.* 2003, *33*, 151–154.

[30] Palmas, S., Polcaro, A. M.,Vacca, A., Mascia, M., Ferrara, F., *J. Appl. Electrochem.* 2007, *37*, 1357–1365.

[31] Coelho, A. D., Sans, C., Agüera, A., Gómez, M. J., Esplugas, S., Dezotti, M., *Sci. Total Environ.* 2009, *407*, 3572–3578.

[32] Vogna, D., Marotta, R., Napolitano, A., Andreozzi, R., d'Ischia, M., *Water Res.* 2004, *38*, 414–422.

[33] Ehling, S., Cole, S., *J. Agric. Food Chem.* 2011, *59*, 2229–2234.

[34] Andreozzi, R., Caprio, V., Insola, A., Marotta, R., *Catal. Today* 1999, *53*, 51–59.

[35] Liu, M., Chen, E. X., Ji, R., Semin, D., *J. Chromatogr. A* 2008, *1188*, 255–263.

[36] Lämmerhofer, M., Richter, M., Wu, J., Nogueira, R., Bicker, W., Lindner, W., *J. Sep. Sci.* 2008, *31*, 2572–2588.

[37] Rodríguez-Alvarez, T., Rodil, R., Quintana, J. B., Triñanes, S., Cela, R., *Water Res.* 2013, *47*, 3220–3230.

[38] Grosse, S., Letzel, T., *J. Chromatogr. A* 2007, *1139*, 75–83.

[39] Greco, G., Grosse, S., Letzel, T., *J. Chromatogr. A* 2012, *1235*, 60–67.

Supporting information

Serial coupling of reversed-phase and zwitterionic hydrophilic interaction LC/MS: suspects screening of diclofenac transformation products by oxidation with boron-doped diamond electrode

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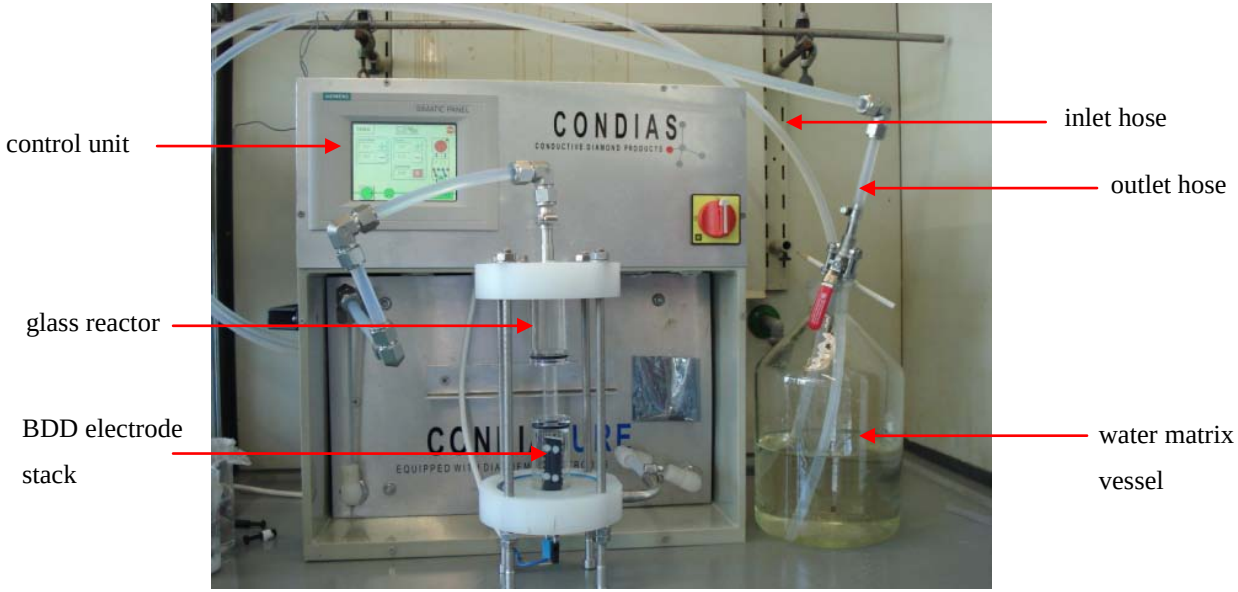


Figure S1. Illustration of the reactor unit and the BDD electrode. The aqueous solution is provided in the water matrix vessel. The solution is circulated over the BDD electrode stack through the inlet hose and pumped back into the vessel. Samples are taken from the outlet hose. The control unit allows adjustment of the applied current and the flow rate.

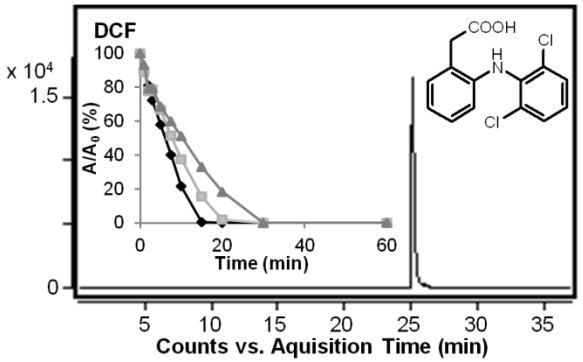
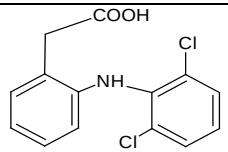
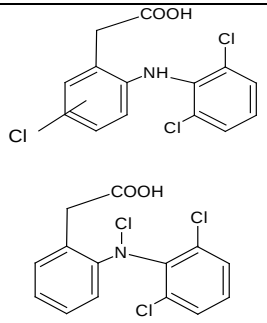
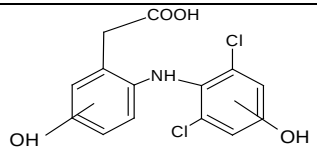
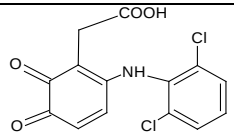
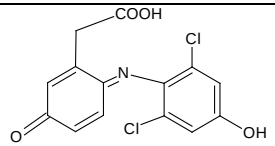
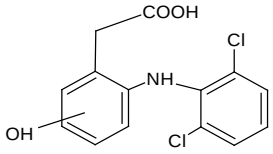
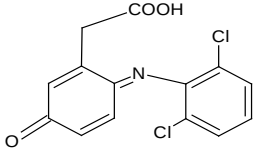
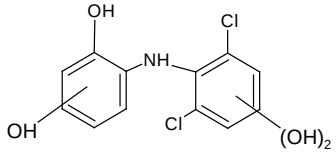
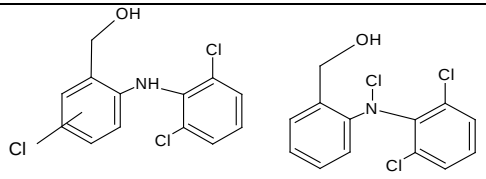
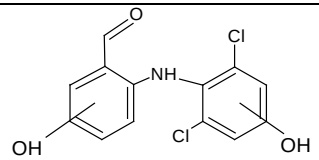
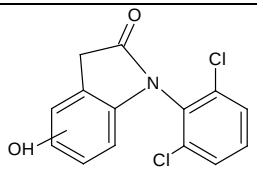
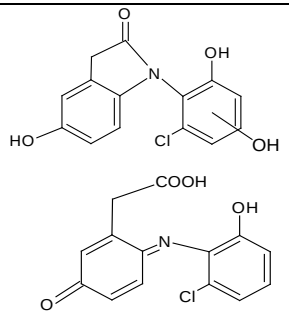
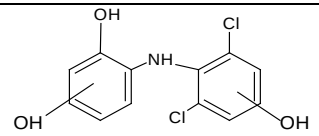
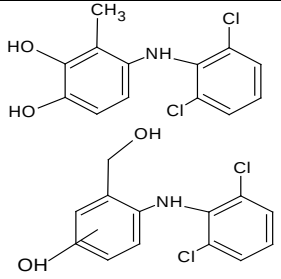


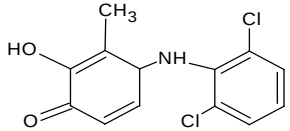
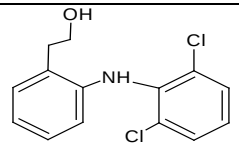
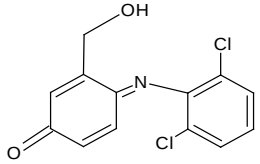
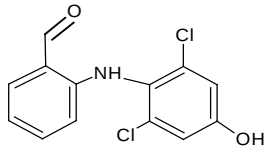
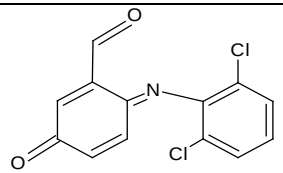
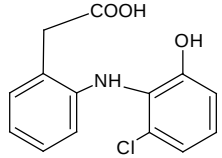
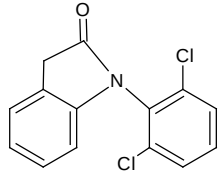
Figure S2. Extracted ion chromatogram of DCF in MilliQ water. (Inset) DCF decay in MilliQ water (black), hard water (light grey), and WWTP effluent (dark grey) by BDD electrode oxidation estimated by the areas (A/A_0) of the relative extracted ion peak.

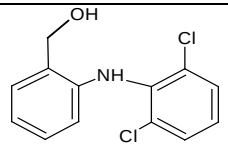
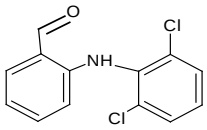
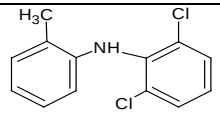
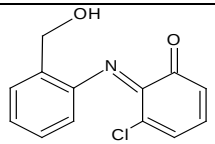
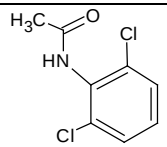
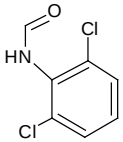
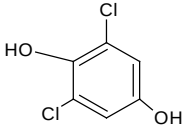
Table S1. List of 47 suspected transformation products selected from literature including the proposed molecular structures, degradation method from which each molecule was produced, analytical method employed and the relative references.

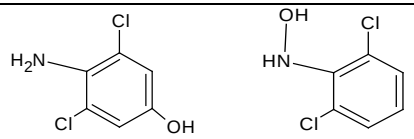
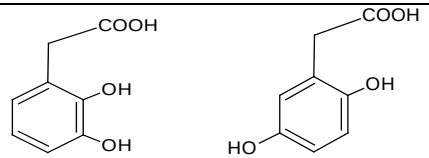
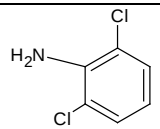
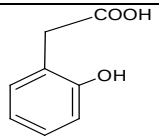
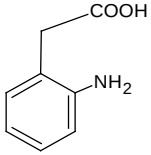
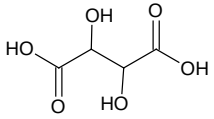
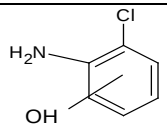
Compound	Proposed structure	Molecular formula	Accurate molecular mass	$[M-H]^-$ (*m/z*)	Degradation method	Analytical method	Reference
DCF		$C_{14}H_{11}NO_2Cl_2$	295.0167	294.0094			
TP_1		$C_{14}H_{10}NO_2Cl_3$	328.9777	327.9704	aqueous chlorination	RP-HPLC	Soufan 2012
TP_2		$C_{14}H_{11}NO_4Cl_2$	327.0065	325.9992	ozonation	RP-HPLC	Coelho 2009
					photocatalysis/TiO2	RP-HPLC	Calza 2006
TP_3		$C_{14}H_9NO_4Cl_2$	324.9909	323.9836	photo-Fenton	RP-HPLC	Pérez-Estrada 2005
					BDD electrode	RP-HPLC	Faber 2012

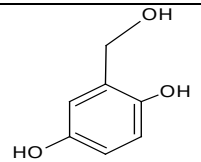
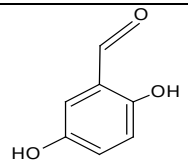
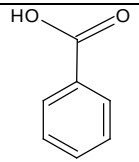
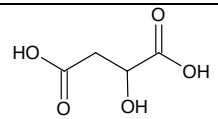
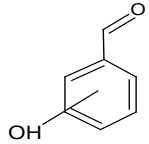
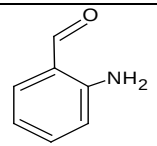
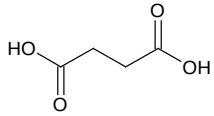
							
TP_4		$C_{14}H_{11}NO_3Cl_2$	311.0116	310.0043	ozonation	RP-HPLC	Coelho 2009
					ozonation UV/H_2O_2	GC	Vogna 2004
					photo-Fenton	RP-HPLC	Pérez-Estrada 2005
					photocatalysis/TiO_2	RP-HPLC	Calza 2006
					ozonation	RP-HPLC	Sein 2008
TP_5		$C_{14}H_9NO_3Cl_2$	308.9959	307.9887	ozonation	RP-HPLC	Coelho 2009
					photocatalysis/TiO_2	RP-HPLC	Calza 2006
TP_6		$C_{12}H_9NO_4Cl_2$	300.9909	299.9836	ozonation	RP-HPLC	Coelho 2009
TP_7		$C_{13}H_{10}NOCl_3$	300.9828	299.9755	aqueous chlorination	RP-HPLC	Soufan 2012

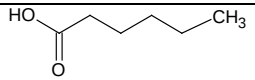
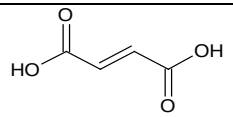
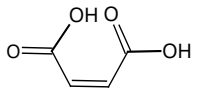
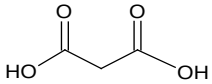
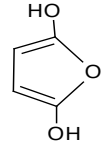
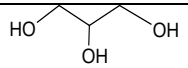
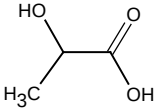
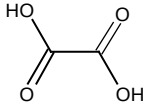
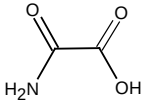
TP_8		$C_{13}H_9NO_3Cl_2$	296.9959	295.9887	ozonation	RP-HPLC	Coelho 2009
TP_9		$C_{14}H_9NO_2Cl_2$	293.0010	291.9938	photo-Fenton	RP-HPLC	Pérez-Estrada 2005
					ozonation	RP-HPLC	Coelho 2009
TP_10		$C_{14}H_{10}NO_4Cl$	291.0298	290.0226	ozonation	RP-HPLC	Coelho 2009
					photo-Fenton	RP-HPLC	Pérez-Estrada 2005
TP_11		$C_{12}H_9NO_3Cl_2$	284.9959	283.9887	ozonation	RP-HPLC	Coelho 2009
TP_12		$C_{13}H_{11}NO_2Cl_2$	283.0167	282.0094	BDD electrode	RP-HPLC	Faber 2012
					aqueous chlorination	RP-HPLC	Soufan 2012

TP_13		$C_{13}H_{10}NO_2Cl_2$	282.0089	281.0016	BDD electrode	RP-HPLC	Faber 2012
TP_14		$C_{14}H_{13}NOCl_2$	281.0374	280.0301	photo-Fenton	GC	Pérez-Estrada 2005
TP_15	 	$C_{13}H_9NO_2Cl_2$	281.0010	279.9938	aqueous chlorination	RP-HPLC	Soufan 2012
					ozonation	RP-HPLC	Coelho 2009
					photo-Fenton	GC	Pérez-Estrada 2005
TP_16		$C_{13}H_7NO_2Cl_2$	278.9854	277.9781	photo-Fenton	RP-HPLC	Pérez-Estrada 2005
TP_17		$C_{14}H_{12}NO_3Cl$	277.0506	276.0433	UV/H_2O_2	GC	Vogna 2004
TP_18		$C_{14}H_9NOCl_2$	277.0061	275.9988	ozonation	RP-HPLC	Coelho 2009
					BDD electrode	GC	Zhao 2009

TP_19		$C_{13}H_{11}NOCl_2$	267.0218	266.0145	aqueous chlorination	RP-HPLC	Soufan 2012
					photo-Fenton	GC	Pérez-Estrada 2005
TP_20		$C_{13}H_9NOCl_2$	265.0061	263.9988	photo-Fenton	GC	Pérez-Estrada 2005
TP_21		$C_{13}H_{11}NCl_2$	251.0269	250.0196	photo-Fenton	GC	Pérez-Estrada 2005
TP_22		$C_{13}H_{10}NO_2Cl$	247.0400	246.0327	ozonation	RP-HPLC	Sein 2008
TP_23		$C_8H_7NOCl_2$	202.9905	201.9832	photo-Fenton	RP-HPLC	Pérez-Estrada 2005
TP_24		$C_7H_5NOCl_2$	188.9748	187.9675	ozonation	RP-HPLC	Coelho 2009
					photo-Fenton	RP-HPLC	Pérez-Estrada 2005
TP_25		$C_6H_4O_2Cl_2$	177.9588	176.9516	ozonation UV/H_2O_2	GC	Vogna 2004
					BDD electrode	RP-HPLC GC	Brillas 2010

TP_26		$C_6H_5NOCl_2$	176.9748	175.9675	ozonation	RP-HPLC	Coelho 2009
					photo-Fenton	RP-HPLC	Pérez-Estrada 2005
TP_27		$C_8H_8O_4$	168.0423	167.0350	BDD electrode	GC	Brillas 2010
					ozonation UV/H_2O_2	GC	Vogna 2004
					BDD electrode	GC	Zhao 2009
TP_28		$C_6H_5NCl_2$	160.9799	159.9726	ozonation	RP-HPLC	Coelho 2009
					ozonation UV/H_2O_2	GC	Vogna 2004
					BDD electrode	GC	Brillas 2010
TP_29		$C_8H_8O_3$	152.0473	151.0401	ozonation UV/H_2O_2	GC	Vogna 2004
TP_30		$C_8H_9NO_2$	151.0633	150.0560	UV/H_2O_2	GC	Vogna 2004
TP_31		$C_4H_6O_6$	150.0164	149.0092	BDD electrode	ion-exclusion HPLC	Brillas 2010
TP_32		C_6H_6NOCl	143.0138	142.0065	ozonation	RP-HPLC	Coelho 2009

TP_33		$C_7H_8O_3$	140.0473	139.0401	BDD electrode	GC	Zhao 2009
TP_34		$C_7H_6O_3$	138.0317	137.0244	BDD electrode	GC	Zhao 2009
TP_35		$C_8H_6O_2$	134.1328	133.1255	BDD electrode	GC	Zhao 2009
TP_36		$C_4H_6O_5$	134.0215	133.0142	BDD electrode	ion-exclusion HPLC	Brillas 2010
TP_37		$C_7H_6O_2$	122.0368	121.0295	ozonation	RP-HPLC	Coelho 2009
TP_38		C_7H_7NO	121.0528	120.0455	ozonation	RP-HPLC	Coelho 2009
TP_39		$C_4H_6O_4$	118.0266	117.0193	BDD electrode	ion-exclusion HPLC	Brillas 2010

					BDD electrode	GC	Zhao 2009
TP_40		$C_6H_{12}O_2$	116.0837	115.0764	BDD electrode	GC	Zhao 2009
TP_41	 	$C_4H_4O_4$	116.0101	115.0037	BDD electrode	ion-exclusion HPLC	Brillas 2010
TP_42		$C_3H_4O_4$	104.0101	103.0037	BDD electrode	GC	Zhao 2009
TP_43		$C_4H_4O_3$	100.0160	99.0088	BDD electrode	GC	Zhao 2009
TP_44		$C_3H_8O_3$	92.0473	91.0401	BDD electrode	GC	Zhao 2009
TP_45		$C_3H_6O_3$	90.0317	89.0244	BDD electrode	GC	Zhao 2009
TP_46		$C_2H_2O_4$	89.9953	88.9880	BDD electrode	ion-exclusion HPLC	Brillas 2010
					BDD electrode	GC	Zhao 2009
TP_47		$C_2H_3O_3N$	89.0113	88.0040	BDD electrode	ion-exclusion HPLC	Brillas 2010

References

Brillas, E., Garcia-Segura, S., Skoumal, M., Arias, C., *Chemosphere* 2010, 79, 605–612.

Calza, P., Medana, C., Baiocchi, C., Pelizzetti, E., *Curr. Anal. Chem.* 2005, 1, 267–287.

Coelho, A. D., Sans, C., Agüera, A., Gómez, M. J., Esplugas, S., Dezotti, M., *Sci. Total Environ.* 2009, 407, 3572-3578.

Faber, H., Melles, D., Brauckmann, C., Wehe, C. A., Wentker, K., Karst, U., *Anal. Bioanal Chem.* 2012, 403, 345–354.

Sein, M. M., Zedda, M., Tuerk, J., Schmidt, T. C., Golloch, A., v. Sonntag, C., *Environ. Sci. Technol.* 2008, 42, 6656–6662.

Pérez-Estrada, L. A., Malato, S., Gernjak, W., Agüera, A., Thurman, E. M., Ferrer, I., Fernández-Alba, A. R., *Environ. Sci. Technol.* 2005, 39, 8300–8306.

Soufan, M., Deborde, M., Legube, B., *Water Res.* 2012, 46, 3377–3386.

Vogna, D., Marotta, R., Napolitano, A., Andreozzi, R., d`Ischia M., *Water Res.* 2004, 38, 414–422.

Zhao, X., Hou, Y., Liu, H., Qiang, Z., Qu, J., *Electrochim. Acta* 2009, 54, 4172–4179.

3.2 Removal of Sulfamethoxazole from Wastewater Treatment Plant Effluents by a Boron-doped Diamond Electrode

SMX is a widely used antibiotic drug that is hardly removed during conventional wastewater treatment. It has been detected in many effluents of wastewater treatment plants, surface and groundwater, as well as in drinking water (Dirany et al., 2010; Luo et al., 2014). The excessive use of antibiotic drugs have been reported as a main reason for the development of anti-resistance bacterium which appeared as a big challenge for the human health worldwide (Levy and Marshall, 2004).

This section of the study has tested the removal of SMX from real secondary effluent of a WWTP using a BDD electrode. The resistance of SMX against other advanced oxidation processes have been reported, hence the goal of this section was to assess the degradation of SMX in real wastewater matrix. The experiments were conducted in a batch system and applying different current densities. The TPs of the degradation were also identified according to the same analytical approach used before (Rajab et al., 2013). An approximately value of the energetic demand of the process was presented.

The conclusion of this section is that BDD electrode is effectively applicable to induce SMX removal in real secondary effluent. Higher current densities led to faster degradation. A longer treatment time resulted in a complete removal of the TPs detected during the degradation process. However, the extension of the process pushed up the total energy consumption of the degradation. Higher current density were able to remove the SMX residue in the treated water within 5 minutes treatment and the process energy was 0.32 Wh L^{-1}. After 10 minutes treatment, almost all TPs were undetectable and the energy consumption as 0.68 Wh L^{-1}.

The results of this section are included in Rajab, M., Heim, C., Greco, G., Helmreich, B., Letzel, T., 2013b. Removal of Sulfamethoxazole from Wastewater Treatment Plant Effluents by a Boron-doped Diamond Electrode. International Journal of Environmental Pollution and Solutions 1, 88–97. Co-authors contributed through valuable insight into overall direction of the research and experimental planning; experimental execution, data analysing, review published data and manuscript preparation were performed by Mohamad Rajab.

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Research Article

Removal of Sulfamethoxazole from Wastewater Treatment Plant Effluents by a Boron-doped Diamond Electrode

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Abstract

The high inflow of pharmaceutical pollutants from wastewater into the aquatic environment requires new technologies for effective wastewater treatment. The current research focusses on the application of boron-doped diamond (BDD) electrodes for the removal of the persistent antibiotic sulfamethoxazole (SMX) from wastewater effluent. Tests were performed with real secondary effluents from a wastewater treatment plant spiked with SMX at the initial concentration of 5.5 µM. The BDD electrode was operated at two different current densities (208 and 333 mA/cm^2). The results showed a very good degradation of SMX. Four previously reported transformation products (TPs) were detected. These intermediates disappeared gradually with the extension of treatment time. SMX was removed during the first 5 to 10 minutes, depending on the current density applied to the electrode. However, much more time was required to remove the majority of the detected TPs. The hazardousness of the TPs is not known and in case it is negligible, the treatment time could be shortened. This will be reflected in less energy consumption and consequently lower costs.

Keywords: Electrochemical oxidation; Wastewater treatment; Sulfamethoxazole; Energy demand; Transformation products

1. Introduction

The growing intake of pharmaceutical substances worldwide leads to an increasing thread for the aquatic environment through wastewaters (Menapace et al., 2008). As some pharmaceuticals cannot be fully degraded under the current conditions in municipal wastewater treatment plants (WWTPs), remarkable amounts are released into the receiving water bodies either in an unaltered form or as stable metabolites and transformation products (TPs) (Ternes et al., 2002; Huber et al., 2005; Menapace et al., 2008). Thus, they appear in the aquatic environment in the nanogram to

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microgram per liter range and some of them even in drinking water in the former range (Huber et al., 2005; Rossi et al., 2013). Even though there should not be acute effects for human beings in this concentration range, pharmaceutical substances are suspected to have long-term adverse effects on humans and aquatic organisms (Huber et al., 2005; Jones et al., 2005). Thus, it is necessary to find new technologies for the removal of such pollutants or their TPs into better degradable compounds during drinking water and wastewater treatment.

