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**Electrochemical Oxidation of Recalcitrant Organic Compounds using  
Electro-Generated Sulfate-based Oxidizing Agents**

Ali Farhat

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Bachelor of Science in Chemistry

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*School of Chemical Engineering  
Advanced Water Management Centre (AWMC)*

## Abstract

Sulfate ions have often been used as background electrolytes in electrochemical degradation of contaminants, and have generally been considered inert even when employing high oxidation power anodes such as boron-doped diamond. Boron-doped diamond (BDD) anodes are widely used in literature for investigating electrochemical oxidation of contaminants due to their excellent capability to form hydroxyl radicals as well as inorganic radicals such as chlorine, phosphate, and sulfate radicals, electro-generated when their corresponding anions are present in the influent water. This study examined the role of sulfate ions and the potential electro-generation of sulfate-based oxidants by comparing electro-oxidation rates for persistent organic contaminants at BDD anodes in the presence of sulfate or nitrate anolytes (considered as inert). The effect of the operating conditions governing this process such as anolyte concentration / conductivity, applied current density, as well as solution volume were explored in this work. The characteristics and the reactive life-time of these electro-chemically generated sulfate-based oxidizing agents were further explored by studying the oxidation extent occurring after the electric current has been switched off or via different modes of intermittent electric current as an option to improve energy efficiency. The effect of chloride ions on the sulfate-based electrooxidation processes for the removal of a natural organic matter surrogate, resorcinol, was also addressed in this work because the anodic oxidation of chloride yields oxidizing species such as chlorine / hypochlorous acid as well as chlorine/chloride radicals, and may compete with sulfate-based oxidizing species, leading to the formation of toxic organic and inorganic chlorinated compounds at higher applied potentials.

The detailed investigations showed that sulfate yielded 10 – 15 times higher electrooxidation rates of all target contaminants compared to the rates achieved with a nitrate anolyte at identical conductivities. The presence of specific radical quenchers (*tert*-butanol, methanol) reported a similar effect on diatrizoate electrooxidation rates, illustrating that hydroxyl radicals ( $\cdot\text{OH}$ ) are most likely influencing the potential anodic formation of sulfate-based oxidizing species. Thus, these results indicate the formation of strong sulfate-derived oxidant species at BDD anodes, where the energy consumption required for a 10-fold removal of diatrizoate was reduced from 45.6 to 2.44 kWh m<sup>-3</sup> by switching from nitrate to sulfate anolyte. This electrochemical activation of sulfate was also observed at low concentrations, relevant for many wastewaters, where even only 1.56 mM sulfate anolyte solution (3.5 mS cm<sup>-1</sup> and 100 A m<sup>-2</sup>) achieved a higher removal rate than 60 mM nitrate with correspondingly higher conductivity (9.0 mS cm<sup>-1</sup>) and operated at double the current density (200 A m<sup>-2</sup>). Chloride addition to Na<sub>2</sub>SO<sub>4</sub> inhibited the resorcinol oxidation and mineralization, unlike its addition to NaNO<sub>3</sub> where it enhanced the oxidation of resorcinol. This inhibitive effect of chloride on sulfate was observed to further decrease the removal rate constants of resorcinol oxidation and mineralization with increasing the chloride concentration from 5 to

40 mM. However, the presence of sulfate is reported to inhibit the electrogeneration of chlorinated organics by ~2 – 4 folds compared to nitrate, especially at low chloride concentrations (i.e.,  $[\text{SO}_4^{2-}]:[\text{Cl}^-]>1$ ). Although increasing the pH from 2 to 7 reduced the amount of chlorinated organics formed by about half, the sulfate-based electrolysis increased the generation of undesired chlorate and perchlorate at both acidic and neutral pH.

Overall findings indicate the formation of strong sulfate-derived oxidant species at BDD anodes when polarized at high potentials, even when operating at low sulfate concentrations such as  $150 \text{ mg L}^{-1}$ , detected in natural water systems. This may have positive implications in electrooxidation of wastewaters containing sulfate because of the substantial energy savings that such systems could achieve, not only attributed to the formation of much stronger oxidants but also due to their extended reactive life-time.

## **Declaration by author**

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

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## Publications during candidature

### Journal Publications

- Farhat, A., Tait, S., Keller, J., Radjenovic, J. (2015). Removal of Persistent Organic Contaminants by Electrochemically Activated Sulfate. *Environ. Sci. Technol.*, 2015, 49 (24), pp 14326–14333. DOI: 10.1021/acs.est.5b02705.