The current focus is on finding alternative and environmentally friendly technologies to efficiently remove pollutants from water, for instance advanced oxidation processes (AOPs) (Andreozzi et al., 1999; Coelho et al., 2009). An emerging technology is the boron-doped diamond (BDD) electrode as an electrochemical AOP, which has already been successfully applied for the removal of a variety of organic pollutants from water and wastewater (Martinez and Quiroz Alfaro, 2008; Menapace et al., 2008; Frontistis et al., 2011). The electrode is mostly more efficient and cost-effective than other AOPs and is characterized by its robustness and a broad electrochemical potential window, which lead to the formation of highly reactive oxidative species (Fryda et al., 2003; Kraft, 2007). Hydroxyl radicals, ozone, hydrogen peroxide and eventually chlorine-derived species are generated *in situ* at the anode and in the bulk. Ideally, they achieve the mineralization of the pollutant (Michaud et al., 2003; Schmalz et al., 2008). The mechanism of the degradation is depending on the chemical nature of the target compound that can be either degraded through selective oxidation (ozonation) or non-selectively oxidized through highly reactive hydroxyl radicals. Ozone reacts preferentially with electron-rich compounds, whereas the radical-driven reaction can affect almost all types of molecules. This makes BDD electrodes applicable for a broad variety of target pollutants (da Silva et al., 2003; Martín de Vidales et al., 2012). However, the degradation efficiency could decrease by a rapid consumption of hydroxyl radicals through a variety of water matrix compounds (Huber et al., 2005; Menapace et al., 2008; Lee and von Gunten, 2010). Up to the present, only few studies were performed in real water matrices to investigate the application of BDD electrodes for the elimination of persistent pharmaceutical compounds from contaminated water bodies.

The aim of the present research was to investigate the application of a BDD electrode for the removal of persistent pharmaceutical pollutants from a real wastewater effluent. The antibiotic sulfamethoxazole (SMX) was used as an exemplary compound. Conventional wastewater treatment removes the substance with only low efficiency resulting in µg/L concentrations detected in WWTP effluents (Trovó et al., 2009a; Trovó et al., 2009b; Dirany et al., 2010). Only few papers have reported the successful degradation of SMX with the BDD electrode from aqueous solutions so far, but no one in real wastewater conditions (Michaud et al., 2003; Dirany et al., 2010; Martín de Vidales et al., 2012). The energy expenditure of this electrochemical water treatment technology is also discussed under varying electrode conditions.

2. Materials and Methods

2.1 Chemicals

SMX was purchased from Sigma Aldrich (St. Louis Missouri, USA). Acetonitrile HiPerSolv Chromanorm was purchased from BDH (Poole, UK). Water LC-MS Chromasolv was bought from Fluka (Buchs, Switzerland). Ammonium acetate was purchased from Sigma-Aldrich (Seelze,

Germany). Indigo bisulfonate (indigo carmine) was purchased from Merck (Darmstadt, Germany). All chemicals were of analytical reagent grade.

2.2 Water matrix

Wastewater was collected from the municipal WWTP Garching, Germany, after secondary sedimentation and before the UV irradiation step (WWTP effluent). The total organic carbon (TOC) was measured with an Elementar High TOC II-Analyser according to Standard Method 5310 (Eaton et al., 2005) after filtration through a 0.45 µm polypropylene membrane filter. TOC concentration was 7.0±0.5 mg/L, the pH of the solution was 8.0, and the conductivity was 1066 µS/cm. The WWTP effluent was spiked with SMX in order to achieve a starting concentration of 5.5 µM.

2.3 Experimental setup

Experiments were conducted with a CONDIAPURE® test system (CONDIAS GmbH, Itzehoe, Germany) using a DIACHEM® electrode stack (CONDIAS) integrated into an optically accessible glass reactor connected to a mixing chamber (Esau & Hueber GmbH, Schrobenhausen, Germany) as described elsewhere (Heim et al., 2011; Ureña de Vivanco et al., 2013). A schematic configuration of the reactor and the operation unit is displayed in Fig. 1.

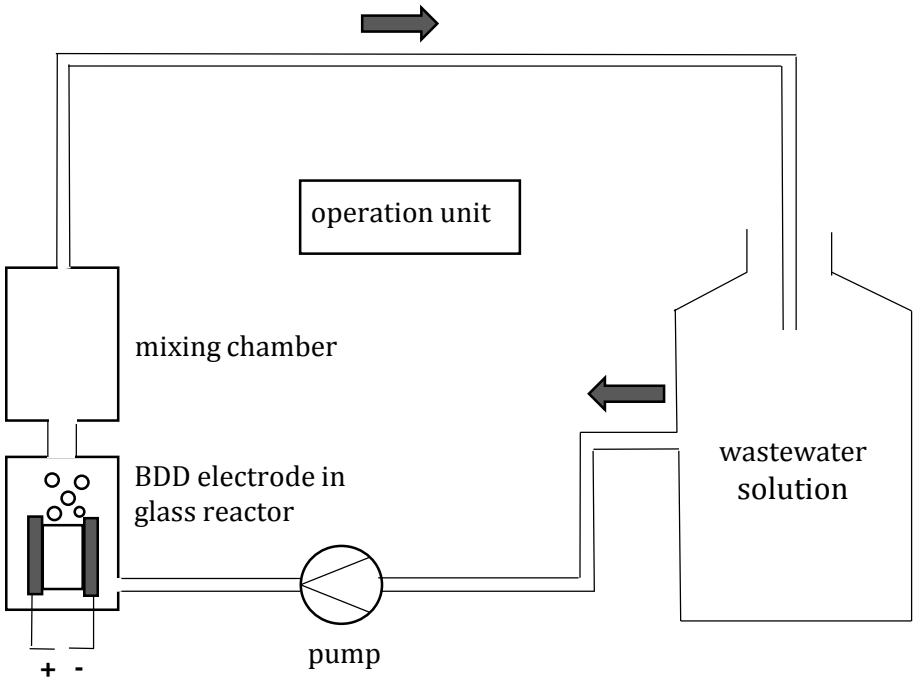


Fig 1. Scheme of the BDD reactor

In situ oxidation was performed with a single anode/cathode pair and a surface of 24 x 50 mm² per electrode. Three litres of SMX solution were prepared in a glass vessel (tempered to 20°C ± 1°C), which was connected to the operation unit with an inlet and outlet tube. The reaction solution was circulated through the glass reactor by a centrifugal pump (PY-2071, Speck Pumpen, Hilpoltstein, Germany) at a flow rate of 4 L/min. Electrolytic treatment was carried out using two current

densities (208 and 333 mA/cm^2) and an overall time of 60 and 10 minutes, respectively. Electricity consumption was monitored using the Energy Monitor 3000 (Voltcraft, Hirschau, Germany).

2.4 Sampling

Samples (2 ml each) were periodically collected directly from the glass vessel, then filtered through 0.22 µm PVDF Pleomax filters before the analysis of SMX and its transformation products with LC-MS.

2.5 LC-MS analysis

Oxidation mixtures were injected on a serial RPLC/ZIC-HILIC/ESI-TOF-MS system containing two Agilent HPLC systems series 1260 Infinity (Waldbronn, Germany) coupled to an Agilent time of flight mass spectrometer (TOF-MS) system series 6230 with a Jet Stream electrospray ionization (ESI) interface (Agilent Technologies, Santa Clara, CA, USA). Chromatographic separation was performed by serial coupling of a Poroshell 120 EC-C18 column (50.0 mm × 3.0 mm, 2.7 µm) (Agilent Technologies, USA) and a ZIC®-HILIC column (150 mm × 2.1 mm, 5 µm, 200 Å) (Merck Sequant, Umeå, Sweden) based on a method recently described (Greco et al., 2013; Rajab et al., 2013). The Jet Stream ESI source was used in negative mode with the conditions described elsewhere (Greco et al., 2013). The HPLC systems, the ESI interface, and the mass spectrometric detector were controlled and data were acquired and processed by MassHunter software (Agilent Technologies, Waldbronn, Germany) using the extracted ion chromatogram (EIC) technique within a mass tolerance of 20 ppm.

2.6 Ozone measurements

Ozone samples were taken directly from the outlet tube after 15 minutes of treatment time. Residual ozone concentrations were quantified by photometric measurement at 610 nm after decolourization of indigo carmine, based on the methods by Bader (Bader and Hoigné, 1981) with modifications described before (Heim et al., 2011). Samples were filtered using a 0.45 µm polyvinylidene difluoride (PVDF) filter to avoid any diffractive effects during the photometric measurement.

3. Results and Discussion

3.1 Degradation of sulfamethoxazole

The degradation process of 5.5 µM of SMX spiked in wastewater treatment effluent solution was carried out with the BDD electrode at two different current densities. The results in Fig. 2 show the percentage decrease of SMX over the time. Applying a current density of 333 mA/cm^2, SMX was completely degraded after 5 minutes, and it took 10 minutes using 208 mA/cm^2. The main species produced by BDD electrode that could be involved in the oxidation process are summarized in equations (1-3) (Michaud et al., 2003).

$$H_2O \rightarrow HO^{\bullet} + H^+ + e^- \quad (1)$$

$$2\ HO^{\bullet} \rightarrow H_2O_2 \quad (2)$$

$$6\ HO^{\bullet} \rightarrow O_3 + 3\ H_2O \quad (3)$$

The faster degradation rate of SMX observed at the higher current density can be related to the higher concentration of oxidants in the solution. For instance, the concentration of dissolved ozone after 15 min of electrolysis was 0.06 mg/L at 208 mA/cm² and 0.24 mg/L for 333 mA/cm², respectively. Ozone concentrations in the WWTP effluent continuously increased over the time.

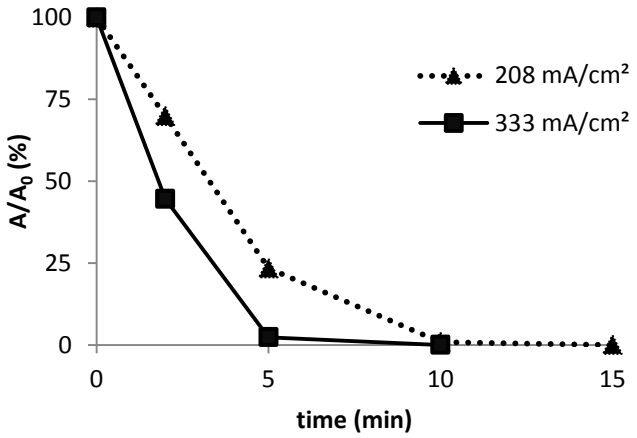


Fig 2. SMX degradation at 208 and 333 mA/cm² estimated by the chromatographic areas (A/A_0) of the relative extracted ion peak

3.2 Formation and removal of sulfamethoxazole transformation products

SMX degradation using AOPs is already the topic of several publications. However, the majority of the studies was conducted in pure water or synthetic model waters. In this study, we have chosen 17 TPs reported in current publications. These TPs were generated by different AOP treatment technologies (Abellán et al., 2008; Dirany et al., 2010; Gómez-Ramos et al., 2011; Martín de Vidales et al., 2012), and they cover a wide range of structure differences. We have recently reported the application of a new LC-TOF-MS method for the analysis of diclofenac transformation products (Rajab et al., 2013). All 17 TPs were undergone a screening procedure described in Rajab et al. (2013) based on the extracted ion chromatogram (EIC) technique, in which the chromatogram is defined by its accurate mass within 20 ppm mass tolerance.

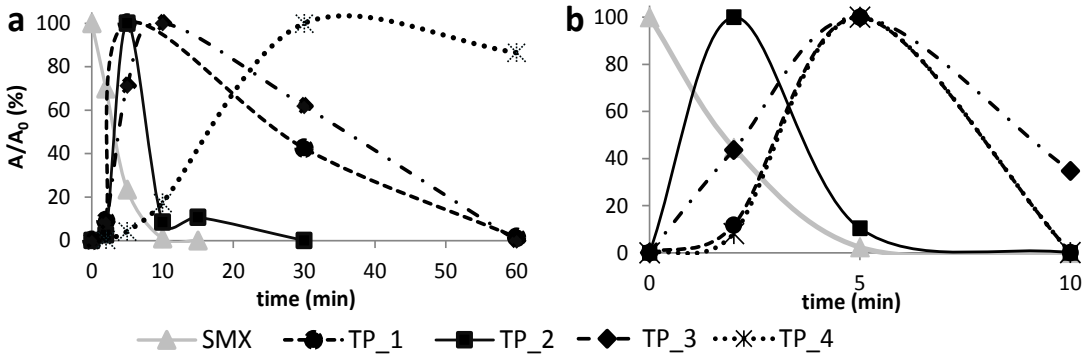
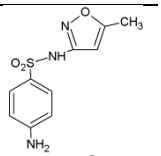
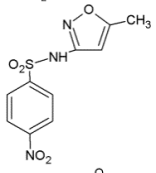
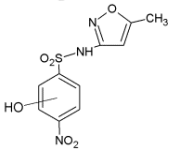
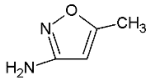
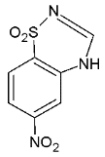


Fig 3. Time course of SMX and the four detected TPs at (a) 208 mA/cm2 and (b) 333 mA/cm² estimated by the chromatographic areas (A/A_0) of the relative extracted ion peak

Table 1 shows SMX and the detected TPs with their molecular formula, reported structure, exact mass, measured mass and the retention time R_t. The RDS% is calculated among all samples, where each sample was injected once. The toxicity of those compounds has not been reported in the literature so far, and was not investigated in this study.

Table 1: Detected TPs after electrochemical oxidation of SMX

compound	R_t (min)	RDS%	molecular formula	exp mass (m/z)	calc mass (m/z)	ppm error	reported structure
SMX	16.63	0.05 (n=7)	$C_{10}H_{11}N_3O_3S$	252.0474	252.0448	-10.2	
TP_1[a]	23.71	0.04 (n=8)	$C_{10}H_9N_2O_5S$	282.0236	282.0190	-16.3	
TP_2[a]	17.84	0.04 (n=6)	$C_{10}H_9N_3O_6S$	298.0183	298.0139	-14.7	
TP_3[b]	7.22	0.04 (n=7)	$C_4H_6N_2O$	97.0418	97.0407	-11.0	
TP_4[b]	23.75	0.63 (n=10)	$C_7H_5N_3O_4S$	225.9964	225.9928	-16.0	

a: (Abellán et al., 2008)
b: (Martín de Vidales et al., 2012)

The time courses of the observed TPs during the SMX degradation process at 208 and 333 mA/cm^2 are shown in Fig. 3. The evolution of all TPs was observed in both experiments and followed similar profiles. During the removal of SMX, TPs were generated gradually. After SMX was completely removed, the TPs were still present and therefore additional treatment time was required for their degradation. TP_1 is formed after the oxidation of the aromatic amino-group, which is converted into a nitro-group. A further hydroxylation on the aromatic ring led to the formation of TP_2. TP_3 has the smallest structure detected, characterized by an isoxazole ring. It derived from the cleavage of the S-N bond in SMX. The TP_3 was recently reported to be formed during aerobic biological treatment of activated sludge, but it was not degradable using this method (Müller et al., 2013). In the present research, TP_3 was successfully removed using the BDD electrode technology. TP_4 may derive from the cleavage of the isoxazole ring of SMX with ensuing re-arrangement of the structure. TP_4 was still detectable after 60 minutes treatment using 208 mA/cm^2.

In general, the disappearance of all TPs was faster at 333 mA/cm^2 than at 208 mA/cm^2. The observed behavior can be explained by higher concentrations of oxidants, namely ozone, at the higher current density, as shown above. This was in agreement with a previous study about the characterization of the BDD electrode (Heim et al., 2011).

3.3 Energy consumption

The total energy (E_{tot}) required for the process consists of two parts: the energy used for the pump operation and the control unit (E_{mix}) and the energy supplied to the electrode (E_{pro}). E_{mix} is independent from the applied current density. In this study conditions, E_{mix} is 0.34 Wh/L*min and it represents the largest contributor of the total energy consumption, as shown in Table 2. E_{pro} depends on the applied current density and it is 0.04 Wh/L*min at 208 mA/cm^2 and 0.07 Wh/L*min at 333 mA/cm^2. In order to evaluate the E_{tot}, the duration of the treatment should be considered. As can be observed in Fig. 2, the time needed to completely remove SMX was two times longer in case of the lower current density. The total energy demand to remove SMX was 3.77 Wh/L at 5 minutes using 208 mA/cm^2 and 2.02 Wh/L at 10 minutes using 333 mA/cm^2. Prolongation of the treatment to achieve also the degradation of the four TPs needed more energy, as shown in Table 2.

Table 2: Energy expenditure for removal of SMX and TPs at (a) 208 and (b) 333 mA/cm^2

(a)	time (min)	0	5	10	30	60
energy required (Wh/L)	E_{pro}	0	0.19	0.38	1.14	2.28
	E_{mix}	0	1.70	3.39	10.15	20.29
	E_{tot}	0	1.89	3.77	11.29	22.57

(b)	time (min)	0	2	5	10
energy required (Wh/L)	E_{pro}	0	0.1	0.32	0.68
	E_{mix}	0	0.68	1.7	3.39
	E_{tot}	0	0.78	2.02	4.07

Considering that using 208 mA/cm^2 a treatment time of 60 minutes was required to achieve a satisfactory degradation of SMX and its TPs, a total of 22.57 Wh/L were needed, whereas using 333 mA/cm^2, the treatment time was 10 minutes and the process consumed 4.07 Wh/L. As already discussed, the current density applied to the electrode affects the generated oxidative spices, resulting in different treatment times. Besides that, the duration of the treatment highly depends on the target compound and the water matrix and it has to be selected taking into account the toxicity of the compound itself and the generated TPs. The balance between the degree of the degradation of both the parent compound and their TPs and the water quality required after the treatment should be struck to meet the best operational parameters for applying the BDD electrode to remove pharmaceuticals from aqueous mediums.

4. Conclusion

It can be concluded that the BDD electrode is effectively applicable to induce sulfamethoxazole degradation in real secondary effluent. The higher the current density applied to the electrode, the faster the degradation process was. The removal of SMX was accompanied by the formation of four previously reported transformation products (TPs). It was possible to degrade all of them increasing the treatment time. Using a higher current density compared to a lower one, the

treatment time decreased and the total energy consumption was lower. The hazardousness of the TPs is not known and in case it is negligible, the treatment time could be shortened. Therefore, the final decision of the operational parameters should take into consideration not only the energy consumption but also the toxicity assays of the TPs.

Acknowledgement

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References

Abellán, M.N., Gebhardt, W., Schröder, H.F., 2008. Detection and identification of degradation products of sulfamethoxazole by means of LC/MS and -MS(n) after ozone treatment. Water Science and Technology 58, 1803–1812.

Andreozzi, R., Caprio, V., Insola, A., Marotta, R., 1999. Advanced oxidation processes (AOP) for water purification and recovery. Catalysis Today 53, 51–59.

Bader, H., Hoigné, J., 1981. Determination of ozone in water by the indigo method. Water Research 15, 449–456.

Beltrán, F.J., Aguinaco, A., García-Araya, J.F., Oropesa, A., 2008. Ozone and photocatalytic processes to remove the antibiotic sulfamethoxazole from water. Water Research 42, 3799–3808.

Beltrán, F.J., Aguinaco, A., García-Araya, J.F., 2009. Mechanism and kinetics of sulfamethoxazole photocatalytic ozonation in water. Water Research 43, 1359-1369.

Coelho, A.D., Sans, C., Agüera, A., Gómez, M.J., Esplugas, S., Dezotti, M., 2009. Effects of ozone pre-treatment on diclofenac: Intermediates, biodegradability and toxicity assessment. Science of the Total Environment 407, 3572-3578.
http://dx.doi.org/10.1016/j.scitotenv.2009.01.013
PMid:19249077

da Silva, L.M., Santana, M.H.P., Boodts, J.F.C., 2003. Electrochemistry and green chemical processes: electrochemical ozone production, Quimica Nova 26, 880–888.

Dirany, A., Sires, I., Oturan, N., Oturan, M.A., 2010. Electrochemical abatement of the antibiotic sulfamethoxazole from water. Chemosphere 81, 594–602.

Eaton, A.D., Clesceri, L.S., Rice, E.W., Greenberg, A.E., Franson, M.A.H., 2005. Standard methods for the examination of water and wastewater, 21st edn. American Public Health Association, Washington, DC

Frontistis, Z., Brebou, C., Venieri, D., Mantzavinos, D., Katsaounis, A., 2011. BDD anodic oxidation as tertiary wastewater treatment for the removal of emerging micro-pollutants, pathogens and organic matter. Journal of Chemical Technology and Biotechnology 86, 1233-1236.
http://dx.doi.org/10.1002/jctb.2669

Fryda, M., Matthée, T., Mulcahy, S., Höfer, M., Schäfer, L., Tröster, I., 2003. Applications of DIACHEM® electrodes in electrolytic water treatment. The Electrochemical Society Interface Spring 2003, 40–44.

Gómez-Ramos, M.d.M., Mezcua, M., Agüera, A., Fernández-Alba, A.R., Gonzalo, S., Rodríguez, A., Rosal, R., 2011. Chemical and toxicological evolution of the antibiotic sulfamethoxazole under ozone treatment in water solution. Journal of Hazardous Materials 192, 18–25.

González, O., Sans, C., Esplugas, S., 2007. Sulfamethoxazole abatement by photo-Fenton. Toxicity, inhibition and biodegradability assessment of intermediates. Journal of Hazardous Materials 146, 459-464.

Greco, G., Grosse, S., Letzel, T., 2013. Serial coupling of reversed-phase and zwitterionic hydrophilic interaction LC/MS for the analysis of polar and nonpolar phenols in wine. Journal of Separation Science 36, 1379–1388.

Heim, C., Ureña de Vivanco, M., Rajab, M., Glas, K., Horn, H., Helmreich, B., Letzel, T., 2011. Ozone II: Characterization of in situ ozone generation using diamond electrodes, Brewing Science 64, 83-88.

Hu, L., Flanders, P., Miller, P.L., Strathmann, T.J., 2007. Oxidation of sulfamethoxazole and related antimicrobial agents by TiO2 photocatalysis. Water Research 41, 2612-2626. http://dx.doi.org/10.1016/j.watres.2007.02.026 PMid:17433403

Huber, M., Göbel, A., Joss, A., Hermann, N., Löffler, D., McArdell, C.S., Ried, A., Siegrist, H., Ternes, T., von Gunten, U., 2005. Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: a pilot study. Environmental Science and Technology 39, 8014-8022. http://dx.doi.org/10.1021/es048396s PMid:16295869

Jones, O., Lester, J., Voulvoulis, N., 2005. Pharmaceuticals: a threat to drinking water? Trends in Biotechnology 23, 163–167.

Kraft, A., 2007. Doped diamond: a compact review on a new, versatile electrode material. International Journal of Electrochemical Science 2, 355-385.

Lee, Y., von Gunten, U., 2010. Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrateVI, and ozone) and non-selective oxidants (hydroxyl radical). Water Research 44, 555–566.

Martín de Vidales, M.J., Robles-Molina, J., Domínguez-Romero, J.C., Cañizares, P., Sáez, C., Molina-Díaz, A., Rodrigo, M.A., 2012. Removal of sulfamethoxazole from waters and wastewater by conductive-diamond electrochemical oxidation. Journal of Chemical Technology and Biotechnology 87, 1441-1449.

Martínez-Huitle, C.A., Quiroz Alfaro, M.A., 2008. Recent environmental applications of diamond electrode: critical review. Journal of Environmental Engineering and Management 18, 155–172.

Menapace, H.M., Diaz, N., Weiss, S., 2008. Electrochemical treatment of pharmaceutical wastewater by combining anodic oxidation with ozonation. Journal of Environmental Science and Health Part A 43, 1–8.

Michaud, P.A., Panizza, A., Ouattara, L., Diaco, T., Foti, G., Comninellis, C., 2003. Electrochemical oxidation of water on synthetic boron-doped diamond thin film anodes. Journal of Applied Electrochemistry 33, 151–154.

Müller, E., Schüssler, W., Horn, H. Lemmer, H., 2013. Aerobic biodegradation of the sulfonamide antibiotic sulfamethoxazole by activated sludge applied as co-substrate and sole carbon and nitrogen source. Chemosphere 92, 969-978.

Rajab, M., Greco, G., Heim, C., Helmreich, B., Letzel, T., 2013. Serial coupling of reversed-phase and zwitterionic hydrophilic interaction LC/MS: suspects screening of diclofenac transformation products by oxidation with boron-doped diamond electrode. Journal of Separation Science 36, 3011-3018.

Rodríguez-Alvarez, T., Rodil, R., Quintana, J.B., Triñanes, S., Cela, R., 2013. Oxidation of non-steroidal anti-inflammatory drugs with aqueous permanganate. Water Research 47, 3220–3230.

Rossi, L., Queloz, P., Brovelli, A., Margot, J., Barry, D.A., 2013. Enhancement of micropollutant degradation at the outlet of small wastewater treatment plants. PLOS ONE 8, 1-12. http://dx.doi.org/10.1371/journal.pone.0058864 PMid:23484055 PMCid:PMC3590130

Royadan, A., Roy, R., Yargeau, V., 2010. Oxidation products of sulfamethoxazole in ozonated secondary effluent. Journal of Hazardous Materials 177, 237-243. http://dx.doi.org/10.1016/j.jhazmat.2009.12.023 PMid:20047796

Schmalz, V., Dittmar, T., Fischer, D., Worch, E., 2008. Diamond electrodes in decentralized wastewater treatment: electrochemical degradation of the chemical oxygen demand (COD) in wastewater with high organic loads from hardening shops. Chemical Engineering and Technology 80, 1545-1550.

Ternes, T.A., Meisenheimer, M., McDowell, D., Sacher, F., Brauch, H.-J, Haist-Gulde, B., Preuss, G., Wilme, U., Zulei-Seibert, N., 2002. Removal of pharmaceuticals during drinking water treatment. Environmental Science and Technology 36, 3855–3863.

Trovó, A.G., Nogueira, R.F.P., Agüera, A., Sirtori, C., Fernández-Alba, A.R., 2009a. Photodegradation of sulfamethoxazole in various aqueous media: persistence, toxicity and photoproducts assessment. Chemosphere 77, 1292-1298.

Trovó, A.G., Nogueira, R.F.P., Agüera, A., Fernández-Alba, A.R., Sirtori, C., Malato, S., 2009b. Degradation of sulfamethoxazole in water by solar photo-Fenton. Chemical and toxicological evaluation. Water Research 43, 3922-3931.

Ureña de Vivanco, M., Rajab, M., Heim, C., Helmreich, B., Letzel, T., 2013. Setup and energetic considerations for three advanced oxidation reactors treating organic compounds. Chemical Engineering and Technology 36, 355-361.

3.3 Electrochemical oxidation of Bisphenol A by a boron-doped diamond electrode in different water matrices: Identification of transformation products and evaluation of inorganic by-products

Plastic industries are considering BPA as a chemical backbone of most polycarbonate goods and resins. The enormous application of this industrial chemical has resulted in more evidences of a contamination in water bodies. Different AOPs were used to remove BPA from water streams, however very few were conducted in real effluent of WWTP.

This section has focused on electrochemical oxidation of BPA in real wastewater matrix and in other two synthetic waters. The effect of both water matrix and the applied current density was tested in a batch system experiments. Beside the BPA degradation, TPs detection, we assessed the formation of inorganic by-products and the specific energy consumption of the process.

The degradation process has been shown to be mainly affected by two factors. Higher current densities accelerate the decomposition process, whereas an increase of inorganic water constituents and organic matter decelerates the process. Independent of the water matrix, the BPA degradation followed a pathway consisting of three main steps: The formation of hydroxylated derivatives followed by the oxidation of the isopropylidene bridge and subsequently the cleavage of the aromatic ring to form small organic molecules. The concentrations of chlorate and perchlorate were relatively high. The formation of these inorganic by-products during the electrochemical oxidation and the specific energy demand are a significant drawback using BDD electrodes. However, further improvement of the BDD electrodes including the electrode design and reactor configurations might help in mitigating these drawbacks.

The results of this section are included in the following manuscript. Rajab, M., Heim, C., Letzel, T, Drewes, J.E., Helmreich, B. Electrochemical oxidation of Bisphenol A by a boron-doped diamond electrode in different water matrices: Identification of transformation products and evaluation of inorganic by-products,. Chemosphere, submitted 17.02.2015. Co-authors contributed through valuable insight into overall direction of the research and experimental planning; experimental execution, data analysing, review published data and manuscript preparation were performed by Mohamad Rajab.

Electrochemical oxidation of Bisphenol A by a boron-doped diamond electrode in different water matrices: Identification of transformation products and evaluation of inorganic by-products

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Abstract

An electrochemical advanced oxidation process employing a boron-doped diamond anode for the treatment of synthetic waters and secondary effluents of wastewater treatment plants (WWTP) was studied. The efficiency and formation of transformation products (TPs) for this treatment process were investigated at different current densities for bisphenol A (BPA) spiked to synthetic water and WWTP effluents. A complete removal of the parent compound was achieved in WWTP effluents. Higher applied current densities resulted in faster removal. At the same time, a correlation between the applied current density and the ozone concentration measured in the bulk solution was revealed. Hence, the observed transformation of BPA is likely due to the generation of reactive oxygen species such as hydroxyl radicals and ozone. Based on a suspected target screening approach, 4 known TPs and two unreported (new) TPs were identified by LC-MS analysis. These results suggest a transformation pathway following three steps: hydroxylation of the aromatic ring, followed by oxidation of the isopropylidene bridge and finally a ring opening and formation of organic acids and other small molecules. The presence of chloride ions in WWTP effluents can result in the generation of excessive concentrations of chlorate and perchlorate during electrochemical oxidation. Applying a current density of 208 mA cm^{-2}, a complete elimination of BPA was achievable after 15 min (Q/V=430 mAh L^{-1}), however, the oxidation resulted in concentrations of chlorate and perchlorate of 2.85 and 5.65 mg L^{-1}, respectively. These values were directly dependent on the exposure time and desired degree of BPA removal.

Keywords:

Boron-doped diamond electrode; electrochemical advanced oxidation process; bisphenol A; by-product formation; transformation products; energy demand

1. Introduction

Due to its biological toxicity and estrogenic activity, bisphenol A (BPA) has received particular focus in the last few years. Since the 1950s, plastic industries are considering BPA as a chemical backbone of most polycarbonate goods and resins (Brede et al., 2003). The applications of such products can results in a direct contact to humans via plastic packaging for food and beverage or thermal paper. BPA might be released during the industrial processes or leaches out of final products and ends up in the water cycle. Many studies have shown that the occurrence of BPA is ranging from microgram per litre in natural waters to much higher levels in streams including industrial runoffs (Arnold et al., 2013; Gasperi et al., 2014; Gültekin and Ince, 2007). Considerable risks are associated with BPA exposure even at low concentrations. Among these risks are spermatogenesis disorder or imbalance of the hormone system (Lang et al., 2008; Qiu et al., 2013; Sharpe, 2011). Consequently, it is important to reduce remaining concentrations of BPA in wastewater to enable a sustainable discharge to the receiving aqueous environment or to engage in water recycling for different reuse applications.

Conventional biological wastewater treatment technologies have limitations in sufficiently reducing the broad spectrum of micropollutants including BPA (Huber et al., 2005; Ternes et al., 2002). Therefore, new treatment processes that are more efficient, less harmful for the environment and offer economic advantages have been proposed for BPA attenuation. Among different available technologies for advanced water treatment, electrochemical advanced oxidation processes (EAOPs) involving *in-situ* generation of oxidant agents are a promising alternative to treat polluted water (Martínez-Huitle and Ferro, 2006; Sirés et al., 2014, Rajab et.al., 2015). To achieve efficient treatment, the anode material plays a critical role in these electrochemical processes. Boron-doped diamond (BDD) has shown remarkable properties to be applied as anodic material (Kraft, 2007; May, 2008). Different studies have shown high treatment efficiencies due to the material characteristic, such as chemical stability and inertness as well as the highest known oxygen evolution overpotential for water electrolysis (Fujishima,

2005). The BDD electrode has the capability to generate different reactive oxygen species (ROS) on the surface of the electrode and in the bulk solution depending on water composition and operational conditions (Kraft et al., 2006; Panizza and Cerisola, 2009).

In recent years, different studies have investigated the removal of BPA by means of AOPs; for example photocatalysis (da Silva et al., 2014; Sarkar et al., 2014), ozonation (Kusvuran and Yildirim, 2013; Umar et al., 2013), Fenton reaction (Arslan-Alaton et al., 2014; Rivero et al., 2014), photo-Fenton-like reaction (Molkenthin et al., 2013), UV/H_2O_2 (Bertanza et al., 2010; Sarkar et al., 2014), as well as electrochemical oxidation applying various anodes (Ju et al., 2012). BDD electrodes were previously used in four studies (Cui et al., 2009; Murugananthan et al., 2008; Pereira et al., 2012; Yoshihara and Murugananthan, 2009), but none of them were applied in real wastewater treatment plant (WWTP) effluents. Wastewater effluent contains abundant chemical components in different concentrations that might affect the efficiency of the electrochemical oxidation of BPA. The interaction between BPA degradation, formation of organic transformation products (TPs) and inorganic by-products is also unknown.

Within this framework, the scope of this study was to investigate the applicability of the BDD electrode to eliminate BPA from different water matrices (deionized water (DI), synthetic drinking water with and without organic content (SW+DOC and SW), and WWTP effluents). The effect of the applied current density as one of the most important factors during the process was examined. The experiments with deionized water were used to identify TPs formed during the process. The novelty aspect of the study has been introduced through assessing a set of degradation experiments using real WWTP effluents spiked with BPA. A special focus was on connecting the development of TPs during the process, energy consumption and formation of inorganic by-products.

2. Experimental Methods

2.1 Chemicals

Phosphoric acid (85%), 5,5-indigodisulphonic acid sodium salt (indigo carmine), sodium hydroxide (NaOH), sodium thiosulfate ($Na_2S_2O_3$), calcium chloride ($CaCl_2$), potassium bromide (KBr), magnesium sulphate heptahydrate ($MgSO_4 \cdot 8H_2O$), sodium hydrogen carbonate ($NaHCO_3$), sodium nitrate ($NaNO_3$) and ethylenediamine monohydrate as well as bovine serum albumin (BSA) were purchased from Merck (Darmstadt, Germany). Native

humic acid (30-40% soil extract) was purchased from Carl Roth (Karlsruhe, Germany). BPA was purchased from Sigma–Aldrich Chemie (Steinheim, Germany). Acetonitrile HiPerSolv Chromanorm was purchased from BDH (Poole, UK). Water LC-MS Chromasolv was bought from Fluka (Buchs, Switzerland). Ammonium acetate was purchased from Sigma-Aldrich (Seelze, Germany). All chemicals were of analytical grade. The solutions were prepared using deionized water ultra-pure water (Milli-Q, 18.2 MΩ·cm).

2.2 Water matrices

Two synthetic waters were prepared by dissolving the salt mix in deionized water. The characteristic of the four water types (DI, SW, SW+DOC and WWTP) used in this study is presented in Table 1.

Table 1. Water quality of the applied water matrices

Parameter [Unit]	DI	SW	SW+ DOC	WWTP
Electrical conductivity [µS cm^{-1}]	0.08	380±27	360±13	1,170
pH	7.8±0.5	8.3±0.3	8.7±0.5	8.0 ± 0.8
c(Cl^-) [mg L^{-1}]	n.d.	20	20	180 ± 10
c(Br^-) [mg L^{-1}]	n.d.	0.1	0.1	n.d.
c(HCO_3^-) [mg L^{-1}]	n.d.	122	122	n.d.
DOC [mg L^{-1}]	n.d.	0	5	12

n.d. not determined

2.3. Experimental setup

Experiments were performed using a conductive diamond electrode system (Figure 1). (CONDIAS GmbH, Itzehoe, Germany). The system consisted of a feed container (1) holding the contaminated water before it was circulated through the single chamber cell (4) (volume =19 cm^3) by means of a centrifugal pump (2) (NPY-2051, Speck Pumpen, Hilpoltstein, Germany) at pre-determined constant flow rate. The electrical power was provided by a

laboratory power supply (5) (EA-PS 3032-10B Heiden Power-Germany). Two sensors (3) placed on the hoses connecting the different parts were placed to measure the temperature, pressure and flow rate.

The electrode stack – located in the cell – consisted of two BDD cathodes and two BDD anodes on a niobium substrate provided by CONDIAS GmbH (Itzehoe, Germany) with an overall effective anode area of 24 cm². A nafion cation exchange membrane was placed in direct contact to each cathode and anode in order to receive a gap-free sandwich structure.

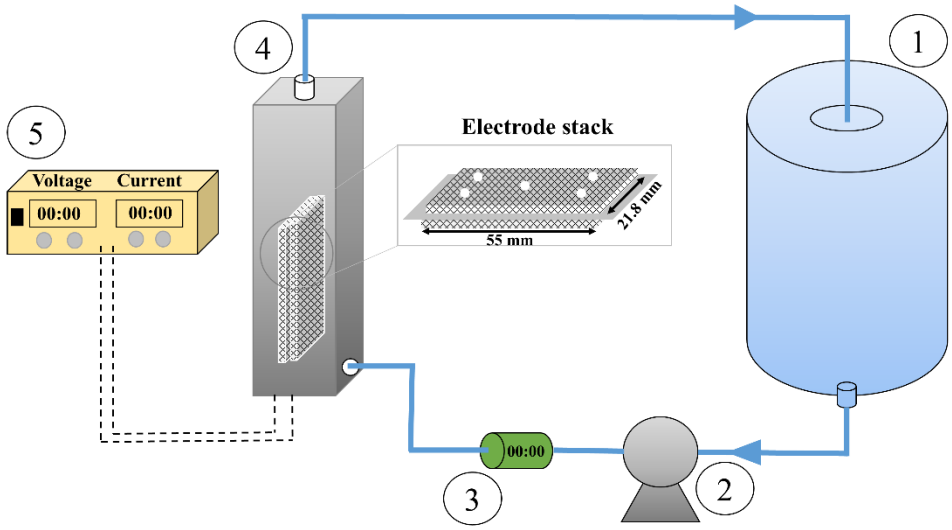

Fig.1. Flow schematic of the bench-scale BDD system. (1) Feed container (2) pump (3) sensor (4) single chamber cell (5) power supply

This enhanced the current density locally and therefore promoted ozone formation enabling electrode operation at low electrical conductivities (Kraft et al., 2006). The applied current could be regulated between 0 and 10 A. All experiments were conducted at room temperature (25 ± 2 °C) and a flow rate of 4 L min^{-1}. Two current densities, 125 and 208 mA cm^{-2}, were applied during this study. Kraft et al (2006) has shown that the best current efficiency for ozone generation (20-24%) is in the range of 50 to 175 mA cm^{-2}. Outside this range the efficiency decreased due to rapid ozone decay in water. Thus, both applied current densities in this study provide a sufficient ozone generation and offer with two different set-points a preliminary assessment of energy demands and inorganic by-product formation. All experiments were carried out in duplicate and showed a good reproducibility within a 95% confidence interval regarding BPA transformation. The mean values of the results of the replicated experiments are presented.

2.4. Bisphenol A oxidation experiments

Three liters of BPA solution (43.8 µM) were prepared and transferred to the feed tank. During treatment, samples (2 ml each) were collected directly after the electrochemical cell at 0, 1, 2, 3, 5, 7.5, 10, 15, 30 and 60 minutes. The oxidation reaction in the samples was terminated by adding 20 µL of 10 mM Na_2SO_3 solution directly after sampling. The samples were filtered through 0.22 µm polyvinylidene fluoride (PVDF) Pleomax filters prior to chromatographic analysis.

2.5. Analyses

The pH was measured using a pH-meter (SenTex 4, WTW, Germany) according to Standard Method 4500-H^+ (Rice et al., 2012). Chemical analysis of dissolved organic carbon (DOC) was performed with an Elementar High TOC II-Analyzer according to Standard Method 5310 after filtration through a 0.45 µm polypropylene membrane filter.

In analogy to the electrochemical oxidation experiments, residual ozone concentrations were measured following the indigo method of Bader and Hoigné (1981) with a modification according to Yates and Stenstrom (2000) replacing the phosphate buffer by phosphoric acid. Bromide (Br^-), chloride (Cl^-), chlorate (ClO_3^-) and perchlorate (ClO_4^-) were analyzed by ion chromatography using a Dionex ICS-1000 (Thermo Scientific Dionex, USA) according to DIN EN ISO 10304-1 DEV E19 (International Organization for Standardization, 2007) (with LODs = 10 µg L^{-1}) after quenching the residual oxidants with 1 mL of ethylenediamine solution (10 mM). The standard deviations of the chemical analyses were found to be 8% for the ozone measurement and 6% for the IC analysis. The quantification of all ROS is impossible in this experimental set-up. Hence, in this study just dissolved ozone concentrations were followed. The quantification of hydroxyl radicals is a goal of other on-going experiments and is not significant for the – qualitatively – analytical approaches of this study.

A detailed description of the chromatographic analysis is described elsewhere (Rajab et al., 2013). Briefly, the samples were injected on a serial RPLC/ZIC©-HILIC/ESI-TOF-MS system combining two Agilent HPLC systems series 1260 Infinity (Waldbronn, Germany) coupled to an Agilent time-of-flight mass spectrometer (TOF-MS) system series 6230 with a Jet Stream electrospray ionization (ESI) interface (Agilent Technologies, Santa Clara, CA, USA). Chromatographic separation was performed by serial coupling of a Poroshell 120 EC-C18

column (50.0 mm × 3.0 mm, 2.7 µm) (Agilent Technologies, USA) and a ZIC©-HILIC column (150 mm × 2.1 mm, 5 µm, 200 Å) (Merck Sequant, Umeå, Sweden). For mass-spectrometric analysis, the negative mode of the jet stream ESI source was used. The method is described elsewhere (Greco et al., 2013). The HPLC systems, the ESI interface, and the mass spectrometric detector were controlled and data were acquired and processed by the MassHunter software (Agilent Technologies, Waldbronn, Germany) using the extracted ion chromatogram (EIC) technique within a mass tolerance of 10 ppm. The logarithm of the distribution coefficient (log *D*) was calculated at pH 7.0 with the MarvinSketch 5.12.4 software.

3. Results and Discussion

In the current experiments, a BDD electrode was applied in order to oxidize BPA in synthetic and real water matrices. First, BPA transformation was studied as a function of both applied current density and composition of the water matrix. The formation of TPs and the stepwise degradation pathway of BPA during BDD treatment were investigated – qualitatively – in deionized water in order to minimize reactions with the water matrix. A quantification was not done. Moving toward applicability under real conditions, the experiments in wastewater effluent were studied with a special focus on understanding the connection of the development of TPs during the process, energy consumption and formation of inorganic by-products.

3.1. Influence of the applied current density and the water matrix content

To test the dependency of the applied current density on the degradation process of BPA, a set of experiments was conducted applying two different current densities (125 and 208 mA cm^{-2}) in wastewater effluent spiked with BPA [43.8 µM]. The relative removal of BPA in wastewater effluent as a function of electrical charge input Q/V is presented in Figure 2. The figure was plotted using the integrated chromatographic peaks' area measured from the extracted-ion chromatograms (EIC) for deprotonated BPA (*m/z* 227.1077) for each collected sample during the experiment.

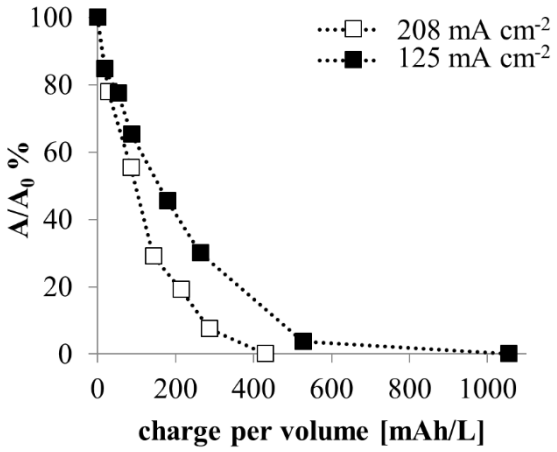

Fig. 2. Normalized removal of BPA in wastewater effluent at two different current densities

The removal of BPA increased with increasing current density and a complete transformation of the parent compound was achieved at a Q/V-value of 430 and 1054 mAh L^{-1} for 208 and 125 mA cm^{-2}, respectively. At a Q/V-value of 286 mAh L^{-1}, a removal level of 92.5% was achieved for a current density of 208 mA cm^{-2}, whereas at the same Q/V-value and applying 125 mA cm^{-2}, just 70% removal was observed. It is important to note that the time needed to introduce this amount of charge in the water matrix is directly depended upon the applied current density. Twenty minutes were required in the case of 125 mA cm^{-2}, whereas the time needed to apply 208 mA cm^{-2} was 10 minutes to introduce a Q/V-value of 286 mAh L^{-1}. The different removal patterns presented in Figure 2 are likely due to the presence of reactive oxygen species – mainly hydroxyl radicals and ozone – generated *in situ* to different degrees. The concentrations of dissolved ozone at a Q/V-value of 286 mAh L^{-1} were 0.17 and 0.07 mg L^{-1} for 208 and 125 mA cm^{-2}, respectively. The higher concentration of ozone in the solution has likely contributed to the faster degradation rate of BPA while applying 208 mA cm^{-2}. As expected, the ozone concentrations during the experiment were low due to the oxidation demand of organic and inorganic constituents in wastewater effluent consuming dissolved ozone quickly. In addition, these constituents also represent scavengers for hydroxyl radicals as a primary product of the BDD electrode. In order to further investigate the role of water chemistry on BPA oxidation efficiency, a new set of experiments was performed. Beside deionized water (DI) and wastewater effluent (WWTP), two synthetic water matrices containing elevated concentrations of inorganic ions (SW) and organic matter (SW + DOC) were prepared. These four water matrices were spiked with BPA and subsequently oxidized using the BDD electrode applying the same current densities (125, 208 mA cm^{-2}) as in previous

experiments. In all water matrices, BPA was effectively removed independent of the applied current density as illustrated in Figure 3. However, the charge input (or exposure time, respectively) required to achieve complete transformation of the parent compound differed among the four matrices.

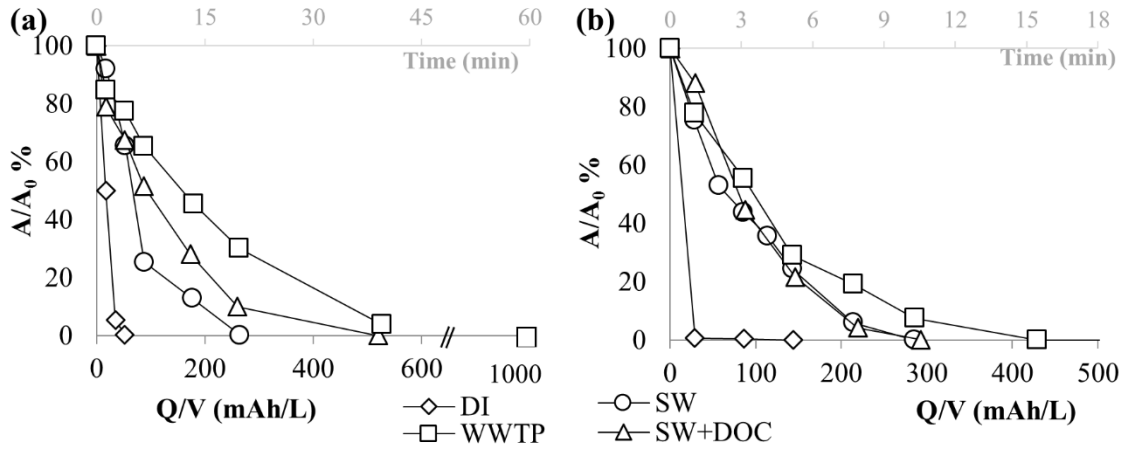

Fig. 3. Electrochemical BPA degradation in four water matrices applying two current densities (a) 125 mA $cm^{-2}$and (b) 208 mA cm^{-2}

At a current density 125 mA cm^{-2} (Fig 3a), BPA removal in a DI water matrix was completed in 3 min (52.2 mAh L^{-1}), in SW in 15 min (265 mAh L^{-1}), and required twice as long for the SW+DOC matrix (30 min/520 mAh L^{-1}). Sixty minutes were required to obtain complete elimination in a wastewater effluent matrix. The variability in the degradation progress among the water matrices is likely due to competitive reactions with elevated concentrations of inorganic constituents and organic matter present in synthetic waters and wastewater effluent. These substances can affect the availability of oxidative species (such as ozone and hydroxyl radicals) leading to a less effective BPA degradation. Furthermore, the presence of radical scavengers, such as carbonate in the used synthetic water and wastewater effluent, may reduce the amount of hydroxyl radicals (Andreozzi, 1999). The organic matter added to SW and present in wastewater effluent include double bonds, activated aromatic rings and non-protonated amines, which can react very quickly with ozone and hydroxyl radicals at a rate of 10^6-10^9 $M^{-1}s^{-1}$ (von Gunten, 2003). As a consequence of these possible reactions, less ozone was likely available in the bulk solution, resulting in a lower BPA degradation rate especially in wastewater effluent. Applying a higher current density (Figure 3b) accelerates the oxidation process and consequently shortens the time needed to degrade BPA in all water matrices.

Higher current densities will generate more hydroxyl radicals on the surface of electrodes, which will react further to form ozone and subsequently result in faster BPA degradation. Due to the higher ozone concentration available in the bulk solution, the differences among the various water matrices regarding BPA oxidation were less significant. As a conclusion, the more electron-donating compounds were present in a water matrix, the less ozone was available in the bulk solution and therefore less BPA degradation took place. Moreover, the expression "removal" used in the discussion means the disappearance of the molecule from the analytical measurements (< LoD) and does not mean total mineralization. Assessing the mineralization requires TOC measurements and different experimental approaches and set-up. Nevertheless, TOC measurements were not done in this study.

3.2. Identification of transformation products in DI water

In order to get a better understanding of transformation processes during the electrochemical oxidation of BPA in absence of competitive reactions with the water matrix, a suspected analytical screening approach (Krauss et al., 2010) was carried out for the treated solution in deionized water. This approach was initiated by generating a list of 37 transformation products (TPs) based on a comprehensive literature review focusing on BPA oxidation applying various AOPs (Table S1). The suspected TPs cover a wide range of structural differences regarding the number of carbon atoms, aromatic rings, and polar groups. Table S1 in the supporting information shows BPA and 37 suspected TPs including their molecular formula, reported structure, exact mass, the applied degradation method, method of analysis, and related references. The analytical procedure using LC-MS has been reported previously (Rajab et al., 2013a, 2013b). Hence, from the 37 suspected TPs (Table S1), a short list of six TPs (4 known TPs and 2 new TPs) were identified in the treated deionized water (Table 1). A further check of the MS spectra of those six TPs did not show any match with possible parent compounds.

As expected, during electrochemical oxidation more polar compounds were formed and therefore the retention times and log*D* values of those compounds were lower than that of BPA. The formation of different hydroxylated derivatives indicates an unselective attack of the OH radicals on the aromatic rings (Oturan and Pinson, 1995) of the BPA molecule. TP1 (*m/z* 243.1027), a mono-hydroxylated BPA, was previously reported as shown in Table S1 with its structure illustrated in Figure 4. The formation of poly-hydroxylated BPA would be also expected as a consequence of the large amount of hydroxyl radicals generated at the BDD anode. Indeed, di-hydroxylated BPAs were reported as TPs formed when water was treated by

AOPs. Hence, the screening procedure of all possible hydroxylated derivatives was executed. A tetra-hydroxylated (4-OH groups) BPA with a molecular mass of *m/z* 291.0874 was detected in deionized water samples (TP2, Figure 4). A formula generation action of the signal at *m/z* 291.0869 was executed and the chemical formula $C_{15}H_{16}O_6$ was generated with a score of 76 and an error of 3 ppm. A new structure for this TP2 was suggested that include four hydroxyl groups on the aromatic rings. The exact position of the hydroxyl groups added to the BPA molecule could not be determined definitively from the information gained from the LC-MS data and is outside this scope of this study.

Table 2. Accurate mass measurements of the identified suspected TPs in deionized water

TPs	Molecular formula	R_t (min)	RSD (%)	Log*D* (pH 7.0)	Exp mass (m/z)	Calc mass (m/z)	ppm error
BPA	$C_{15}H_{16}O_2$	26.84	0.02 (54)	4.04	227.1081	227.1077	-1.8
known							
TP1	$C_{15}H_{16}O_3$	25.87	0.03 (13)	3.74	243.1021	243.1027	2.5
TP3	$C_8H_8O_4$	7.15	0.07 (46)	-2.71	167.0351	167.0350	-0.6
TP5	$C_7H_8O_3$	6.57	0.08 (51)	-1.85	139.0404	139.0401	-2.4
TP6	$C_4H_4O_4$	5.22	0.04 (64)	-5.80 / -4.55	115.0040	115.0037	-2.7
new							
TP2	$C_{15}H_{16}O_6$	21.67	0.14 (24)	2.82	291.0869	291.0874	1.6
TP4	$C_6H_4O_4$	6.87	0.04 (24)	-1.98	139.0031	139.0037	4.0

The retention times of BPA in comparison with its detected hydroxylated derivatives (TP1 and TP2) reveal the differences in polarity, where the most polar molecule (TP2) eluted faster from the RP chromatographic column followed by TP1 and finally the parent compound BPA.

After the hydroxylation step of the BPA molecule, further reactions might lead to ring opening. At this level of oxidation, different possibilities are expected. Among others, the splitting of the phenolic moiety at the connection point with the isopropylidene bridge and further oxidation of this linking bridge by hydroxyl radicals are possible reactions. For the pathway, TP3 (*m/z* 167.0351) could be formed (see also Figure 4).

The formation of benzoquinone compounds is reported in almost all literature studies dealing with oxidation of BPA. Those compounds have the characteristic of shifting the color of the solution from colorless to light-brownish. This color change was observed during the oxidation of BPA in deionized water applying 208 mA cm^{-2} for a few minutes, then it disappeared after extended treatment. However, the screening of the LC-MS data did not reveal a match with any of the reported benzoquinone from Table S1, but a compound with a molecular mass of *m/z* 139.0037 was detected. The retention time of this molecule was 6.87

min with a log*D* value of -1.98, which is in agreement with the retention behavior of hydrophilic molecules. As no significant signal appears in the MS spectrum of the sample, a formula generation action of the signal at *m/z* 139.0039 was operated and the chemical formula $C_6H_4O_4$ was generated with a score of 71 and an error of 3.1 ppm. Based on this formula and the color changing of the solution, and because no TP with this formula was previously reported, a new structure was proposed including a benzoquinone molecule with two hydroxyl groups on the ring (TP4, Figure 4).

The cleavage of the aromatic ring leads to the formation of aliphatic acids and small molecules. In this study, two different aliphatic acids TP5 with *m/z* 139.0401 and TP6 with *m/z* 115.0037 were identified. An additional piece of evidence for the formation of such organic acids could be the decreasing pH value during the experiments (from an initial value of 7.8±0.5 to 6.5±0.3 at the end of the experiments). This effect was also reported in previous studies (Cui et al., 2009; Yoshihara and Murugananthan, 2009). In conclusion, four reported TPs of BPA were identified and two more TPs were proposed based on the analytical data generated. Considering the properties of those compounds, with the current LC coupling system, it was possible to separate the molecules of a large polarity range in just one single injection, whereas other studies used separate analytical instruments (RPLC, GC, and IC) to identify and verify the same compounds.

3.3. Proposed electrochemical oxidation scheme for BPA degradation in DI water

Based on the identified TPs, a general stepwise scheme of the BPA degradation with the BDD electrode was proposed (Figure 4). As illustrated in the figure, three main steps are considered. The first step involves the non-selective attack of hydroxyl radicals generated on the surface of the electrode and the ozonation reaction of the BPA molecule in the bulk solution leading mainly to hydroxylated derivatives and in the second step to aromatic ring openings. Ring opening, phenolic moiety cleavage and oxidation of the isopropylidene bridge are – among others – different reaction pathways at this level. The third proposed step is a more advanced oxidation level, where the aromatic rings undergo a cleavage resulting in the generation of organic acids and small molecules. Further steps can be expected ending with the mineralization of BPA to CO_2 and H_2O, but this will require much longer exposure times.

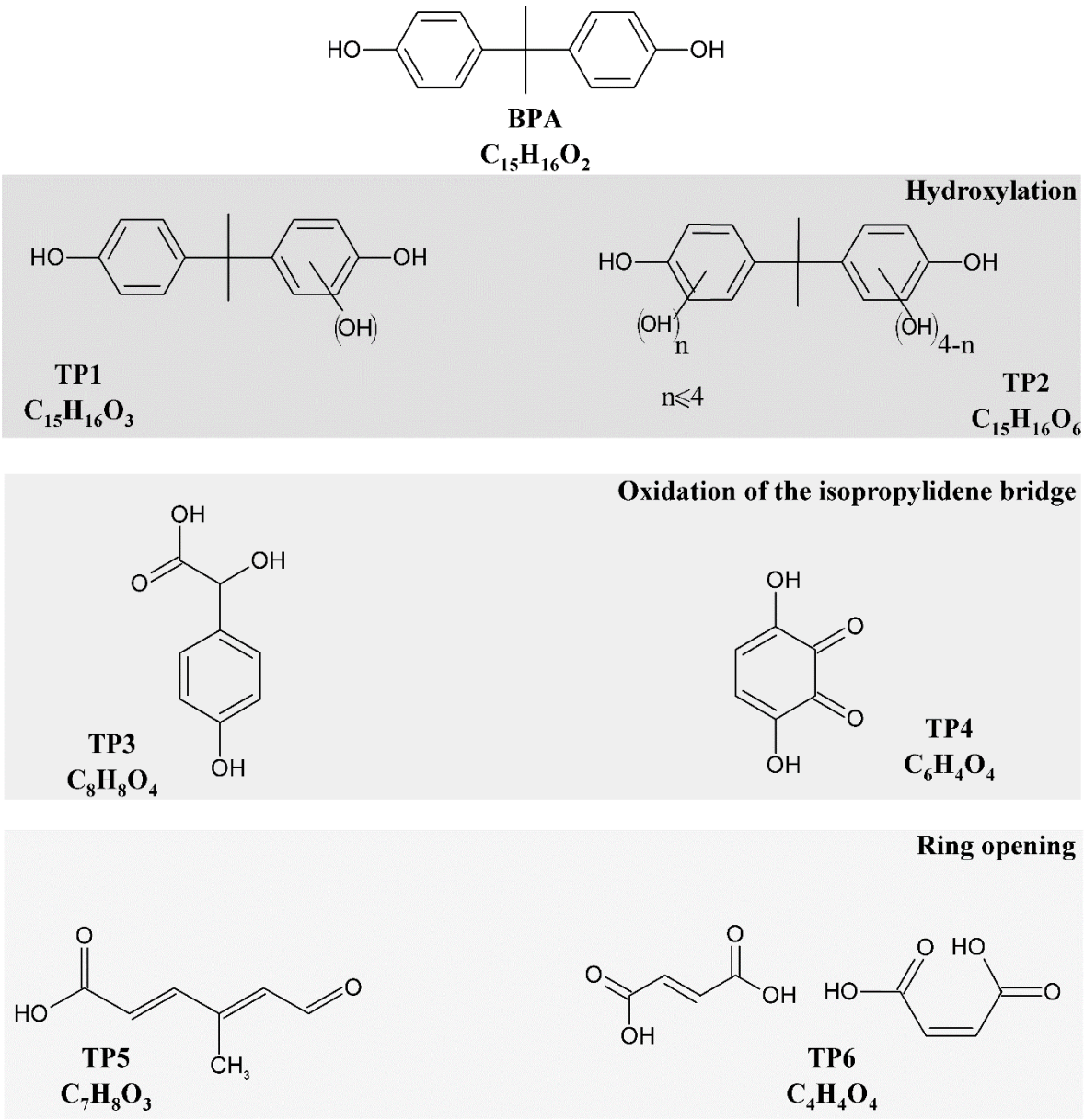

Fig. 4.. Proposed stepwise BPA degradation pathway during oxidation with the BDD electrode

3.4. BPA degradation in wastewater treatment plant effluent: operational perspective

Several publications have already reported BPA degradation using different AOPs. However, the majority of these studies was conducted in deionized water matrices or synthetic model waters. In this study, experiments were also performed in real wastewater effluent. The results obtained from those experiments will pinpoint to the important role of the water matrix for TP formation. In addition, these experiments allow an approximate estimation of the

specific energy demand of the process. The TPs reported in Table S1 followed the same screening procedure as described before for deionized water. Four TPs (TP1, TP3, TP5 and TP6) were detected in wastewater effluent samples. Compared to deionized water, wastewater effluent has higher content complexity. Thus, the oxidants (OH radicals and ozone) would be less available for BPA poly-hydroxylation and further degradation. This could be a reason for the undetected TP2. Despite the differences between both water matrices, the presence of the targeted TPs indicates that the underlying degradation mechanism could be the same.

In this context, it is noteworthy that the role of ionic species, such as chloride present in wastewater effluent needs to be considered in the formation pathway of TPs as also additional chlorinated or brominated TPs can be formed. While these compound were reported in other studies (Bourgin et al., 2013; Dupuis et al., 2012), the analysis of these species was beyond the scope of this study.

The formation of three targeted TPs (TP1, TP3 and TP5) during the BPA degradation process at 208 mA cm^{-2} is illustrated in Figure 5. During the removal of BPA, TPs were generated simultaneously and gradually. The TPs appeared and disappeared (partially or completely) at different times depending on the degradation step as described previously (Figure 4). Consequently, TP1 (hydroxylated BPA) appeared directly after initiating the process and disappeared within 30 minutes. The other two TPs (TP3 and TP5) increased to their maximum at 10 minutes then decreased gradually to 0% for TP3 and 40% for TP5 at 60 minutes. This raises the question, how long an oxidation process should be performed to achieve "complete removal" of a target compound? The answer to this question is associated with the economic aspect. From an energetic point of view as BPA disappeared completely after introducing a charge Q/V of 430 mAh L^{-1} (15 min), the process could be terminated at that point. With the given reactor design, this mode of operation would represent a specific energy demand of 7.4 kWh m^{-3}. This high value is due to the severed limitations of the chosen batch system. The unfavorable hydrodynamic conditions of the reaction cell as well as the imperfect diamond structure of the electrode are reasons that pushed the specific energy demand up to this level. An extrapolation of the values reported here to a large-scale continuous-flow reactor is not possible and these values should be seen only as a preliminary approximation. Continuous-flow experiments are planned and will be published in nearby future.

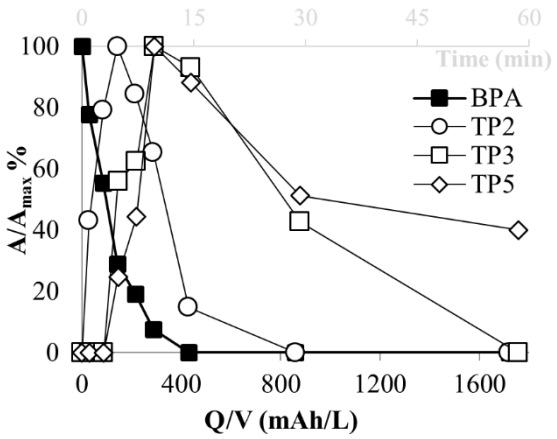

Fig 5. BPA degradation and the formation of three TPs in a wastewater effluent matrix applying 208 mA cm^{-2}

Beside a potentially very high specific energy demand, an additional drawback of electrochemical oxidation using BDD electrodes in chloride-containing waters is the formation of inorganic by-products and halogenated organic compounds (such as chlorate, perchlorate, adsorbable organic halides (AOX) and trihalomethanes (THMs)) (Anglada et al., 2011; Azizi et al., 2011). In this study, considering rather worst-case reactor and process design conditions the generation of chlorate and perchlorate during BPA oxidation in a wastewater effluent matrix was quantified. As BPA was completely eliminated (Q/V=430 mAh L^{-1}, 15 min), the chlorate and perchlorate concentrations were 2.85 and 5.65 mg L^{-1}, respectively. However, lower chlorate and perchlorate concentrations would be achievable while aiming at a BPA degradation of 70-80% and the formation of TP1, TP3 and TP5. To the best of our knowledge, no toxicity has been reported for those TPs so far. Due to the carcinogenic potential of perchlorate, different measures should be considered to reduce the concentration, in order to meet discharge regulations (e.g. US Environmental Protect Agency: 15 µg L^{-1} (Bergmann et. al 2014)). In this context, it is important to stress that BDD electrodes might not be seen as suitable drinking water treatment technology. The water matrix used in the experiments here represents a scenario similar to an industrial effluent highly contaminated with BPA. Other applications of electrochemical oxidation are the treatment of industrial wastewater, cooling water and ballast water, for which higher initial chloride and bromide concentrations are expected. The inorganic by-products regulations of such treated waters are different than those for drinking water and might be less stringent. In Canada for example, the recommended interim guideline for chlorate in freshwater was set at 30 mg L^{-1} (Warrington 2002).

4. Conclusion

The BDD electrode is effective in oxidizing BPA in different water matrices. The degradation process has been shown to be mainly affected by two factors. Higher current densities accelerate the decomposition process, whereas an increase of inorganic water constituents and organic matter decelerates the process. The generated oxygen reactive species – mainly hydroxyl radicals and ozone – are responsible for the oxidation process. Independent of the water matrix, the BPA degradation followed a pathway consisting of three main steps: The formation of hydroxylated derivatives followed by the oxidation of the isopropylidene bridge and subsequently the cleavage of the aromatic ring to form small organic molecules. For water compositions like wastewater effluent, BPA abatement and the formation of TPs were evaluated regarding specific energy consumption of the process. Depending on the extent of oxidation, the energy required for complete BPA removal in a batch process was 7.37 kWh m^{-3}. However, an even higher energy demand was needed to achieve a complete oxidation of the formed TPs. Excessive amounts of chlorate and perchlorate were formed during the batch treatment increasing in concentrations with longer treatment time. The formation of these inorganic by-products during the electrochemical oxidation and the specific energy demand are a significant drawback using BDD electrodes. However, further improvement of the BDD electrodes including the electrode design and reactor configurations as well as continuous-flow experiments might help in mitigating these drawbacks.

Acknowledgments

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References

Andreozzi, R., 1999. Advanced oxidation processes (AOP) for water purification and recovery. Catal. Today. 53, 51–59.

Anglada, A., Urtiaga, A., Ortiz, I., Mantzavinos, D., Diamadopoulos, E., 2011. Boron-doped diamond anodic treatment of landfill leachate: evaluation of operating variables and formation of oxidation by-products. Water Res. 45, 828–838.

Arnold, S.M., Clark, K.E., Staples, C.A., Klecka, G.M., Dimond, S.S., Caspers, N., Hentges, S.G., 2013. Relevance of drinking water as a source of human exposure to bisphenol A. J Expo Sci Environ Epidemiol.23, 137–144.

Arslan-Alaton, I., Aytac, E., Kusk, K.O., 2014. Effect of Fenton treatment on the aquatic toxicity of bisphenol A in different water matrices. Environ Sci Pollut Res Int. 21, 12122–12128.

Azizi, O., Hubler, D., Schrader, G., Farrell, J., Chaplin, B.P., 2011. Mechanism of perchlorate formation on boron-doped diamond film anodes. Environ. Sci. Technol. 45, 10582–10590.

Bader, H., Hoigné, J., 1981. Determination of ozone in water by the indigo method. Water Res. 15, 449–456.

Bergmann, M.E:H., Koparal, A.S., Iourtchouk, T., 2014. Electrochemical advanced oxidation processes, formation of halogenate and perhalogenate species-a critical review. Crit Rev Environ Sci Technol. 44, 348 – 390

Bertanza, G., Pedrazzani, R., Zambarda, V., Grande, M.D., Icarelli, F., Baldassarre, L., 2010. Removal of endocrine disrupting compounds from wastewater treatment plant effluents by means of advanced oxidation. Water Sci. Technol. 61, 1663–1671.

Bourgin, M., Bichon, E., Antignac, J.-P., Monteau, F., Leroy, G., Barritaud, L., Chachignon, M., Ingrand, V., Roche, P., Le Bizec, B., 2013. Chlorination of bisphenol A: non-targeted screening for the identification of transformation products and assessment of estrogenicity in generated water. Chemosphere 93, 2814–2822.

Brede, C., Fjeldal, P., Skjevrak, I., Herikstad, H., 2003. Increased migration levels of bisphenol A from polycarbonate baby bottles after dishwashing, boiling and brushing. Food Addit. Contam. 20, 684–689.

Cui, Y.-h., Li, X.-y., Chen, G., 2009. Electrochemical degradation of bisphenol A on different anodes. Water Res. 43, 1968–1976.

da Silva, J.C.C, Reis Teodoro, J.A, Afonso, R.J, Aquino, S.F., Augusti, R., 2014. Photodegradation of bisphenol A in aqueous medium: monitoring and identification of by-

products by liquid chromatography coupled to high-resolution mass spectrometry. Rapid Commun. Mass Spectrom. 28, 987–994.

Dupuis, A., Migeot, V., Cariot, A., Albouy-Llaty, M., Legube, B., Rabouan, S., 2012. Quantification of bisphenol A, 353-nonylphenol and their chlorinated derivatives in drinking water treatment plants. Environ Sci Pollut Res Int. 19, 4193–4205.

Fujishima, A., 2005. Diamond electrochemistry. BKC; Elsevier, Tokyo, Amsterdam, Boston, xxii, 586.

Gasperi, J., Sebastian, C., Ruban, V., Delamain, M., Percot, S., Wiest, L., Mirande, C., Caupos, E., Demare, D., Kessoo, M Diallo Kessoo, Saad, M., Schwartz, J.J., Dubois, P., Fratta, C., Wolff, H., Moilleron, R., Chebbo, G., Cren, C., Millet, M., Barraud, S., Gromaire, M.C., 2014. Micropollutants in urban stormwater: occurrence, concentrations, and atmospheric contributions for a wide range of contaminants in three French catchments. Environ Sci Pollut Res Int. 21, 5267–5281.

Greco, G., Grosse, S., Letzel, T., 2013. Serial coupling of reversed-phase and zwitterionic hydrophilic interaction LC/MS for the analysis of polar and nonpolar phenols in wine. J. Sep. Sci. 36, 1379–1388.

Gültekin, I., Ince, N.H., 2007. Synthetic endocrine disruptors in the environment and water remediation by advanced oxidation processes. J. Environ. Manage. 85 (4), 816–832.

Huber, M.M., Göbel, A., Joss, A., Hermann, N., Löffler, D., McArdell, C.S., Ried, A., Siegrist, H., Ternes, T.A., Gunten, U. von, 2005. Oxidation of Pharmaceuticals during Ozonation of Municipal Wastewater Effluents: A Pilot Study. Environ. Sci. Technol. 39, 4290–4299.

International Organization for Standardization, 2007. Water quality - determination of dissolved anions by liquid chromatography of ions. International Organization for Standardization, Geneva, v, 15.

Ju, P., Fan, H., Guo, D., Meng, X., Xu, M., Ai, S., 2012. Electrocatalytic degradation of bisphenol A in water on a Ti-based PbO2–ionic liquids (ILs) electrode. Chem Eng. J. 179, 99–106.

Kraft, A., 2007. Doped diamond: A compact review on a new, versatile electrode material. Int. J. Electrochem. Sci. 2, 355–383.

Kraft, A., Stadelmann, M., Wünsche, M., Blaschke, M., 2006. Electrochemical ozone production using diamond anodes and a solid polymer electrolyte. Electrochem. Commun. 8, 883–886.

Krauss, M., Singer, H., Hollender, J., 2010. LC-high resolution MS in environmental analysis: from target screening to the identification of unknowns. Anal. Bioanal. Chem. 397, 943–951.

Kusvuran, E., Yildirim, D., 2013. Degradation of bisphenol A by ozonation and determination of degradation intermediates by gas chromatography–mass spectrometry and liquid chromatography–mass spectrometry. Chem Eng. J. 220, 6–14.

Lang, I.A., Galloway, T.S., Scarlett, A., Henley, W.E., Depledge, M., Wallace, R.B., Melzer, D., 2008. Association of urinary bisphenol A concentration with medical disorders and laboratory abnormalities in adults. JAMA. 300, 1303–1310.

Martínez-Huitle, C.A., Ferro, S., 2006. Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes. Chem Soc Rev. 35, 1324–1340.

May, P.W., 2008. Materials science. The new diamond age? Science 319 (5869), 1490–1491.

Molkenthin, M., Olmez-Hanci, T., Jekel, M.R., Arslan-Alaton, I., 2013. Photo-Fenton-like treatment of BPA: effect of UV light source and water matrix on toxicity and transformation products. Water Res. 47, 5052–5064.

Murugananthan, M., Yoshihara, S., Rakuma, T., Shirakashi, T., 2008. Mineralization of bisphenol A (BPA) by anodic oxidation with boron-doped diamond (BDD) electrode. J. Hazard. Mater. 154, 213–220.

Oturan, M.A., Pinson, J., 1995. Hydroxylation by Electrochemically Generated OH.bul. Radicals. Mono- and Polyhydroxylation of Benzoic Acid: Products and Isomer Distribution. J. Phys. Chem. 99, 13948–13954.

Panizza, M., Cerisola, G., 2009. Direct and mediated anodic oxidation of organic pollutants. Chem. Rev. 109, 6541–6569.

Pereira, G.F., Rocha-Filho, R.C., Bocchi, N., Biaggio, S.R., 2012. Electrochemical degradation of bisphenol A using a flow reactor with a boron-doped diamond anode. Chem Eng J. 198-199, 282–288.

Qiu, L.-L., Wang, X., Zhang, X.-h., Zhang, Z., Gu, J., Liu, L., Wang, Y., Wang, X., Wang, S.-L., 2013. Decreased androgen receptor expression may contribute to spermatogenesis failure in rats exposed to low concentration of bisphenol A. Toxicol. Lett. 219, 116–124.

Rajab, M., Greco, G., Heim, C., Helmreich, B., Letzel, T., 2013a. Serial coupling of RP and zwitterionic hydrophilic interaction LC-MS: suspects screening of diclofenac transformation products by oxidation with a boron-doped diamond electrode. J. Sep. Sci. 36, 3011–3018.

Rajab, M., Heim, C., Greco, G., Helmreich, B., Letzel, T., 2013b. Removal of Sulfamethoxazole from Wastewater Treatment Plant Effluents by a Boron-doped Diamond Electrode. International Journal of Environmental Pollution and Solutions 1, 88–97.

Rajab, M., Heim, C., Letzel, T., Drewes, J.D., Helmreich, B, 2015. Electrochemical disinfection using boron-doped diamond electrode-The synergetic effects on in situ ozone and free chlorine generation. Chemosphere 121, 3011–3018.

Rice, E.W., Baird, R.B., Eaton, A.D., Clesceri, L.S., 2012. Standard Methods for Examination of Water and Wastewater 2012, 22nd edition ed. American Public Health Assn., Washington, DC.

Rivero, M.J., Alonso, E., Dominguez, S., Ribao, P., Ibañez, R., Ortiz, I., Irabien, A., 2014. Kinetic analysis and biodegradability of the Fenton mineralization of bisphenol A. J. Chem. Technol. Biotechnol. 89, 1228–1234.

Sarkar, S., Ali, S., Rehmann, L., Nakhla, G., Ray, M.B., 2014. Degradation of estrone in water and wastewater by various advanced oxidation processes. J. Hazard. Mater. 278, 16–24.

Sharpe, R.M., 2011. Pediatrics: endocrine disruption and human health effects--a call to action. Nat Rev Endocrinol 7, 633–634.

Sirés, I., Brillas, E., Oturan, M.A., Rodrigo, M.A., Panizza, M., 2014. Electrochemical advanced oxidation processes: today and tomorrow. A review. Environ Sci Pollut Res Int 21, 8336–8367.

Ternes, T.A., Meisenheimer, M., McDowell, D., Sacher, F., Brauch, H.-J., Haist-Gulde, B., Preuss, G., Wilme, U., Zulei-Seibert, N., 2002. Removal of Pharmaceuticals during Drinking Water Treatment. Environ. Sci. Technol. 36, 3855–3863.

Umar, M., Roddick, F., Fan, L., Aziz, H.A., 2013. Application of ozone for the removal of bisphenol A from water and wastewater--a review. Chemosphere 90, 2197–2207.

von Gunten, U., 2003. Ozonation of drinking water: Part I. Oxidation kinetics and product formation. Water Res. 37, 1443–1467.

Warrington, P., 2002. Ambient water quality guidelines for chlorate. National Library of Canada Cataloguing in Publication Data. (http:// http://www.env.gov.bc.ca/wat/wq/BCguidelines/chlorate/chlorate.html) (retrieved 11.02.2015).

Yates, R., Stenstrom, M.K., 2000. Gravimetric sampling procedure for aqueous ozone concentrations. Water Res. 34, 1413–1416.

Yoshihara, S., Murugananthan, M., 2009. Decomposition of various endocrine-disrupting chemicals at boron-doped diamond electrode. Electrochim. Acta. 54, 2031–2038.

Supporting information

Electrochemical oxidation of Bisphenol A by a boron-doped diamond electrode in different water matrices: Identification of transformation products and evaluation of inorganic by-products

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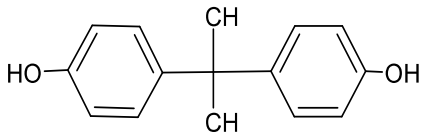
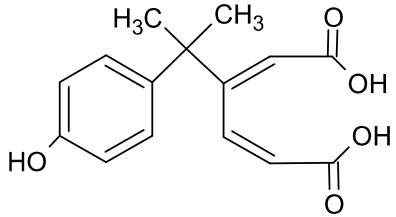
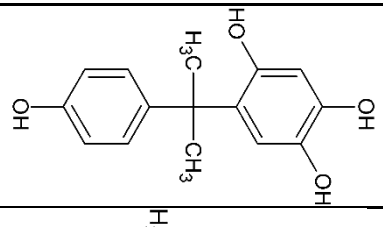
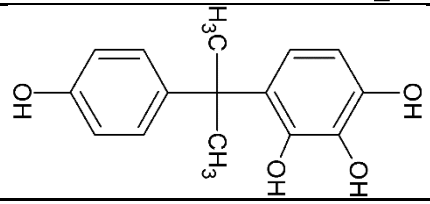
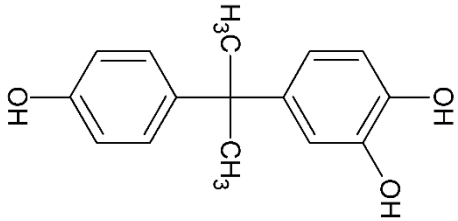
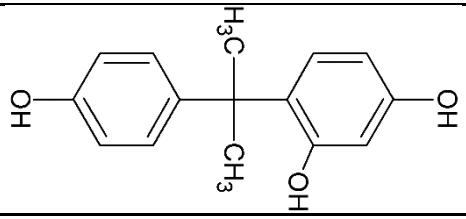
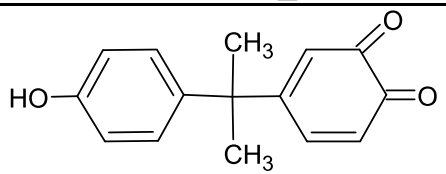
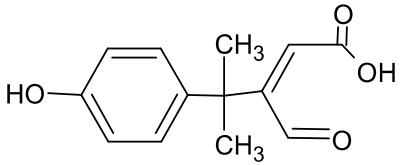
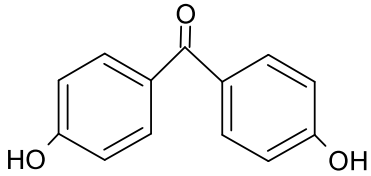
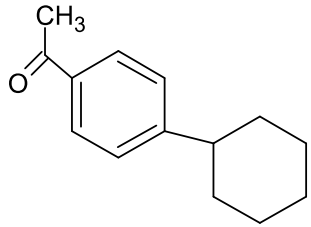
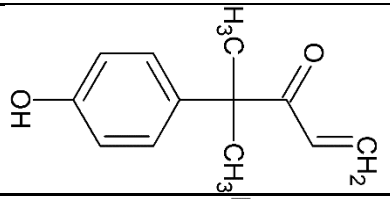
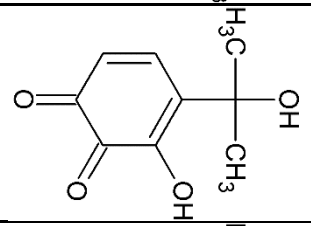
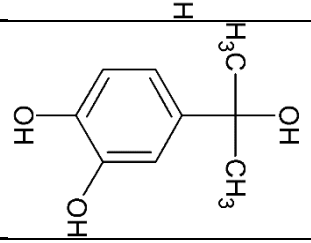
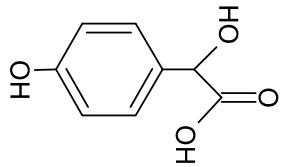
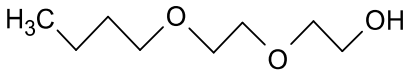
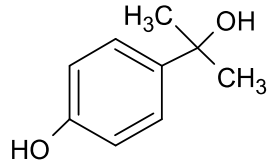
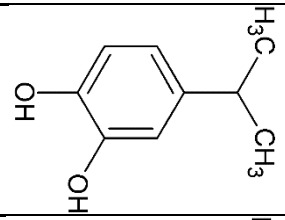
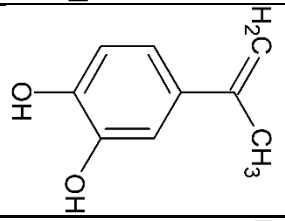
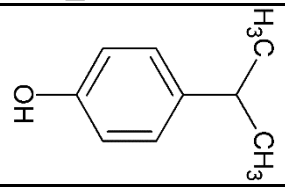
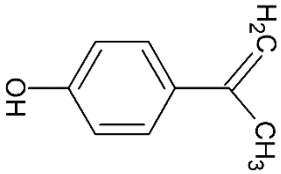
Table S1.

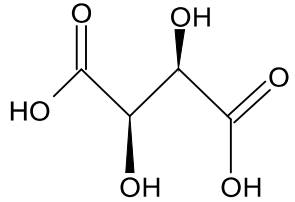
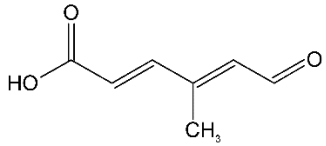
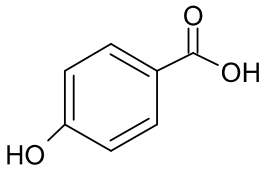
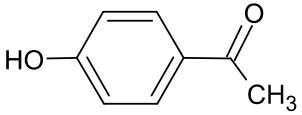
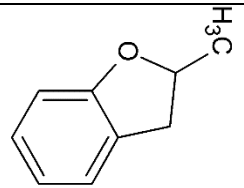
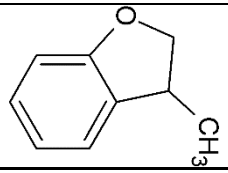
List of 37 suspected transformation products of BPA selected from literature including the proposed molecular structures, the applied degradation method, analytical method employed and the relative references.

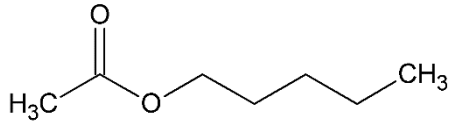
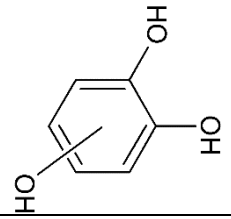
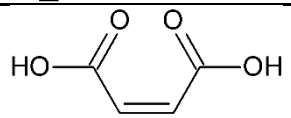
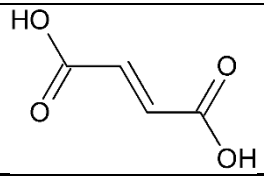
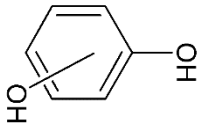
Compound	***Proposed structure***	***Molecular formula***	***Accurate molecular mass***	***[M-H]$^-$ (m/z)***	***Degradation method***	***Analytical method***	***Reference***
Bisphenol A		*$C_{15}H_{16}O_2$*	*228.1150*	*227.1077*			
1		*$C_{15}H_{16}O_5$*	*276.0998*	*275.0925*	*Photo- Fenton-like*	*GC-MS*	*[1]*
					Ozonation	*LC-MS RP-HPLC*	*[2,3]*
2		*$C_{15}H_{16}O_4$*	*260.1049*	*259.0976*	*Electrochemically generated Fenton's reagent (EF)*	*LC-MS*	*[4]*
3		*$C_{15}H_{16}O_4$*	*260.1049*	*259.0976*	*Photodegradation*	*RP-HPLC LC-MS*	*[5]*

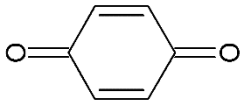
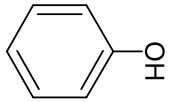
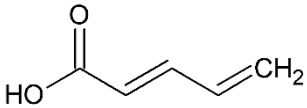
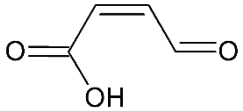
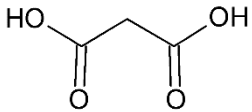
4 (TP1)		*$C_{15}H_{16}O_3$*	*244.1099*	*243.1027*	*EF*	*RP-HPLC LC-MS GC-MS*	*[4]*
					Ozonation	*LC-MS RP-HPLC*	*[3]*
					Photodegradation	*RP-HPLC LC-MS*	*[5]*
5 (TP1)		*$C_{15}H_{16}O_3$*	*244.1099*	*243.1027*	*EF*	*RP-HPLC LC-MS GC-MS*	*[4]*
					Electrochemical	*RP-HPLC*	*[6]*
6		*$C_{15}H_{14}O_3$*	*242.0943*	*241.0870*	*Ozonation*	*LC-MS RP-HPLC*	*[2][3]*
					Photodegradation	*RP-HPLC LC-MS*	*[5]*
7		*$C_{13}H_{14}O_4$*	*234.0892*	*233.0819*	*Ozonation*	*LC-MS RP-HPLC*	*[3]*
					Photo- Fenton-like	*GC-MS*	*[1]*
8		*$C_{13}H_{10}O_3$*	*214.0630*	*213.0557*	*Photo- Fenton-like*	*GC-MS*	*[1]*

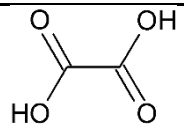
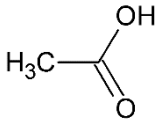
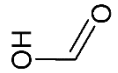
9		*$C_{14}H_{18}O$*	*202.1358*	*201.1285*	*Photo- Fenton-like*	*GC-MS*	*[1]*
10		*$C_{12}H_{14}O_2$*	*190.0994*	*189.0921*	*Ozonation*	*LC-MS* *RP-HPLC*	*[2]*
11		*$C_9H_{10}O_4$*	*182.0579*	*181.0506*	*Photodegradation*	*RP-HPLC* *LC-MS*	*[5]*
12		*$C_9H_{12}O_3$*	*168.0786*	*167.0714*	*Photodegradation*	*RP-HPLC* *LC-MS*	*[5]*
13 (TP3)		*$C_8H_8O_4$*	*168.0423*	*167.0350*	*EF*	*RP-HPLC* *LC-MS* *GC-MS*	*[4]*
14		*$C_8H_{18}O_3$*	*162.1256*	*161.1183*	*Photo- Fenton-like*	*GC-MS*	*[1]*

15		*$C_9H_{12}O_2$*	*152.0837*	*151.0764*	*Ozonation*	*LC-MS RP-HPLC*	*[2,3]*
					Photo-Fenton	*GC-MS*	*[7]*
					Electrocatalytic Ti-PbO2-ionic liquids	*LC-MS*	*[8]*
16		*$C_9H_{12}O_2$*	*152.0837*	*151.0764*	*Electrochemical*	*RP-HPLC*	*[6]*
17		*$C_9H_{10}O_2$*	*150.0681*	*149.0608*	*Photo- Fenton-like*	*GC-MS*	*[1]*
18		*$C_9H_{12}O$*	*136.0888*	*135.0815*	*Electrochemical*	*RP-HPLC*	*[6]*
					Photo-Fenton	*GC-MS*	*[7]*
					Electrocatalytic Ti-PbO2-ionic liquids	*LC-MS*	*[8]*
19		*$C_9H_{10}O$*	*134.0732*	*133.0659*	*EF*	*RP-HPLC LC-MS GC-MS*	*[4]*
					Photo-Fenton	*GC-MS*	*[7]*
					Electrochemical	*RP-HPLC*	*[6]*

20		*$C_4H_6O_6$*	*150.0164*	*149.0092*	*Electrochemical*	*RP-HPLC*	*[6]*
21 (TP5)		*$C_7H_8O_3$*	*140.0473*	*139.0401*	*Photo- Fenton-like*	*GC-MS*	*[1]*
22		*$C_7H_6O_3$*	*138.0317*	*137.0244*	*EF*	*RP-HPLC LC-MS GC-MS*	*[4]*
					Ozonation	*LC-MS RP-HPLC*	*[2]*
23		*$C_8H_8O_2$*	*136.0524*	*135.0451*	*Photo-Fenton*	*GC-MS*	*[7]*
					Photo- Fenton-like	*GC-MS*	*[1]*
24		*$C_9H_{10}O$*	*134.0732*	*133.0659*	*Electrocatalytic Ti-PbO2-ionic liquids*	*LC-MS*	*[8]*
					Photo-Fenton	*GC-MS*	*[7]*
25		*$C_9H_{10}O$*	*134.0732*	*133.0659*	*Photo-Fenton*	*GC-MS*	*[7]*

26		*$C_7H_{14}O_2$*	*130.0994*	*129.0921*	*Photo- Fenton-like*	*GC-MS*	*[1]*
27		*$C_6H_6O_3$*	*126.0317*	*125.0244*	*Electrochemical*	*RP-HPLC*	*[6]*
					Ozonation	*LC-MS* *RP-HPLC*	*[2]*
28 (TP6)		*$C_4H_4O_4$*	*116.0110*	*115.0037*	*EF*	*RP-HPLC* *LC-MS* *GC-MS*	*[4]*
					*Electrochemical*	*RP-HPLC*	*[6]*
29		*$C_6H_6O_2$*	*110.0368*	*109.0295*	*Photo- Fenton-like*	*GC-MS*	*[1]*
					EF	*RP-HPLC* *LC-MS* *GC-MS*	*[4]*
					Electrochemical	*RP-HPLC*	*[6]*
					Ozonation	*LC-MS* *RP-HPLC*	*[3]*
					Ozonation	*LC-MS* *RP-HPLC*	*[2]*
					Photo-Fenton	*GC-MS*	*[7]*

30		*$C_6H_4O_2$*	*108.0211*	*107.0138*	*EF*	*RP-HPLC LC-MS GC-MS*	*[4]*
					Ozonation	*LC-MS RP-HPLC*	*[3]*
					Electrochemical	*RP-HPLC*	*[6]*
					Photo-Fenton	*GC-MS*	*[7]*
					Electrocatalytic Ti-PbO2-ionic liquids	*LC-MS*	*[8]*
31		*C_6H_6O*	*94.0419*	*93.0346*	*EF*	*RP-HPLC LC-MS GC-MS*	*[4]*
					Photo-Fenton	*GC-MS*	*[7]*
					Electrocatalytic Ti-PbO2-ionic liquids	*LC-MS*	*[8]*
32		*$C_5H_6O_2$*	*98.0368*	*97.0295*	*Electrocatalytic Ti-PbO2-ionic liquids*	*LC-MS*	*[8]*
33		*$C_4H_4O_3$*	*100.0160*	*99.0088*	*EF*	*RP-HPLC LC-MS GC-MS*	*[4]*
34		*$C_3H_4O_4$*	*104.0110*	*103.0037*	*Ozonation*	*LC-MS RP-HPLC*	*[2]*

35		*$C_2H_2O_4$*	*89.9953*	*88.9880*	*Ozonation*	*LC-MS* *RP-HPLC*	*[2]*
36		*$C_2H_4O_2$*	*60.0211*	*59.0138*	*EF*	*RP-HPLC* *LC-MS* *GC-MS*	*[4]*
					Electrochemical	*RP-HPLC*	*[6]*
37		*CH_2O_2*	*46.0055*	*44.9982*	*EF*	*RP-HPLC* *LC-MS* *GC-MS*	*[4]*

References

1. Molkenthin, M.; Olmez-Hanci, T.; Jekel, M.R.; Arslan-Alaton, I. Photo-Fenton-like treatment of BPA: effect of UV light source and water matrix on toxicity and transformation products. *Water Res.* **2013**, *47*, 5052–5064.
2. Kusvuran, E.; Yildirim, D. Degradation of bisphenol A by ozonation and determination of degradation intermediates by gas chromatography–mass spectrometry and liquid chromatography–mass spectrometry. *Chemical Engineering Journal* **2013**, *220*, 6–14.
3. Deborde, M.; Rabouan, S.; Mazellier, P.; Duguet, J.-P.; Legube, B. Oxidation of bisphenol A by ozone in aqueous solution. *Water Res.* **2008**, *42*, 4299–4308.
4. Gözmen, B.; Oturan, M.A.; Oturan, N.; Erbatur, O. Indirect Electrochemical Treatment of Bisphenol A in Water via Electrochemically Generated Fenton's Reagent. *Environ. Sci. Technol.* **2003**, *37*, 3716–3723.
5. da Silva, Júlio César Cardoso; Reis Teodoro, Janaina Aparecida; Afonso, Robson José de Cássia Franco; Aquino, S.F.; Augusti, R. Photodegradation of bisphenol A in aqueous medium: monitoring and identification of by-products by liquid chromatography coupled to high-resolution mass spectrometry. *Rapid Commun. Mass Spectrom.* **2014**, *28*, 987–994.
6. Cui, Y.-h.; Li, X.-y.; Chen, G. Electrochemical degradation of bisphenol A on different anodes. *Water Res.* **2009**, *43*, 1968–1976.
7. Katsumata, H.; Kawabe, S.; Kaneco, S.; Suzuki, T.; Ohta, K. Degradation of bisphenol A in water by the photo-Fenton reaction. *Journal of Photochemistry and Photobiology A: Chemistry* **2004**, *162*, 297–305.
8. Ju, P.; Fan, H.; Guo, D.; Meng, X.; Xu, M.; Ai, S. Electrocatalytic degradation of bisphenol A in water on a Ti-based PbO2–ionic liquids (ILs) electrode. *Chemical Engineering Journal* **2012**, *179*, 99–106.

3.4 Electrochemical disinfection using boron-doped diamond electrode – The synergetic effects of in situ ozone and free chlorine generation

Poor water quality worldwide causes disease breakouts that endanger public health. The need to disinfect water (drinking water, process water or effluents of wastewater treatment plants (WWTPs)) has encouraged both scientists and engineers to develop new and cost-effective methods for effective water disinfection. The conventional disinfection technologies have some drawbacks. High turbidity or higher dissolved organic limits the applicability of traditional processes (UV, chlorination or ozonation). Electrochemical disinfection by BDD electrode is a promising process that achieves high level of disinfection independent on the application environment. Reactive oxygen species and reactive chlorine species are generated simultaneously in real water matrix where chloride ions are present.

The scope of this study was to investigate the influence of chloride ion concentration on the disinfection performance of a BDD electrode on the ubiquitous model organism *Pseudomonas aeruginosa* (*P.aeroginosa*) and the formation of disinfection by-products (DBPs). *P.aeruginosa* was chosen because of its important role in public health, particularly with regards to nosocomial infection and diseases in immunodeficient patients. The experiments were conducted in batch mode. Two parameters were tested: (1) the applied current density and (2) the effect of chloride ions in the treated water. Both DBP and energy consumption were assessed during the process.

Based on the result obtained in this study, the BDD electrode was a viable technology to achieve a complete inactivation of the microorganisms. The measured concentrations of ozone and free chlorine were affected by the applied current density and the chloride content in the treated water with tendency towards generating ozone at higher current densities. Reactive chlorine species enhanced disinfection at low current densities where ozone was not generated in sufficient amounts. Depending on the applied current density, the formation of chlorate and perchlorate could be controlled.

The results of this section are presented with permission from Rajab, M., Heim, C., Letzel, T., Drewes, J.D., Helmreich, B, 2015. Electrochemical disinfection using boron-doped diamond electrode-The synergetic effects on in situ ozone and free chlorine generation. Chemosphere 121, 3011–3018. Copyright 2015 Elsevier Ltd. Co-authors contributed through a valuable insight into overall direction of the research and experimental planning; experimental execution, data analysing, review published data were performed by Mohamad Rajab.

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Electrochemical disinfection using boron-doped diamond electrode – The synergetic effects of *in situ* ozone and free chlorine generation

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HIGHLIGHTS

- BDD electrode is capable to achieve high disinfection level of *P. aeruginosa*.
- Synergetic effect of *in situ* generated O_3 and Cl_2 enhances the disinfection process.
- High current density boosts disinfection level; DBPs formation and energy demand.
- DBP formation and energy demand can be controlled over the applied current density.

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ABSTRACT

This work investigated the capability of using a boron-doped diamond (BDD) electrode for bacterial disinfection in different water matrices containing varying amounts of chloride. The feed water containing *Pseudomonas aeruginosa* was electrochemically treated while applying different electrode conditions. Depending on the applied current density and the exposure time, inactivation between 4- and 8-log of the targeted microorganisms could be achieved. The disinfection efficiency was driven by the generation of free chlorine as a function of chloride concentration in the water. A synergetic effect of generating both free chlorine and ozone *in situ* during the disinfection process resulted in an effective bactericidal impact. The formation of the undesired by-products chlorate and perchlorate depended on the water matrix, the applied current density and the desired target disinfection level. In case of synthetic water with a low chloride concentration (20 mg L^{-1}) and an applied current density of 167 mA cm^{-2}, a 6-log inactivation of *Pseudomonas aeruginosa* could be achieved after 5 min of exposure. The overall energy consumption ranged between 0.3 and 0.6 kW h m^{-3} depending on the applied current density and water chemistry. Electrochemical water disinfection represents a suitable and efficient process for producing pathogen-free water without the use of any chemicals.

1. Introduction

Due to the insufficient management of water resources in urban and rural areas in many parts of the world, millions of people are exposed every day to unsafe levels of microbiological and chemical pollutants in their drinking water. Poor water quality worldwide causes disease breakouts that endanger public health and especially children (World Health Organization, 2013). The need to disinfect both drinking water and effluents of wastewater treatment plants (WWTPs) has encouraged both scientists and engineers to develop new and cost-effective methods for effective water disinfection. Well-established chemical disinfection technologies such as chlorination or ozonation have different drawbacks that limit their application in some cases. The chemicals used in such technologies require high safety specifications to be considered, thus enhancing the operation costs. Furthermore, formation of disinfection by-products (DBPs) during chlorination or ozonation and the loss of disinfection efficiency through the presence of organic matter are crucial when considering those technologies (Sedlak and von Gunten, 2011; Li and Ni, 2012). The applicability of physical disinfection processes such as UV irradiation, membrane separation and thermal disinfection is associated with high cost and maintenance efforts and does not fulfil the requirements for primary and residual water disinfection (Martínez-Huitle and Brillas, 2008; Schmalz et al., 2009).

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In the last few decades, alternative systems to conventional disinfection methods were developed. The most promising ones are based on the *in situ* electrogeneration of disinfection agents (Kraft, 2008; Martínez-Huitle and Brillas, 2008; Ghernaout and Ghernaout, 2010). It offers an environmentally friendly, economically and operationally competitive technology, which is known to be applicable against a wide range of microbiological contaminations in water. A critical factor in these electrochemical processes is the role of the anode material. Among others, boron-doped diamond (BDD) has shown remarkable properties to be applied as anodic material (Kraft, 2007; May, 2008). Beside its inertness and the chemical stability, it has the highest known oxygen evolution overpotential due to its low adsorption capacity leading to the formation of other oxidants before oxygen evolves (Fujishima, 2005). Reactive oxygen species (ROS), such as hydroxyl radicals, ozone, singlet oxygen and hydrogen peroxide, are formed during the operation in water on the surface of the electrode and in the bulk solution leading to a high efficiency during the oxidation process. In the presence of ions, such as chloride, sulfate and bicarbonate, free chlorine, peroxodisulphate and other weak oxidants can be produced during the electrolysis, which are known to be powerful disinfectants (Polcaro et al., 2009; Pérez et al., 2010). A potential drawback of electrochemical disinfection using BDD electrodes is the formation of disinfection by-products (DBPs) (Bergmann and Rollin, 2007; Bergmann et al., 2011; Haaken et al., 2012). The highly reactive oxidant species formed during the electrolysis process – mainly hydroxyl radicals and ozone - are able to oxidize halogenated ions present in water (von Gunten and Pinkernell, 2000; Deborde and von Gunten, 2008). Among the generated inorganic by-products, bromate, chlorate and perchlorate are of great concern because of their negative impact and possible carcinogenic effect on human health (Bergmann et al., 2010, 2011). Moreover, the reaction of halogen species with organic molecules found in water will promote the formation of the harmful adsorbable organically bound halogens (AOX) and the trihalomethanes (THMs).

The applicability of BDD electrodes for electrochemical disinfection has been tested at laboratory and pilot scale. Different operational parameters, microorganism species and water matrices were investigated. For instance, the applied current density shows a significant role in the bactericidal kinetics (Furuta et al., 2004; Schmalz et al., 2009; Griessler et al., 2011; Yao et al., 2011). The applied current density and the chloride content in the feed water have been identified as the most influential factors (Polcaro et al., 2009; Schmalz et al., 2009; Pérez et al., 2010; Yao et al., 2011). The role of hydroxyl radicals in the disinfection process also depends on the water content. In case of the presence of chloride and bicarbonate, its role is almost negligible. The direct disinfection effect of hydroxyl radicals in absence of radical scavengers is obvious (Diao et al., 2004; Jeong et al., 2006; Schmalz et al., 2009). However, past studies have not considered the relationship between the studied parameters, the formatted DBPs and the energy demand of the process.

The scope of this study was to investigate the influence of chloride ion concentration on the disinfection performance of a BDD electrode on the ubiquitous model organism *Pseudomonas aeruginosa (P. aeroginosa)* and the formation of disinfection by-products. *P. aeruginosa* was chosen because of its important role in public health, particularly with regards to nosocomial infection and diseases in immunodeficient patients (Panis et al., 2009). Bacterial inactivation was tested under variation of the applied current density and different chloride ion concentrations. The major objective of this study was to link the bacterial inactivation capacity of BDD diamond with the energy demand and the formation of inorganic DBPs in order to define optimal process conditions.

2. Experimental section

2.1. Experimental setup

Experiments were performed using a conductive diamond electrode system (CONDIAPURE®- CONDIAS GmbH, Germany). The batch reactor system consisted of a flow through cell with a volume of 45 cm^3 equipped with a BDD electrode stack, pump, a 20 L tank, power supply, and two sensors placed on the hoses connecting the different parts (Fig. 1).

The electrode stack consisted of two BDD cathodes and two BDD anodes on a niobium substrate (CONDIAS GmbH, Germany) with an overall effective anode area of 24 cm^2. A nafion cation exchange membrane was placed in direct contact to each cathode and anode in order to receive a gap-free sandwich structure. This enhanced the current density locally and therefore promoted ozone formation and enabled to operate the electrode at low conductivities (Kraft et al., 2006a, 2006b). The system was operated in a recirculation that flow rate could be adjusted between 0.5 and 10 L min^{-1}. The applied current could be regulated between 0 and 10.0 A. All experiments were conducted at room temperature (25 ± 2 °C) and slightly alkaline pH value (8.5 ± 0.5). Two current densities, 42 and 167 mA cm^{-2}, were applied during this study. Kraft et al. (2006b) has shown that the best current efficiency (20–24%) for ozone generation to be located in the range of 50–175 mA cm^{-2}, after this range the efficiency decreased owing to an increase in ozone decay in the water. Prior studies (Heim et al., 2011; Ureña de Vivanco et al., 2013) have shown that efficient ozone production applying the same BDD electrode at lower current densities than 42 mA cm^{-2} is not sufficient. This could be due to the confined of generated hydroxyl radicals to the electrode surface. In this context, the lowest applied current density in this study (42 mA cm^{-2}) was chosen with respect to the possibility of efficient ozone production as well as a minimum energy consumption during the process. The other applied current density (167 mA cm^{-2}) was selected to assure a sufficient ozone generation and simultaneously a worst-case scenario for DBPs formation. All experiments were carried out in duplicate and showed a good reproducibility within a 95% confidence interval within the microbiological method. The mean values of the results of the replicated experiments are presented.

2.2. Chemicals

Phosphoric acid (85%), 5,5-indigodisulphonic acid sodium salt (indigo carmine), sodium hydroxide (NaOH), sodium thiosulfate ($Na_2S_2O_3$), calcium chloride ($CaCl_2$), potassium bromide (KBr), potassium iodide (KI), magnesium sulphate heptahydrate ($MgSO_4$ $8H_2O$), sodium hydrogen carbonate ($NaHCO_3$) and sodium nitrate

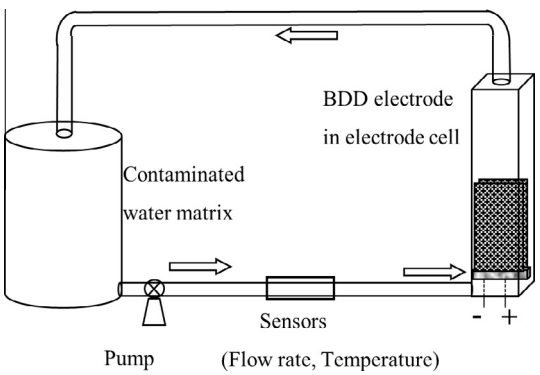

Fig. 1. Experimental setup of the BDD electrode and the reactor unit.

($NaNO_3$), as well as ethylenediamine monohydrate were purchased from Merck (Germany). All chemicals were of analytical grade. Two synthetic waters that differed in chloride concentrations were prepared by dissolving the salt mix in deionized water. The composition of the synthetic water types is presented in Table 1.

2.3. Preparation of bacteria suspensions

Bacterial strains of *P. aeruginosa* (ATCC 10145) were provided by the Institute of Microbial Ecology at Technische Universität München. *P. aeruginosa* were cultured using Plate Count (PC) bouillon containing 5.0 g L^{-1} caseine peptone, 2.5 g L^{-1} yeast extract and 1.0 g L^{-1} glucose (pH 7.0) and incubated at 37 °C for 18 h with continuous shaking. Following centrifugation, the resulting cell pellets were resuspended in 16 mL of ¼ concentrated Ringer's solution (Merck Inc., Germany). The 20 mL highly concentrated bacteria suspensions were used directly for the experiment. The contaminated aqueous solutions were prepared by mixing 10 L of the particular water matrix with 20 mL bacteria suspension to obtain initial bacteria concentrations of approximately 10^7–10^8 CFU mL^{-1}. During electrode operation, the feed solution was the temperature was controlled at 25 ± 1 °C.

2.4. Microbial analysis

A sodium thiosulfate solution (1.5 g L^{-1}) was added to quench the residual oxidants in each microbiological sample (Haaken et al., 2012). The *P. aeruginosa* cell population was determined following the EU drinking water directive (Council directive 98/83/EC of 3 November 1998). *P. aeruginosa* solutions were diluted with ¼ concentrated Ringeŕs solution prior to filtration according to ISO 16266 (International Organization for Standardization, 2006). Filters were placed on selective agar and incubated for 48 h at 37 °C. Based on the change in the bacterial count of the sample after a certain disinfection period, the inactivation rate was calculated as the logarithmic reduction of bacteria ($\log N/N_0$), where N_0 represents the initial bacterial concentration and N the bacterial count at the respective sampling time.

2.5. Analytical methods

In analogy to the disinfection experiments, both residual ozone and free/total chlorine concentrations were quantified. Residual ozone concentrations were measured following the indigo method of Bader and Hoigné (1981) with a modification according to Yates and Stenstrom (2000) replacing phosphate buffer by phosphoric acid. Free/total chlorine concentrations were determined using N,N-diethyl-p-phenylenediamine (DPD) using a colorimetric test kit (Hach-Lange LCK 310; limit of detection (LOD) = 50 μgL^{-1} Cl_2). Chloride (Cl^-), chlorate (ClO_3^-) and perchlorate (ClO_4^-) were analyzed by ion chromatography using a DIONEX ICS-1000 (Thermo Scientific Dionex, USA) according to DIN EN ISO 10304-1 DEV E19 (International Organization for Standardization, 2007) (LOD = 10 μg L^{-1}) after quenching the residual oxidants with 1 mL of ethylenediamine solution (10 mM).

The standard deviations of the chemical analyses were found to be 6% for the ozone measurement, 7.3% for the DPD method (free/total chlorine) and 5.9% for the anion analysis (chloride, chlorate and perchlorate). The pH of the treated solution was measured with a pH-meter (SenTex 4, WTW, Germany).

3. Results and discussion

Different parameters can affect the inactivation of microorganisms using BDD electrodes. The effects of applied current density and chloride content were studied regarding the inactivation of *P. aeruginosa* in deionized and synthetic water matrices. During the experiments, the degree of inactivation, ozone and free chlorine concentrations, inorganic disinfection by-products and energy consumption were determined. Noteworthy, it has to be mentioned that the spectrum of the chlorine species generated during the process is complex. In addition to HClO and ClO^- measured as free chlorine, Cl_2 is also possibly generated. Therefore, the sum of the three different dissolved chlorine species (Cl_2, HClO, and ClO^-) is called active chlorine (Kraft et al., 1999a, 1999b).

3.1. Effect of the applied current density on the inactivation rate

The first series of experiments was conducted to study the dependency of the applied current density on inactivation of *P. aeruginosa* in deionized water by applying two different current densities (42 and 167 mA cm^{-2}). Inactivation results in deionized water at 42 and 167 mA cm^{-2} over the electrical charge input *Q*/*V* are presented in Fig. 2. At a *Q*/*V*-value of 105 mA h L^{-1} in deionized water, inactivation levels of almost 4-log units and 8-log units were observed applying a current density of 42 and 167 mA cm^{-2}, respectively (Fig. 2). The results reveal that a higher current density resulted in faster disinfection. This behavior is likely caused by the electrical charge (*Q*/*V*) that passed through the electrolyte. However, the time needed to introduce this amount of electrical charge to the electrolyte quadruplicates moving from the higher to the lower current density (from 15 min to 60 min). This difference in inactivation efficiency is likely due to the *in situ* generation of ozone. While a maximum ozone concentration of 0.46 mg L^{-1} was measured applying the higher current density, the ozone concentration was only 0.07 mg L^{-1} at the lower current density. The shape of the inactivation curves in both experiments revealed an initial rapid inactivation phase followed by a phase with an insignificant change in the log removal values (tailing phenomenon). It is hypothesized that the following factors have caused this behavior. First, the concentration of the bacteria at beginning of the experiment is higher thus leading to a higher probability of the bacteria to come in direct contact with the anode (hydroxyl radical zone). Hydroxyl radicals generated on the surface of the BDD anode- in chloride-free water- are a lethal factor responsible for the disinfection (Jeong et al., 2006) and second, the clumping behavior of microorganisms that occurs during treatment (Mamane, 2008) reduces opportunities of oxidants to reach and eliminate every single cell. The third factor might be

Table 1
Chemical parameters of deionized water and the model waters (synthetic water I–II).

Parameter	Unit	Deionized water	Synthetic water I	Synthetic water II
Conductivity	μS cm^{-1}	0.08	850–926	1230
pH	–	7.0	8.9	8.7
c(Cl^-)	mg L^{-1}	n.d.	20	250
c(Br^-)	mg L^{-1}	n.d.	1.0	1.0
c(HCO_3^-)	mg L^{-1}	n.d.	122	122

n.d. not determined.

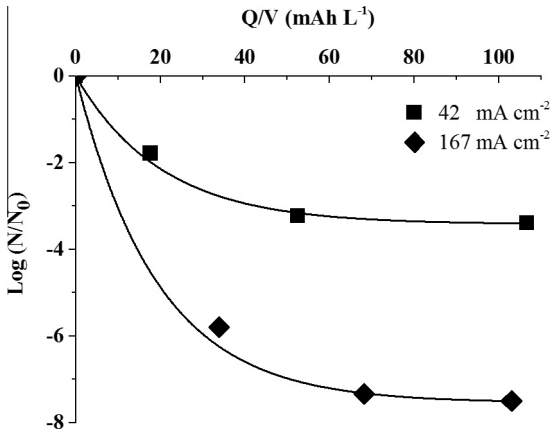

Fig. 2. Disinfection kinetics of *P. aeruginosa* in deionized water in dependence of the applied charge per volume at two current densities (mean values of the results are plotted).

the loss of oxidant effectivity caused by the reaction of residual cellular material from inactivated bacteria with the oxidants. Another perspective to explain this plateau phenomenon would be the accuracy of the microbial analytical method. The total inactivation at 167 mA cm^{-2} was achieved at 68 mAh L^{-1}. Therefore, the curve flattens from that point on and further treatment did not result in enhanced inactivation levels.

3.2. Investigation of the variation and effectiveness of generated oxidant species

The composition of the water matrix has a significant effect on the disinfection process due to the variation of the formed oxidants and its effectiveness. However, the *in situ* analysis of each single oxidant produced during an electrochemical process is not trivial and in many cases is not practical to conduct (Bergmann, 2006). This study focused on the effect of chloride present in the feed water resulting in the generation of different chlorine-derived oxidants in solution. Possible synergetic effects with other oxidant agents on the disinfection process were also considered. Hence, disinfection experiments were conducted in two synthetic water types containing different chloride concentrations in comparison to chloride-free water.

The log-removal results for *P. aeruginosa* in synthetic water I (containing 20 mg L^{-1} Cl^-), synthetic water II (containing 250 mg L^{-1} Cl^-) as well as in deionized water are presented in Fig. 3 for current densities of 42 (Fig. 3a) and 167 mA cm^{-2} (Fig. 3b). As the current density was kept constant for each experiment, *Q*/*V* values can be directly linked to the applied disinfection time. Measured concentrations of ozone and free chlorine are also presented for the three water matrices during bacterial inactivation (Table 2). Applying the lower current density (Fig. 3a), the inactivation of microorganisms in deionized water matrix followed a first-order decay curve after initiating the process, but disinfection efficiency declined after approximately 30 min. The poor overall inactivation level in deionized water is likely due to the generation of relatively low ozone concentrations in solution. After reaching a maximum concentration of 0.07 mg L^{-1} after 5 min, the ozone concentration decreased constantly and no more ozone was dissolved in the solution during the remainder of the experiment (Table 2). Organic and inorganic residues of bacterial cells might consume the ozone molecules in the water leading to a decrease of the measurable ozone values. In contrast to deionized water, it appears that in both synthetic waters containing chloride, disinfection was delayed and only effective after an initial period. The delay time was needed in case of synthetic water I and II to produce proper concentrations of disinfectants such as ozone and free chlorine. The concentrations of both oxidants increased as disinfection progressed and more charge was introduced into the solution. The ozone concentration increased from 0.02 to 0.19 mg L^{-1} in synthetic water I and from 0.04 to 0.58 mg L^{-1} in synthetic water II. At the same time, we observed an increase in free chlorine concentrations in both water matrices during the process (Table 2). The combination of the bactericidal effects of both species results in a synergetic effect. Another factor that could contribute to higher inactivation levels after the initial phase is the pH value of the solution during the experiments (decreasing from 8.52 ± 0.4 to 7.25 ± 0.2). Even though, this drop-off is not significant, it has an enormous effect on the relative distribution of the chlorine species HClO and ClO^-. Moving from the higher pH level to the lower one leads to shifting the percentage ration HClO/ClO^- from (≈12/88 to 70/30) (Metcalf and Eddy, 2003) which increases the inactivation process taking into account the killing efficiencies of both species. The kinetic behavior of inactivation when applying the higher current density (Fig. 3b) is different. In all water matrices used, the inactivation started directly after initiating the process. The reason is likely due to the increased concentrations of ozone and free chlorine. Relatively high concentrations of ozone were measured after a few minutes of starting the experiments (0.25, 0.31 and 0.38 mg L^{-1} in deionized water, synthetic water I and synthetic water II, respectively) (Table 2). The effectiveness of ozone as a strong disinfectant in deionized water contributes to a maximum of more than 7-log inactivation units for a charge value of 69 mA h L^{-1} (10 min). It is worth mentioning that the initial bacteria concentrations were comparable for all water matrices investigated. The inactivation capacity in synthetic water I reached its limitation at *Q*/*V* value of 69 mA h L^{-1} (10 min) with a reduction of 6-log units and after that no more disinfection was possible. The changes in the oxidant concentrations after this time point could be contributed to such steady-phase of inactivation. The ozone concentration slightly decreased (0.37–0.31 mg L^{-1}), whereas the free chlorine concentration increased moderately from 0.25 to 0.33 mg L^{-1}, but no effect was noticeable regarding microorganisms inactivation. In case of synthetic water II, the higher concentrations of oxidant species formed after 15 min (0.62 and 0.59 mg L^{-1} for ozone and free chlorine, respectively) (Table 2) caused higher inactivation levels at this time point.

3.3. Generation of inorganic disinfection by-products (DBPs)

The formation of DBPs during electrochemical disinfection in water containing inorganic ions such as chloride and bromide has been reported previously (von Gunten, 2003a, 2003b; Bergmann and Rollin, 2007). Reaction scheme in Fig. 4 displays the stepwise mechanism for chloride oxidation based on several studies (von Gunten, 2003b; Palmas et al., 2007; Bergmann et al., 2009). The formation of hydroxyl radicals at the surface of the diamond electrode and ozone in the bulk solution – in case of the presence of chloride in the treated water – leads to the formation of undesired species like chlorate and perchlorate (Palmas et al., 2007). In this study, the generation of chlorate and perchlorate as inorganic disinfection by-products originating from chloride for electrochemical disinfection using a BDD electrode reactor were quantified. The two synthetic water matrices with different chloride content were applied under different current densities. Higher initial chloride concentrations lead to an increase in the formation of chlorate and further to perchlorate (Fig. 5). During the experiment with 167 mA cm^{-2}, the chlorate concentration was 0.33 mg L^{-1} in synthetic water I after 10 min exposure time (68 mA h L^{-1}) (Fig. 5a), this was 0.72 mg L^{-1} in synthetic water II at the same time (Fig. 5b). By enhancing the current density, the

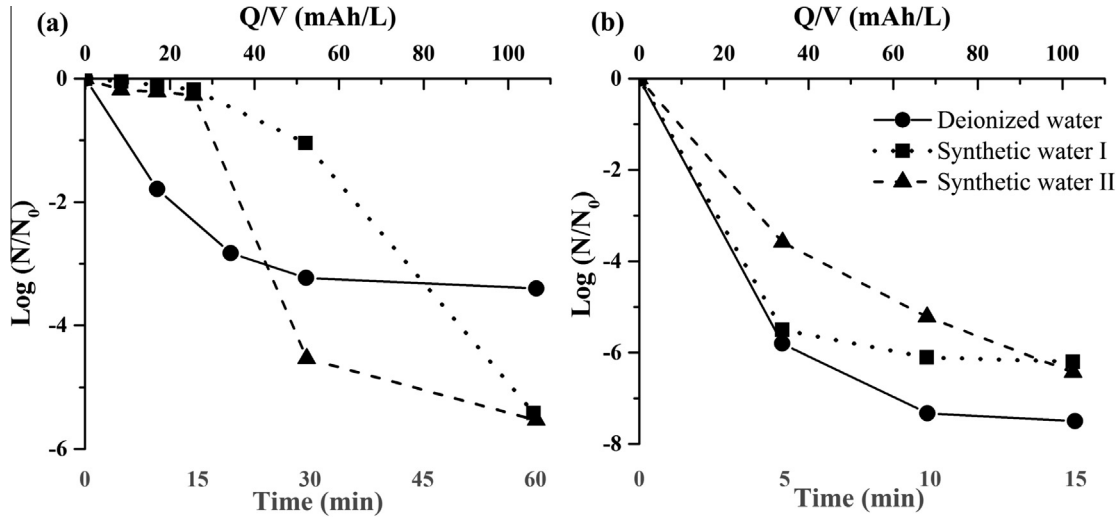

Fig. 3. Disinfection kinetics of *P. aeruginosa* in water with varying chloride concentrations (synthetic water I: 20 mg L^{-1}; synthetic water II: 250 mg L^{-1}) in dependence of the applied charge per volume for two current densities ((a) =42 mA cm^{-2}; (b) =167 mA cm^{-2}). The time axis is for reference only.

Table 2
Development of ozone and free chlorine concentrations in three water matrices during the electrochemical disinfection applying two current densities. (DW: deionized water, SW I/II: synthetic water I/II).

42 mA cm^{-2}						167 mA cm^{-2}				
Q/V (time)	0 (0)	8.44 (5)	25.63 (15)	52.21 (30)	106.68 (60)	Q/V (time)	0 (0)	33.82 (5)	68.09 (10)	102.98 (15)
O_3 concentration (mg L^{-1})										
DW	0	0.07	0.04	0.03	0.01	DW	0	0.25	0.34	0.46
SW I	0	0.12	0.06	0.04	0.19	SW I	0	0.31	0.37	0.31
SW II	0	0.04	0.14	0.33	0.58	SW II	0	0.38	0.59	0.62
Free chlorine concentration (mg L^{-1})										
DW	0	n.d.	n.d.	n.d.	0.13	DW	n.d.	n.d.	n.d.	n.d.
SW I	0.10	0.16	0.18	0.26	0.43	SW I	0.10	0.13	0.25	0.33
SW II	0.11	n.d.	0.31	0.51	0.67	SW II	0.09	0.28	0.37	0.59

n.d. not determined.

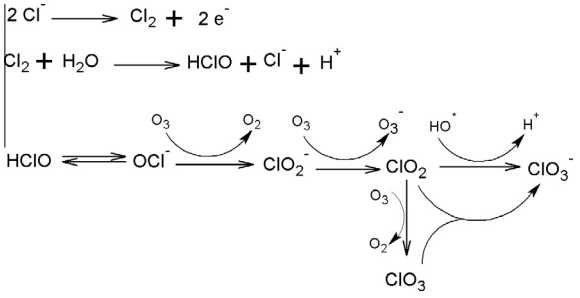

Fig. 4. The stepwise mechanism for chloride oxidation.

formation of inorganic by-products increased, probably due to the higher ozone concentration. The difference between chlorate and perchlorate concentrations -at each time point- depends mainly on the applied current density. This could be noticed in Fig. 5(a and b) for chlorate and perchlorate data in case of 167 mA cm^{-2} in both water matrices (black colored points and bars). The difference in the initial chloride concentrations between synthetic water I and II (×10 times) was not evident in the observed chlorate and perchlorate concentrations measured in both matrices. The concentrations of both molecules were just two times higher in synthetic water II than they were in synthetic water I.

Due to the carcinogenic potential of perchlorate (Urbansky and Schock, 1999; Charnley, 2008), different measures should be considered to reduce the concentration in order to meet the drinking water regulations. While EU legislation currently do not regulate chlorate and perchlorate in drinking water, some states in the USA have already set a maximum contaminant level of perchlorate ranging between 2 and 6 μg L^{-1} (Stanford et al., 2011). The WHO has set the value of 700 μg L^{-1} as a maximum concentration of chlorate (World Health Organization, 2011). In this context, it is important to highlight the fact that not only drinking water can be treated using BDD electrodes. Other applications of electrochemical disinfection are the treatment of swimming pool water, cooling water and ballast water, for which higher initial chloride and bromide concentrations are expected. The regulations of such treated waters are different than those for drinking water. The WHO recommends a chlorate concentration lower than 3 mg L^{-1} for swimming pool water (World Health Organization, 2006). In this study, the concentrations of DBPs measured, where a 5–6 log reduction value of microorganisms was achieved, are still in the range of the reported regulations (gray areas in Fig. 5).

3.4. Energy demand of the process

The results discussed previously illustrate the effectiveness of the electrochemical disinfection process using BDD electrodes, apart from the content of the water matrix. To link those data with energy requirements, the energy demand was monitored over the entire disinfection process.

The energy needed during the treatment was calculated by Eq. 1:

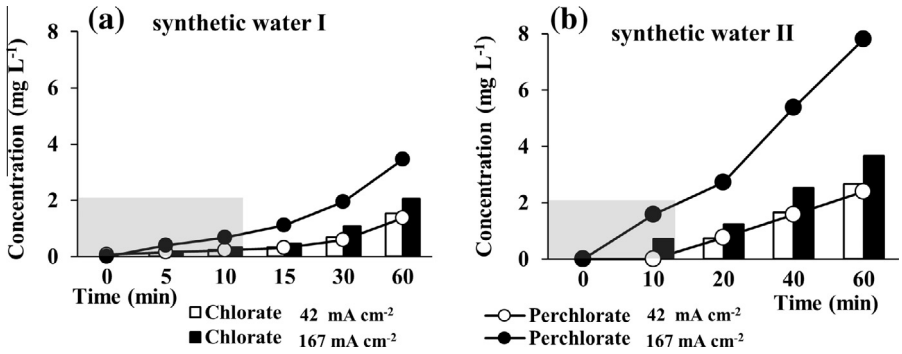

Fig. 5. Development of chlorate and perchlorate concentrations during the disinfection of *P. aeruginosa* in synthetic water I (a) and II (b) under varying current densities. Gray areas represent the desired disinfection of a 6-log unit reduction.

$$E\left(\frac{\text{kW h}}{\text{m}^3}\right) = \frac{E_{\text{cell}} * I * T}{V} \quad (1)$$

where E_{cell} is the cell voltage (volt), I is the applied current (ampere), T the treatment time (h) and V is the volume of the treated water (m^3).

In general, the energy demand depends on the desired inactivation level and thus the disinfection time, as well as the current density in a certain water matrix. Under the applied experimental conditions in both synthetic water types, the energy consumption was 0.63 kW h m^{-3} at a current density of 42 mA cm^{-2} to achieve a 6-log reduction of the target microorganisms (60 min). In case of the higher current density (167 mA cm^{-2}), the time needed to achieve the 6-log reduction was relatively short (up to 10 min) and therefore the energy consumption ranged between 0.3 and 0.4 kW h m^{-3}. Cano et al. (2012) reported a power consumption as low as 0.2 kW h m^{-3} to achieve a complete inactivation of *E. coli* ($N_0 = 10^3$ CFU mL^{-1}) during wastewater treatment using a BDD electrode. In this context, it is worth mentioning here that this study was conducted using a laboratory unit. The calculation of energy consumption does not consider the upscaling effects of optimized hydrodynamic conditions for a large-scale installation. Moreover, the initial microorganism concentrations used in this study ($N_0 = 10^7$–10^8 CFU mL^{-1}) are relatively high, which should be considered when comparing the energy consumption with other studies. Literature data for electrochemical disinfection of *E. coli* ($N_0 = 10^3$–10^5 CFU mL^{-1}) showed a relatively high energy consumption (between 1.0 and 2.6 kW h m^{-3}) to achieve complete disinfection, which is economically impracticable for drinking water applications (Kerwick et al., 2005; Haaken et al., 2012).

4. Conclusions

The BDD electrode is a viable technology for inactivation of *P. aeruginosa* in different water matrices. The process provides a high degree of removal of the microorganisms without any additional chemical substances even under worst-case conditions as applied in the current study. The measured concentrations of ozone and free chlorine were affected by the applied current density and the chloride content in the treated water with tendency towards generating ozone at higher current densities. Reactive chlorine species enhanced disinfection at low current densities where ozone was not generated in sufficient amounts. The role of pH is very important as the presence of chlorine species is changing significantly. Hence, shifting the pH value to slightly under pH 7 could improve the inactivation level. Chlorate and perchlorate as DBPs were formed and concentrations of both by-products also depended on the applied current density. The formation of perchlorate during disinfection using BDD electrodes is shown as a significant drawback. However, when applying either a water matrix with elevated chloride concentrations or a high current density, the overall treatment time could be significantly reduced to achieve the desired disinfection level. This keeps the formation of undesired by-products at a minimum level as well as the energy demand. Further improvement of the disinfection potential of BDD electrodes including the electrode design is currently in process.

Acknowledgments

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References

Bader, H., Hoigné, J., 1981. Determination of ozone in water by the indigo method. Water Res. 15, 449–456.
Bergmann, M.E.H., 2006. Application of DPD-method in electrochemical drinking water disinfection (in German). Wasser Abwasser. 12, 780–786.
Bergmann, M.E.H., Rollin, J., 2007. Product and by-product formation in laboratory studies on disinfection electrolysis of water using boron-doped diamond anodes. Catal. Today 124, 198–203.
Bergmann, M.E.H., Rollin, J., Iourtchouk, T., 2009. The occurrence of perchlorate during drinking water electrolysis using BDD anodes. Electrochim. Acta 54, 2102–2107.
Bergmann, M.E.H., Rollin, J., Koparal, A.S., 2010. Chlorate and perchlorate- new criterions for environmentally-friendly processes in advanced oxidation. Water Pract. Technol. 5.
Bergmann, M.E.H., Iourtchouk, T., Rollin, J., 2011. The occurrence of bromate and perbromate on BDD anodes during electrolysis of aqueous systems containing bromide: first systematic experimental studies. J. Appl. Electrochem. 41, 1109–1123.
Cano, A., Cañizares, P., Barrera-Díaz, C., Sáez, C., Rodrigo, M.A., 2012. Use of conductive-diamond electrochemical-oxidation for the disinfection of several actual treated wastewaters. Chem. Eng. J. 211, 463–469.
Charnley, G., 2008. Perchlorate: overview of risks and regulation. Food. Chem. Toxicol. 46, 2307–2315.
Deborde, M., von Gunten, U., 2008. Reactions of chlorine with inorganic and organic compounds during water treatment—kinetics and mechanisms: a critical review. Water Res. 42, 13–51.
Diao, H., Li, X., Gu, J., Shi, H., Xie, Z., 2004. Electron microscopic investigation of the bactericidal action of electrochemical disinfection in comparison with chlorination, ozonation and Fenton reaction. Process Biochem. 39, 1421–1426.
Fujishima, A. (Ed.), 2005. Diamond Electrochemistry, vol. XXII. Elsevier, Amsterdam u.a. 586 S.
Furuta, T., Tanaka, H., Nishiki, Y., Pupunat, L., Haenni, W., Rychen, P., 2004. Legionella inactivation with diamond electrodes. Diam. Relat. Mater. 13, 2016–2019.
Ghernaout, D., Ghernaout, B., 2010. From chemical disinfection to electro-disinfection: the obligatory itinerary? Desalin. Water Treat. 16, 156–175.
Griessler, M., Knetsch, S., Schimpf, E., Schmidhuber, A., Schrammel, B., Wesner, W., Sommer, R., Kirschner, A.K.T., 2011. Inactivation of Pseudomonas aeruginosa in electrochemical advanced oxidation process with diamond electrodes. Water Sci. Technol. 63, 2010–2016.

Haaken, D., Dittmar, T., Schmalz, V., Worch, E., 2012. Influence of operating conditions and wastewater-specific parameters on the electrochemical bulk disinfection of biologically treated sewage at boron-doped diamond (BDD) electrodes. Desalinat. Water Treat. 46, 160–167.
Heim, C., Ureña de Vivanco, M., Rajab, M., Glas, K., Horn, H., Helmreich, B., Letzel, T., 2011. Ozone II: characterization of in situ ozone generation using diamond electrodes. Brew. Sci. 64, 83–88.
International Organization for Standardization ISO, 2006. Water Quality – Detection and Enumeration of *Pseudomonas aeruginosa* – Method by Membrane Filtration. ISO, Geneva ISO 16266, 12p.
International Organization for Standardization ISO, 2007. Water Quality – Determination of Dissolved Anions by Liquid Chromatography of Ions, Geneva ISO 10304–1, vol. 15.
Jeong, J., Kim, J.Y., Yoon, J., 2006. The role of reactive oxygen species in the electrochemical inactivation of microorganisms. Environ. Sci. Technol. 40, 6117–6122.
Kerwick, M.I., Reddy, S.M., Chamberlain, A., Holt, D.M., 2005. Electrochemical disinfection, an environmentally acceptable method of drinking water disinfection? Electrochim. Acta 50, 5270–5277.
Kraft, A., 2007. Doped diamond: a compact review on a new, versatile electrode material. Int. J. Electrochem. Sci. 2, 355–385.
Kraft, A., 2008. Electrochemical water disinfection: a short review. Platin. Met. Rev. 52, 177–185.
Kraft, A., Stadelmann, M., Blaschke, M., Kreysig, D., Sandt, B., Schröder, F., Rennau, J., 1999a. Electrochemical water disinfection. Part I: Hypochlorite production from very dilute chloride solutions. J. Appl. Electrochem. 29, 861–868.
Kraft, A., Blaschke, M., Kreysig, D., Sandt, B., Schröder, F., Rennau, J., 1999b. Electrochemical water disinfection. Part II: hypochlorite production from potable water, chlorine consumption and the problem of calcareous deposits. J. Appl. Electrochem. 29, 895–902.
Kraft, A., Stadelmann, M., Wünsche, M., Blaschke, M., 2006a. Electrochemical destruction of organic substances in deionized water using diamond anodes and a solid polymer electrolyte. Electrochem. Commun. 8, 155–158.
Kraft, A., Stadelmann, M., Wünsche, M., Blaschke, M., 2006b. Electrochemical ozone production using diamond anodes and a solid polymer electrolyte. Electrochem. Commun. 8, 883–886.
Li, H., Ni, J., 2012. Electrogeneration of disinfection byproducts at a boron-doped diamond anode with resorcinol as a model substance. Electrochim. Acta 69, 268–274.
Mamane, H., 2008. Impact of particles on UV disinfection of water and wastewater effluents: a review. Rev. Chem. Eng. 24, 67–157.
Martínez-Huitle, C.A., Brillas, E., 2008. Electrochemical alternatives for drinking water disinfection. Angew. Chem. Int. Ed. 47, 1998–2005.
May, P.W., 2008. The new diamond age? Science 319 (5869), 1490–1491.
Metcalf and Eddy Inc., 2003. Wastewater Engineering Treatment and Reuse, fourth ed. McGraw Hill, New York, USA. p. 1234.
Palmas, S., Polcaro, A.M., Vacca, A., Mascia, M., Ferrara, F., 2007. Influence of the operating conditions on the electrochemical disinfection process of natural waters at BDD electrodes. J. Appl. Electrochem. 37, 1357–1365.
Panis, C., Matsuo, T., Reiche, E.M.V., 2009. Nosocomial infections in human immunodeficiency virus type 1 (HIV-1) infected and AIDS patients: major microorganisms and immunological profile. Braz. J. Microbiol. 40, 155–162.
Pérez, G., Gómez, P., Ibañez, R., Ortiz, I., Urtiaga, A.M., 2010. Electrochemical disinfection of secondary wastewater treatment plant (WWTP) effluent. Water Sci. Technol. 62, 892–897.
Polcaro, A.M., Vacca, A., Mascia, M., Palmas, S., Rodiguez Ruiz, J., 2009. Electrochemical treatment of waters with BDD anodes: kinetics of the reactions involving chlorides. J. Appl. Electrochem. 39, 2083–2092.
Schmalz, V., Dittmar, T., Haaken, D., Worch, E., 2009. Electrochemical disinfection of biologically treated wastewater from small treatment systems by using boron-doped diamond (BDD) electrodes – contribution for direct reuse of domestic wastewater. Water Res. 43, 5260–5266.
Sedlak, D.L., von Gunten, U., 2011. The chlorine dilemma. Science 331, 42–43.
Stanford, B.D., Pisarenko, A.N., Snyder, S.A., Gordon, G., 2011. Perchlorate, bromate, and chlorate in hypochlorite solutions: guidelines for utilities. J. AWWA 103, 71–83.
Urbansky, E.T., Schock, M.R., 1999. Issues in managing the risks associated with perchlorate in drinking water. J. Environ. Manage. 56, 79–95.
Ureña de Vivanco, M., Rajab, M., Heim, C., Letzel, T., Helmreich, B., 2013. Setup and energetic considerations for three advanced oxidation reactors treating organic compounds. Chem. Eng. Technol. 36, 355–361.
von Gunten, U., 2003a. Ozonation of drinking water: Part I. Oxidation kinetics and product formation. Water Res. 37, 1443–1467.
von Gunten, U., 2003b. Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. Water Res. 37, 1469–1487.
von Gunten, U., Pinkernell, U., 2000. Ozonation of bromide-containing drinking waters: a delicate balance between disinfection and bromate formation. Water Sci. Technol. 41, 53–59.
World Health Organization, 2006. Guidelines for Safe Recreational Water Environments. World Health Organization, Geneva. p. 118.
World Health Organization, 2011. Guidelines for Drinking-Water Quality, fourth ed. World Health Organization, Geneva. 632pp.
World Health Organization, 2013. Water Quality and Health Strategy 2013–2020. (http://www.who.int/water_sanitation_health/publications/2013/water_quality_strategy/en/) (retrieved 01.08.14).
Yao, Y., Kubota, Y., Murakami, T., Ochiai, T., Ishiguro, H., Nakata, K., Fujishima, A., 2011. Electrochemical inactivation kinetics of boron-doped diamond electrode on waterborne pathogens. J Water Health 9, 534–543.
Yates, R., Stenstrom, M.K., 2000. Gravimetric sampling procedure for aqueous ozone concentrations. Water Res. 34, 1413–1416.

4 Chapter Four
General Conclusions

Wastewater treatment and reuse are some of the main strategies drawn to minimize the effects of water scarcity. Due to the presence of residual micropollutants in water sources, new treatment technologies are now the foci of academic and industrial research. The risk of residual organic traces in water on human and ecological health, is still poorly understood (Oaks et al., 2004). Electrochemical oxidation, using BDD electrode, present an environmentally-friendly and economical technology to remove micropollutants from the effluents of municipal and industrial wastewater treatment plants.

4.1 Summary of Research Conclusion

A number of parameters control the applicability of BDD electrode for water and wastewater treatment. Among these parameters, the present research focused on the influence of water matrix components and the applied current density on the degradation of three CECs (DCF, SMX, and BPA). The mechanism of the inactivation of *P.aeroginosa* was also investigated to assess the role of oxidation species during the process. Conclusions drawn are presented in the following sections.

4.1.1 Task 1: Influence of water matrices on the DCF degradation

The *in-situ* generation of oxidants using BDD electrode depends on the water matrix and its components. Task 1 – presented as point 3.1 – studied the degradation of DCF in three different water matrices at constant current density. The main goal of the study was the application of analytical approach to identify the TPs formed during the process. This approach suggests a suspected screening based on a list of known TPs and the data gained from a serial coupling of RP and zwitterionic hydrophilic interaction LC–MS. The major conclusions from this chapter are:

- The removal of DCF was achieved after 15, 20 and 30 minutes in MilliQ water, hard water and WWTP effluent, respectively. The variability in the degradation process amongst the water matrices was ascribed to competitive reactions between the DCF and the inorganic and organic constituents present in hard water and WWTP effluent.
- The serial coupling of RP-HILIC LC-MS was applied for a comprehensive investigation of different suspected TPs and eleven suspected TPs were identified. The key step in the identification procedure was the integration of chemical and physical characteristics of the compounds – namely the accurate mass detection and the qualitative relationship of the retention time and the logarithm of the distribution coefficient (log*D*) – during the screening process.
- The majority of the TPs were undetectable after 30 minutes treatment in the deionized water matrix. In hard water and WWTP effluent, some TPs were found after 60 minutes of treatment. This could be related to the chemical structure of the TP and the availability of oxidant species in the water matrix.

4.1.2 Task 2: Influence of applied current densities on the degradation of SMX in wastewater effluent

The applied current density is the most important parameter during electrochemical oxidation, using a BDD electrode. It effects the kinetic of the degradation as well as the formation of inorganic by-products. Task 2 – presented as point 3.2 – focused on the degradation of SMX in a wastewater effluent at two different current densities. The objectives of this task were to apply the degradation study under real conditions and to follow the energy consumption during the process. Key conclusions drawn from this chapter are:

- Increasing the applied current density (from 208 to 333 mA cm^{-2}) led to a higher dissolved ozone concentrations in the matrix (0.06 mg L^{-1} to 0.24 mg L^{-1}). Hence, faster degradation rate of SMX was observed.
- The formation of TPs occurred simultaneously with the SMX degradation. At higher current density, the disappearance of TPs in the matrix was faster due to the high ozone concentration. A complete removal of all TPs was not achievable even with longer treatment time. However, the BDD electrode removed TP with an isoxazole ring, which was non-degradable in the biological treatment step under aerobic condition.

- The energy demand of the process depends on the applied current density and the treatment time, to achieve the water quality required after treatment. In this study, the process energy demand for the total degradation of SMX was 0.38 and 0.32 kWh m^{-3} at 208 and 333 mA cm^{-2}, respectively. The prolongation of the treatment time from 10 to 60 min at 208 mA cm^{-2} or from 5 to 10 min at 333 mA cm^{-2} resulted in simultaneous degradation of some TPs. Nonetheless, this prolongation increased the process energy demand to 2.28 and 0.68 kWh m^{-3} for 208 and 333 mA cm^{-2}, respectively. The experimental set up contributed in those high values, and therefore they should be seen only as a preliminary approximation.

4.1.3 Task 3: Degradation of BPA in different water matrices and different applied current densities

The efficiency of BPA degradation in deionized water, synthetic waters and WWTP effluent and the formation of TPs were investigated at different current densities. The approach of task 3 was to apply the gained knowledge of the previous tasks on the degradation of the industrial micropollutant BPA. The effect of water matrix on the formation of TPs and, consequently, the degradation pathway was assessed in this task. Inorganic by-products (chlorate and perchlorate) were quantified and presented in a combination with the energy demand of the process. Key conclusions from this task included:

- As in the previous tasks, higher current densities accelerated the degradation process, whereas an increase in inorganic constituents and organic matter of the water matrix decelerated the process.
- Independent of the water matrix, the BPA degradation followed a pathway consisting of three main steps: The formation of hydroxylated derivatives, followed by the oxidation of the isopropylidene bridge and subsequently the cleavage of the aromatic ring to form small organic molecules
- Depending on the extent of oxidation, the energy required for complete BPA removal in a batch process was 7.37 kWh m^{-3}. Excessive amounts of chlorate and perchlorate were formed during the treatment, which increased with longer treatment time. This high energy demand and the excessive inorganic by-products formation were seen as a drawback of the process. Nevertheless, changing the experimental set up (continuous

flow system, flow rate and hydrodynamic feature of the reactor) will give reliable values for a scale-up approach.

4.1.4 Task 4: Electrochemical disinfection using BDD electrode

This task investigated the influence of chloride ion concentration on the disinfection performance of a BDD electrode on the ubiquitous model organism *Pseudomonas aeruginosa* (*P. aeruginosa*). Two parameters were tested, namely applied current density and chloride ion concentration. The major objective of this study was to link the bacterial inactivation capacity of BDD diamond with the energy demand and the formation of inorganic DBPs, in order to define the optimal process conditions. The foremost conclusions drawn from this chapter are:

- High degree of microorganism's removal was possible using BDD electrode without adding any chemical substances, even under worst-case conditions such as experimental design and reactor geometry.
- Beside reactive oxygen species, reactive chlorine species were formed. The *in-situ* generation of both species resulted in a synergy effect on the inactivation of *P. aeruginosa.*
- The pH of the water matrix affected the relative distribution of the chlorine species (i.e. HClO and ClO^-). Hence, the inactivation capacity of those species increased at lower pH.
- Higher initial chloride concentrations led to an increase in the formation of chlorate and further to perchlorate. However, a 5-6 log reduction value of microorganisms was achieved and, at the same time, the concentrations of chlorate and perchlorate were still in the acceptable level under regulation of swimming pool, for instance.
- Under the applied experimental conditions, in the synthetic water, the energy consumption was 0.63 kWh m^{-3}, at a current density of 42 mA cm^{-2}, to achieve a 6-log reduction of the target microorganisms (60 min). In case of the higher current density (167 mA cm^{-2}), the time needed to achieve the 6-log reduction was relatively short (up to 10 min) and therefore the energy consumption ranged between 0.3 and 0.4 kWh m^{-3}. Those energy demand values do not consider upscaling effects of optimized hydrodynamic conditions for a large-scale installation.

4.2 Research Contributions and Significance

The components of the water matrix affect the kinetic of micropollutants degradation, using BDD electrode. Water matrix with high organic and inorganic contents decelerates the degradation process and lead to higher inorganic by-products concentrations. The applied current density is another major factor that control the degradation process. Increasing the applied current density will result in faster degradation process. However, this action boosts the consumption of energy and the formation of inorganic by-products. The research focused on application in real WWTP effluents to define the optimal operational parameters. Hence, an applied current density that ranged between 100 and 200 mA cm^{-2} has been shown to be sufficient to remove the target micropollutant and many of the formed TPs. At this range of current densities, chlorate and perchlorate concentrations are in the acceptable levels for industrial effluents. Nonetheless, those concentration levels are high for drinking water applications.

The research tested another applicability for BDD electrode, namely disinfection. The results showed a sufficient inactivation levels of *P. aeruginosa.* The chloride content in the water matrix has a positive impact on the disinfection process, where a synergic effect could be gained from oxygen and chloride oxidant species. The formation of DBPs could be managed and kept in the legalised levels for non-drinking water applications.

4.3 Recommendations for Future Research

The results acquired through this research contributed to the understanding of the BDD applications in water and wastewater treatment and the optimized operational parameters for such applications. A number of important issues, identified as worthy of further research include:

- The upscaling approach is a fundamental objective in the development of a BDD-based treatment system. In order to achieve this goal, a set of experiments have to be executed applying a continuous-flow system. Those experiments will provide more accurate data, especially for the specific energy demand of the process.
- Identifying the chemical characteristic of the TPs is an interesting aspect from the chemistry point of view. However, from an engineering and applicability perspectives, the toxicity characteristic of those TPs is more meaningful. If none of the TPs is toxic,

there is no need to extend the process for longer time. Hence, lower energy demand and less inorganic by-products formation would be achieved.

- The structure of diamonds over the electrode has an important effect on the formation of ozone molecules. This structure could be controlled during the manufacturing process of the electrodes. More researches should focus on modifying the electrode and getting the optimal structure that enhance the ozone formation and minimize the formation of inorganic by-products.
- The hydrodynamics of the system is an important factor that affects the process. Hydroxyl radicals are the primer product over the BDD electrode. Thus, the efficiency of those radicals is coupled with an intensive contact between the treated water (the parent compound) and the surface of the electrode. This was - partially – achieved using the *CONDIAPURE SHORTY* ® reactor (Figure 4). Different modifications of the reactor and changing the hydraulic retention time should be assessed.
- Moving forward to the real applications, a real industrial wastewater matrix has to be considered. Micropollutants removal, TPs and inorganic by-products evaluation should be among the objectives of such experiments. In addition, the halogenated organic by-products (AOX, THMs) should be quantified.

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5 References

Al Aukidy, M., Verlicchi, P., Voulvoulis, N., 2014. A framework for the assessment of the environmental risk posed by pharmaceuticals originating from hospital effluents. Sci. Total Environ. 493, 54-64.

Alidina, M., Hoppe-Jones, C., Yoon, M., Hamadeh, A.F., Li, D., Drewes, J.E., 2014. The occurrence of emerging trace organic chemicals in wastewater effluents in Saudi Arabia. Sci. Total Environ. 478, 152–162.

Alves, S.A., Ferreira, T.C., Migliorini, F.L., Baldan, M.R., Ferreira, N.G., Lanza, M.R., 2013. Electrochemical degradation of the insecticide methyl parathion using a boron-doped diamond film anode. J. Electroanal. Chem. 702, 1–7.

Ambuludi, S.L., Panizza, M., Oturan, N., Özcan, A., Oturan, M.A., 2013. Kinetic behavior of anti-inflammatory drug ibuprofen in aqueous medium during its degradation by electrochemical advanced oxidation. Environ Sci Pollut Res. 20, 2381–2389.

Andreozzi, R., 1999. Advanced oxidation processes (AOP) for water purification and recovery. Catal. Today 53, 51–59.

Arihara, K., Terashima, C., Fujishima, A., 2006. Application of Freestanding Perforated Diamond Electrodes for Efficient Ozone-Water Production. Electrochem. Solid-State Lett. 9, D17.

Bahamonde, P.A., Fuzzen, M.L., Bennett, C.J., Tetreault, G.R., McMaster, M.E., Servos, M.R., Martyniuk, C.J., Munkittrick, K.R., 2015. Whole organism responses and intersex severity in rainbow darter (Etheostoma caeruleum) following exposures to municipal wastewater in the Grand River basin, ON, Canada. Part A. Aquat. Toxicol. 159, 290–301.

Barrera-Díaz, C., Cañizares, P., Fernández, F.J., Natividad, R., Rodrigo, M.A., 2014. Electrochemical Advanced Oxidation Processes: An Overview of the Current Applications to Actual Industrial Effluents. J. Mex. Chem. Soc. 58, 256–275.

Bergmann, H., 2010. Zur Bewertung von Diamantelektroden für die Wasserdesinfektionselektrolyse (german language). gwf-Wasser | Abwasser (Juni), 604–612.

Bergmann, M. Henry E., Iourtchouk, T., Rollin, J., 2011. The occurrence of bromate and perbromate on BDD anodes during electrolysis of aqueous systems containing bromide: first systematic experimental studies. J Appl Electrochem 41, 1109–1123.

Bergmann, M. Henry E., Rollin, J., 2007. Product and by-product formation in laboratory studies on disinfection electrolysis of water using boron-doped diamond anodes. Catal. Today 124, 198–203.

Bergmann, M. Henry E., Rollin, J., Koparal, A.S., 2010. Chlorate and perchlorate- new criterions for environmentally-friendly processes in advanced oxidation. Water Pract Tech 5.

Borràs, N., Arias, C., Oliver, R., Brillas, E., 2013. Anodic oxidation, electro-Fenton and photoelectro-Fenton degradation of cyanazine using a boron-doped diamond anode and an oxygen-diffusion cathode. J. Electroanal. Chem 689, 158–167.

Brian, J.V., Harris, C.A., Scholze, M., Backhaus, T., Booy, P., Lamoree, M., Pojana, G., Jonkers, N., Runnalls, T., Bonfà, A., Marcomini, A., Sumpter, J.P., 2005. Accurate Prediction of the Response of Freshwater Fish to a Mixture of Estrogenic Chemicals. Environ Health Perspect 113, 721–728..

Brillas, E., Martínez-Huitle, C.A., 2011. Synthetic diamond films: Preparation, electrochemistry, characterization, and applications. Wiley, Hoboken, N.J., 1 online resource.

Brodin, T., Fick, J., Jonsson, M., Klaminder, J., 2013. Dilute concentrations of a psychiatric drug alter behavior of fish from natural populations. Science 339, 814–815.

Brozinski, J.-M., Lahti, M., Meierjohann, A., Oikari, A., Kronberg, L., 2013. The Anti-Inflammatory Drugs Diclofenac, Naproxen and Ibuprofen are found in the Bile of Wild Fish Caught Downstream of a Wastewater Treatment Plant. Environ. Sci. Technol. 47, 342–348.

Campos-González, E., Frontana-Uribe, B.A., Vasquez-Medrano, R., Macías-Bravo, S., Ibanez, J.G., 2014. Advanced electrochemical oxidation of Methyl Parathion at boron-doped diamond electrodes. J. Mex. Chem. Soc. 58, 315–321.

Carson, R., Darling, L., Darling, L., 1962. Silent spring. Houghton Mifflin; Riverside Press, Boston, Cambridge, Mass., x, 368.

Cavalcanti, E.B., -Segura, S.G., Centellas, F., Brillas, E., 2013. Electrochemical incineration of omeprazole in neutral aqueous medium using a platinum or boron-doped diamond anode: Degradation kinetics and oxidation products. Water Res. 47, 1803–1815.

Chen, T.-S., tsai, R.-W., chen, Y.-S., Huang, K.-l., 2014. Electrochemical Degradation of Tetracycline on BDD in Aqueous Solutions. Int. J. Electrochem. Sci.9, 8422–8434.

Comninellis, C., Chen, G., ©2010. Electrochemistry for the environment. Springer, New York, xi, 563.

Comninellis, C., Kapalka, A., Malato, S., Parsons, S.A., Poulios, I., Mantzavinos, D., 2008. Advanced oxidation processes for water treatment: advances and trends for R&D. J. Chem. Technol. Biotechnol. 83, 769–776.

Cordeiro, G.S., Rocha, R.S., Valim, R.B., Migliorini, F.L., Baldan, M.R., Lanza, M., Ferreira, N.G., 2013. Degradation of profenofos in an electrochemical flow reactor using boron-doped diamond anodes. Diamond Relat. Mater. 32, 54–60.

Coria, G., Nava, J.L., Carreno, G., 2014. Electrooxidation of Diclofenac in Synthetic Pharmaceutical Wastewater Using an Electrochemical Reactor Equipped with a Boron Doped Diamond Electrode. J. Mex. Chem. Soc. 58, 303–308.

Davison, J., 1999. Genetic Exchange between Bacteria in the Environment. Plasmid 42, 73–91.

de Amorim, Kamila P., Romualdo, L.L., Andrade, L.S., 2013. Electrochemical degradation of sulfamethoxazole and trimethoprim at boron-doped diamond electrode: Performance, kinetics and reaction pathway. Sep. Purif. Technol. 120, 319–327.

Deborde, M., von Gunten, U., 2008. Reactions of chlorine with inorganic and organic compounds during water treatment—Kinetics and mechanisms: A critical review. Water Res. 42, 13–51.

Dirany, A., Sirés, I., Oturan, N., Oturan, M.A., 2010. Electrochemical abatement of the antibiotic sulfamethoxazole from water. Chemosphere 81, 594–602.

Donn, J., Mendoza, M., Pritchard, J., 2008. AP: Probe Finds Drugs in Drinking Water. <http://hosted.ap.org/specials/interactives/pharmawater_site/> (retrieved 30.03.15).

El-Ghenymy, A., Cabot, P.L., Centellas, F., Garrido, J.A., Rodríguez, R.M., Arias, C., Brillas, E., 2013. Electrochemical incineration of the antimicrobial sulfamethazine at a boron-doped diamond anode. Electrochim. Acta 90, 254–264.

Errami, M., Salghi, R., Ebenso, Eno. E, Messali, M, Al-Deyab, S.S, Hammouti, B, 2014. Anodic Destruction of abamectin Acaricide Solution By BDD-Anodic Oxidation. Int. J. Electrochem. Sci. 9, 5467–5478.

Fabiańska, A., Białk-Bielińska, A., Stepnowski, P., Stolte, S., Siedlecka, E.M., 2014. Electrochemical degradation of sulfonamides at BDD electrode: Kinetics, reaction pathway and eco-toxicity evaluation. J. Hazard. Mater. 280, 579–587.

Ferro, S., 2002. Synthesis of diamond. J. Mater. Chem. 12, 2843–2855.

Fryda, M., Matthée, T., Mulcahy, S., Hampel, A., Schäfer, L., Tröster, I., 2003. Fabrication and application of Diachem® electrodes. Diamond Relat. Mater. 12, 1950–1956.

Fujishima, A. (Ed.), 2005. Diamond electrochemistry. Elsevier, Amsterdam u.a, XXII, 586 S.

Ganzenko, O., Huguenot, D., van Hullebusch, Eric D., Esposito, G., Oturan, M.A., 2014. Electrochemical advanced oxidation and biological processes for wastewater treatment: a review of the combined approaches. Environ Sci Pollut Res 21, 8493–8524.

Glaze, W.H., Kang, J.-W., Chapin, D.H., 1987. The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation. Ozone-Sci. Eng. 9, 335–352.

Haaken, D., Dittmar, T., Schmalz, V., Worch, E., 2012. Influence of operating conditions and wastewater-specific parameters on the electrochemical bulk disinfection of biologically treated sewage at boron-doped diamond (BDD) electrodes. Desalin. Water Treat. 46, 160–167.

Heim, C., Ureña de Vivanco, M., Rajab, M., Glas, K., Horn, H., Helmreich, B., Letzel, T., 2011. Ozone II: characterization of in situ ozone generation using diamond electrodes. Brewing science 64, 83–88.

Heim, C., Ureña de Vivanco, M., Rajab, M., Müller, E., Letzel, T., Helmreich, B., 2014. Rapid inactivation of waterborne bacteria using boron-doped diamond electrodes. Int. J. Environ. Sci. Technol.

Hoigne, J., 1997. Inter-calibration of oh radical sources and water quality parameters. Water Sci. Technol. 35, 1–8.

Isse, A.A., Lin, C.Y., Coote, M.L., Gennaro, A., 2011. Estimation of Standard Reduction Potentials of Halogen Atoms and Alkyl Halides. J. Phys. Chem. B 115, 678–684.

Jobling, S., Williams, R., Johnson, A., Taylor, A., Gross-Sorokin, M., Nolan, M., Tyler, C.R., van Aerle, R., Santos, E., Brighty, G., 2005. Predicted Exposures to Steroid Estrogens in U.K. Rivers Correlate with Widespread Sexual Disruption in Wild Fish Populations. Environ Health Perspect 114, 32–39.

Kidd, K.A., Blanchfield, P.J., Mills, K.H., Palace, V.P., Evans, R.E., Lazorchak, J.M., Flick, R.W., 2007. Collapse of a fish population after exposure to a synthetic estrogen. PANS.104, 8897–8901.

Kleywegt, S., Pileggi, V., Yang, P., Hao, C., Zhao, X., Rocks, C., Thach, S., Cheung, P., Whitehead, B., 2011. Pharmaceuticals, hormones and bisphenol A in untreated source and finished drinking water in Ontario, Canada — Occurrence and treatment efficiency. Sci. Total Environ. 409, 1481–1488.

Kraft, A., 2007. Doped Diamond: A Compact Review on a New, Versatile Electrode Material. Int. J. Electrochem. Sci. 2, 355–385.

Kraft, A., Stadelmann, M., Blaschke, M., 2003. Anodic oxidation with doped diamond electrodes: a new advanced oxidation process. J. Hazard. Mater 103, 247–261.

Kraft, A., Stadelmann, M., Wünsche, M., Blaschke, M., 2006a. Electrochemical destruction of organic substances in deionized water using diamond anodes and a solid polymer electrolyte. Electrochem. Commun. 8, 155–158.

Kraft, A., Stadelmann, M., Wünsche, M., Blaschke, M., 2006b. Electrochemical ozone production using diamond anodes and a solid polymer electrolyte. Electrochem. Commun. 8, 883–886.

Kümmerer, K., 2001. Drugs in the environment: emission of drugs, diagnostic aids and disinfectants into wastewater by hospitals in relation to other sources – a review. Chemosphere 45, 957–969.

Levy, S.B., Marshall, B., 2004. Antibacterial resistance worldwide: causes, challenges and responses. Nat Med 10, S122.

Li, H., Ni, J., 2012. Electrogeneration of disinfection byproducts at a boron-doped diamond anode with resorcinol as a model substance. Electrochim. Acta 69, 268–274.

Luo, Y., Guo, W., Ngo, H.H., Nghiem, L.D., Hai, F.I., Zhang, J., Liang, S., Wang, X.C., 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Sci. Total Environ. 473-474, 619–641.

Madsen, H.T., Søgaard, E.G., Muff, J., 2015. Study of degradation intermediates formed during electrochemical oxidation of pesticide residue 2,6-dichlorobenzamide (BAM) in chloride medium at boron doped diamond (BDD) and platinum anodes. Chemosphere 120, 756–763.

Marselli, B., Garcia-Gomez, J., Michaud, P.-A., Rodrigo, M.A., Comninellis, C., 2003. Electrogeneration of Hydroxyl Radicals on Boron-Doped Diamond Electrodes. J. Electrochem. Soc. 150, D79.

Martín de Vidales, María J., Robles-Molina, J., Domínguez-Romero, J.C., Cañizares, P., Sáez, C., Molina-Díaz, A., Rodrigo, M.A., 2012. Removal of sulfamethoxazole from waters and wastewaters by conductive-diamond electrochemical oxidation. J. Chem. Technol. Biotechnol. 87, 1441–1449.

Martínez-Huitle, C.A., Brillas, E., 2008. Electrochemical Alternatives for Drinking Water Disinfection. Angew. Chem. Int. Ed. 47, 1998–2005.

Martínez-Huitle, C.A., Brillas, E., 2009. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review. Appl. Catal., B. 87, 105–145.

Martínez-Huitle, C.A., Ferro, S., 2006. Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes. Chem Soc Rev 35, 1324–1340.

Michael, I., Rizzo, L., McArdell, C.S., Manaia, C.M., Merlin, C., Schwartz, T., Dagot, C., Fatta-Kassinos, D., 2013. Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: A review. Water Res. 47, 957–995.

Michaud, P.-A., Panizza, M., Ouattara, L., Diaco, T., Foti, G., Comninellis, C., 2003. Electrochemical oxidation of water on synthetic boron-doped diamond thin film anodes. J. Appl. Electrochem. 33, 151–154.

Nakada, N., Kiri, K., Shinohara, H., Harada, A., Kuroda, K., Takizawa, S., Takada, H., 2008. Evaluation of Pharmaceuticals and Personal Care Products as Water-soluble Molecular Markers of Sewage. Environ. Sci. Technol. 42, 6347–6353.

Oaks, J.L., Gilbert, M., Virani, M.Z., Watson, R.T., Meteyer, C.U., Rideout, B.A., Shivaprasad, H.L., Ahmed, S., Iqbal Chaudhry, Muhammad Jamshed, Arshad, M., Mahmood, S., Ali, A., Ahmed Khan, A., 2004. Diclofenac residues as the cause of vulture population decline in Pakistan. Nature 427, 630–633.

Oturan, M.A., Aaron, J.-J., 2014. Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review. Crit. Rev. Env. Sci. Tec. 44, 2577–2641.

Pal, A., Gin, K.Y.-H., Lin, A.Y.-C., Reinhard, M., 2010. Impacts of emerging organic contaminants on freshwater resources: Review of recent occurrences, sources, fate and effects. Sci. Total Environ. 408, 6062–6069.

Palmas, S., Polcaro, A.M., Vacca, A., Mascia, M., Ferrara, F., 2007. Influence of the operating conditions on the electrochemical disinfection process of natural waters at BDD electrodes. J Appl Electrochem 37, 1357–1365.

Peng, X., Yu, Y., Tang, C., Tan, J., Huang, Q., Wang, Z., 2008. Occurrence of steroid estrogens, endocrine-disrupting phenols, and acid pharmaceutical residues in urban riverine water of the Pearl River Delta, South China. Sci. Total Environ. 397, 158–166.

Pereira, G.F., Rocha-Filho, R.C., Bocchi, N., Biaggio, S.R., 2012. Electrochemical degradation of bisphenol A using a flow reactor with a boron-doped diamond anode. Chem. Eng. J. 198-199, 282–288.

Pérez, G., Gómez, P., Ibañez, R., Ortiz, I., Urtiaga, A.M., 2010. Electrochemical disinfection of secondary wastewater treatment plant (WWTP) effluent. Water Sci. Technol. 62, 892.

Pills Report, 2012. Pharmaceutical residues in the aquatic system – a challenge for the future: Insights and activities of the European cooperation project PILLS. <http://www.pills-project.eu/content/136/documents/PillsBrochure-en.pdf.> (retrieved 24.02.15).

Polcaro, A.M., Vacca, A., Mascia, M., Palmas, S., Rodiguez Ruiz, J., 2009. Electrochemical treatment of waters with BDD anodes: kinetics of the reactions involving chlorides. J Appl Electrochem 39, 2083–2092.

Rajab, M., Greco, G., Heim, C., Helmreich, B., Letzel, T., 2013. Serial coupling of RP and zwitterionic hydrophilic interaction LC-MS: suspects screening of diclofenac transformation products by oxidation with a boron-doped diamond electrode. J. Sep. Sci. 36, 3011–3018.

Reis, R.M., Baio, José Augusto Fragale, Migliorini, F.L., Rocha, Robson da Silva, Baldan, M.R., Ferreira, N.G., Lanza, Marcos Roberto de Vasconcelos, 2013. Degradation of dipyrone in an electrochemical flow-by reactor using anodes of boron-doped diamond (BDD) supported on titanium. J. Electroanal. Chem. 690, 89–95.

Schmalz, V., Dittmar, T., Haaken, D., Worch, E., 2009. Electrochemical disinfection of biologically treated wastewater from small treatment systems by using boron-doped diamond (BDD) electrodes – Contribution for direct reuse of domestic wastewater. Water Res. 43, 5260–5266.

Schwarzenbach, R.P., Escher, B.I., Fenner, K., Hofstetter, T.B., Johnson, C.A., von Gunten, U., Wehrli, B., 2006. The challenge of micropollutants in aquatic systems. Science 313, 1072–1077.

Sedlak, D.L., von Gunten, U., 2011. The Chlorine Dilemma. Science 331, 42–43.

Sidrach-Cardona, R., Hijosa-Valsero, M., Marti, E., Balcázar, J.L., Becares, E., 2014. Prevalence of antibiotic-resistant fecal bacteria in a river impacted by both an antibiotic production plant and urban treated discharges. Sci. Total Environ. 488-489, 220–227.

Sirés, I., Brillas, E., 2012. Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: a review. Environ Int 40, 212–229.

Sirés, I., Brillas, E., Oturan, M.A., Rodrigo, M.A., Panizza, M., 2014. Electrochemical advanced oxidation processes: today and tomorrow. A review. Environ Sci Pollut Res Int 21, 8336–8367.

Snyder, S.A., Westerhoff, P., Yoon, Y., Sedlak, D.L., 2003. Pharmaceuticals, Personal Care Products, and Endocrine Disruptors in Water: Implications for the Water Industry. Enviro. Eng. Sci. 20, 449–469.

Soufan, M., Deborde, M., Legube, B., 2012. Aqueous chlorination of diclofenac: Kinetic study and transformation products identification. Water Res. 46, 3377–3386.

Souza, F.L., Teodoro, T.Q., Vasconcelos, V.M., Migliorini, F.L., Lima Gomes, P., Ferreira, N.G., Baldan, M.R., Haiduke, R., Lanza, M., 2014. Electrochemical oxidation of imazapyr with BDD electrode in titanium substrate. Chemosphere 117, 596–603.

Spongberg, A.L., Witter, J.D., Acuña, J., Vargas, J., Murillo, M., Umaña, G., Gómez, E., Perez, G., 2011. Reconnaissance of selected PPCP compounds in Costa Rican surface waters. Water Res.45, 6709–6717.

Strempel, S., Scheringer, M., Ng, C.A., Hungerbühler, K., 2012. Screening for PBT Chemicals among the “Existing” and “New” Chemicals of the EU. Environ. Sci. Technol. 46, 5680–5687.

Takagi, T., Ramachandran, C., Bermejo, M., Yamashita, S., Yu, L.X., Amidon, G.L., 2006. A provisional biopharmaceutical classification of the top 200 oral drug products in the United States, Great Britain, Spain, and Japan. Mol. Pharmacol. 3,631–643.

Tang, J.Y., Busetti, F., Charrois, J.W., Escher, B.I., 2014. Which chemicals drive biological effects in wastewater and recycled water? Water Res. 60, 289–299.

Ternes, T.A., 1998. Occurrence of drugs in German sewage treatment plants and rivers1Dedicated to Professor Dr. Klaus Haberer on the occasion of his 70th birthday.1. Water Res. 32, 3245–3260.

Tetreault, G.R., Bennett, C.J., Shires, K., Knight, B., Servos, M.R., McMaster, M.E., 2011. Intersex and reproductive impairment of wild fish exposed to multiple municipal wastewater discharges. Aquat. Toxicol. 104, 278–290.

Tröster, I., Fryda, M., Herrmann, D., Schäfer, L., Hänni, W., Perret, A., Blaschke, M., Kraft, A., Stadelmann, M., 2002. Electrochemical advanced oxidation process for water treatment using DiaChem® electrodes. Diamond Relat. Mater. 11, 640–645.

Tröster, I., Schäfer, L., Fryda, M., Matthée, T., 2004. Electrochemical advanced oxidation process using DiaChem® electrodes. Water Sci. Technol. 49, 207–212.

Ureña de Vivanco, M., 2013. Characterisation of a boron-doped deiamond electrode and applications for the oxidation of pharmaceutical substances and disinfection in water. Doctor Thesis (Dr. rer. nat.), Technische Universität München-Germany.

Ureña de Vivanco, M., Rajab, M., Heim, C., Letzel, T., Helmreich, B., 2013. Setup and Energetic Considerations for Three Advanced Oxidation Reactors Treating Organic Compounds. Chem. Eng. Technol. 36, 355–361.

Vedenyapina, M.D., Borisova, D.A., Rosenwinkel, K.-H., Weichgrebe, D., Stopp, P., Vedenyapin, A.A., 2013. Kinetics and mechanism of the deep electrochemical oxidation of sodium diclofenac on a boron-doped diamond electrode. Russ. J. Phys. Chem. 87, 1393–1396.

von Gunten, U., 2003. Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. Water Res. 37, 1469–1487.

von Gunten, U., Pinkernell, U., 2000. Ozonation of bromide-containing drinking waters: a delicate balance between disinfection and bromate formation. Water Sci. Technol. 41, 53–59.

Zorrilla, I., Martinez, R., Taggart, M.A., Richards, N., 2014. Suspected Flunixin Poisoning of a Wild Eurasian Griffon Vulture from Spain. Conserv. Biol. 29, 587-592.

6 List of Publications, Oral Presentations and Scientific Posters

Publications

Mohamad Rajab, Carolin Heim, Thomas Letzel, Jörg E Drewes, Brigitte Helmreich., Electrochemical oxidation of Bisphenol A by a boron-doped diamond electrode in different water matrices: Identification of transformation products and evaluation of inorganic by-products. Submitted to *Chemosphere*- February 2015

Mohamad Rajab, Carolin Heim, Thomas Letzel, Jörg E Drewes, Brigitte Helmreich., 2014 Electrochemical disinfection using boron-doped diamond electrode - The synergetic effects of *in situ* ozone and free chlorine generation *Chemosphere* 121, 47-53.

Heim, C., Urena de Vivanco, M., **Rajab, M**., Müller, E, Letzel, T, Helmreich, B., 2014 Rapid inactivation of waterborne bacteria using boron-doped diamond electrodes *International journal of Environmental Science and Technology*, DOI:10.1007/s13762-014-0722-9

Urena de Vivanco, M**., Rajab, M**., Heim, C., Letzel, T., Helmreich, B., 2013, Setup and Energetic Considerations for Three Advanced Oxidation Reactors Treating Organic Compounds, *Chemical Engineering and Technology*, 2013, 36, No. 2, 355-361

Mohamad Rajab, Giorgia Greco, Carolin Heim, Brigitte Helmreich, Thomas Letzel., 2013 Serial coupling of RP and zwitterionic hydrophilic interaction LC-MS: Suspects screening of diclofenac transformation products by oxidation with a boron-doped diamond electrode. *Journal of separation science,* 36, (18), 3011-3018

Mohamad Rajab, Carolin Heim, Giorgia Greco, Brigitte Helmreich, Thomas Letzel., 2013 Removal of Sulfamethoxazole from Wastewater Treatment Plant Effluents by a Boron-doped Diamond Electrode *International Journal of Environmental Pollution and Solutions*, 1,88-97.

Heim, C., Urena de Vivanco, M., **Rajab**, **M**., Glas, K., Horn, H., Helmreich, B., Letzel, T., 2011, Ozone II: Characterization of In Situ Ozone Generation Using Diamond Electrodes. *Brewing Science*, 64, 83-88.

Oral Presentations

Rajab, M., Heim, C., Letzel, T., Drewes, J.E., Helmreich, B., 2014, Electrochemical disinfection combined with micropollutant degradation using a boron-doped diamond (BDD) electrode. *EcoTechnologies for Wastewater Treatment (ecoSTP2014),*Verona-Italy

Rajab, M., Urena de Vivanco, M., Heim, C., Letzel, T., Helmreich, B., 2011, The Applicability of a Boron-Doped Diamond Electrode for Water Disinfection-Short presentation-, *6th IWA Specialist Conference: Oxidation Technologies for Water and Wastewater Treatment* Goslar-Germany.

Scientific Poster

Rajab, M., Greco, G., Heim, C., Helmreich, B., Letzel, T., 2013, Removal of Diclofenac from secondary effluent of sewage treatment plant using a boron-doped diamond (BDD) electrode.*: 6th Late Summer Workshop "Micropollutants in the water cycle",* Schloss Maurach-Lake Constance-Germany

Urena de Vivanco, M**.**, **Rajab, M**, Heim, C., Helmreich, B., Letzel, T., 2013, Degradation Pathways of organic compounds as a Tool for the Characterisation of Advanced oxidation Processes, *ANAKON-Tagung*, Essen-Germany

Heim, C., Ureña de Vivanco, M., **Rajab, M**., Helmreich, B., Glas, K., Letzel, T., Horn, H., Parlar, H., 2011, Desinfektion von Wasser und Abwasser unter Einsatz einer Diamantelektrode. *5te*. *Wasserseminar für die Getränke- und Lebensmittelindustrie: H2O - Quell radikaler Desinfektionstechnologien und ökologischer Strategien*. Waidring /Tirol, Österreich,

Rajab, M., Urena de Vivanco, M., Heim, C., Letzel, T., Helmreich, B., 2011, The Applicability of a Boron-Doped Diamond Electrode for Water Disinfection, *6th IWA Specialist Conference: Oxidation Technologies for Water and Wastewater Treatment* Goslar-Germany.

Rajab, M., Urena de Vivanco, M., Heim, C., Letzel, T., Helmreich, B., 2011, Electrochemical degradation of the emerging contaminant sulfamethoxazole in secondary effluent using a boron doped diamond electrode, *8th IWA Specialized Conference on Assessment and control of micropollutants and Hazardous substances in water –Micropol & Ecohazard 2013*- Zurich-Switzerland.