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Contributor	Statement of contribution
Ali Farhat (Candidate)	Designed experiments and Data Analysis (60%) Wrote the paper (60%)
Jelena Radjenovic	Designed experiments and Data Analysis (30%) Wrote and edited paper (30%)
Stephan Tait	Wrote and edited paper (10%) Assisted with Statistical Analysis of Data
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## **Statement of parts of the thesis submitted to qualify for the award of another degree**

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## Table of Contents

Abstract.....	2
Declaration by author .....	4
Publications during candidature .....	5
Journal Publications .....	5
Conference Presentations and Posters .....	5
Publications included in this thesis .....	6
Contributions by others to the thesis .....	6
Statement of parts of the thesis submitted to qualify for the award of another degree .....	6
Acknowledgements .....	7
Keywords.....	8
Australian and New Zealand Standard Research Classifications (ANZSRC) .....	8
Fields of Research (FoR) Classification.....	8
Table of Contents .....	9
List of Tables .....	12
List of Figures.....	14
List of Abbreviations.....	16
1. Chapter 1: Introduction .....	17
1.1. Background .....	17
1.2. Research Motivation.....	19
1.3. Research Objectives .....	20
2. Chapter 2: Literature Review .....	22
2.1 Occurrence of Trace Organic Contaminants in the Environment .....	22
2.2 Advanced Oxidation Processes (AOPs) for Removal of Organic Compounds .....	25
2.2.1 Hydroxyl Radicals-based Advanced Oxidation Processes .....	26
2.2.2 Sulfate Radicals-based Advanced Oxidation Processes .....	27
2.3 Electrochemical processes for wastewater treatment .....	32
2.3.1 Mechanisms of electrochemical oxidation and importance of electrode material .....	33
2.4 Electrochemical Formation of Persulfate .....	37
2.5 Concluding Summary and Thesis Objectives .....	39
3. Chapter 3: Major Research Methodology .....	42
3.1 Reactor Design and Specifications .....	43
3.2 Chemicals and Reagents.....	45
3.3 Chemical Analysis.....	45

3.3.1	Liquid Chromatography - Mass Spectrometry .....	45
3.3.2	High Performance Liquid Chromatography .....	48
3.3.3	Ion Chromatography .....	49
3.3.4	Adsorbable Organic Chlorides (AOCl) .....	49
3.3.5	Hydrogen Peroxide and Persulfate Quantification .....	49
3.4	Sampling Procedure and Data Analysis .....	52
3.5	Energy Consumption .....	53
4.	Chapter 4: Role of Sulfate Electrolyte in Electrochemical Oxidation of Recalcitrant Organics at Boron-doped Diamond Anodes .....	54
4.1	Introduction .....	55
4.2	Materials and Methods .....	56
4.2.1	Experimental Setup .....	56
4.2.2	Chemical Analysis .....	57
4.3	Results and Discussion .....	58
4.3.1	Effect of anolyte on electrooxidation rates of persistent organic contaminants .....	58
4.3.2	Persulfate electro-generation and potential role in the electrooxidation .....	61
4.3.3	Potential role of electro-generated $\text{SO}_4^{\cdot-}$ in the electrooxidation of diatrizoate .....	64
4.3.4	Effect of specific radical quenchers on electrooxidation of diatrizoate .....	67
4.3.5	Electrooxidation of nitrobenzene in $\text{Na}_2\text{SO}_4$ anolyte .....	69
4.3.6	Energy Consumption .....	70
4.4	Concluding Remarks .....	71
5.	Chapter 5: Effect of Operating Parameters on the Electrooxidation Rates of Diatrizoate ..	72
5.1	Introduction .....	73
5.2	Materials and Methods .....	74
5.3	Results and Discussion .....	75
5.3.1	Effect of anolyte concentration and conductivity on diatrizoate electrooxidation .....	75
5.3.2	Effect of applied current density on electrooxidation rates of diatrizoate .....	78
5.3.3	Effect of combined low sulfate concentration and current on diatrizoate removal .....	80
5.3.4	Effect of anolyte volume on diatrizoate removal rates .....	80
5.4	Concluding Remarks .....	82
6.	Chapter 6: Long-life Oxidizing Species in Sulfate-based Electrochemical Systems .....	84
6.1	Introduction .....	85
6.2	Materials and Methods .....	86
6.2.1	Delayed Quenching Experiments .....	86
6.2.2	Pulse Electric Current Experiments .....	87

6.2.3 Off-line Diatrizoate Oxidation Experiments .....	87
6.3 Results .....	89
6.3.1 Effect of Delayed Quenching on Oxidation of Diatrizoate .....	90
6.3.2 Effect of the Pulse Electric Current Modes on Diatrizoate Oxidation .....	93
6.3.3 Effect of Off-line Diatrizoate Oxidation by pre-Oxidized Sulfate Anolyte .....	94
6.4 Discussion .....	95
6.4.1 Possible Mechanisms of the Formation of Long-life Sulfate-based Oxidants .....	95
6.4.2 Energy Savings Induced by the Sulfate-based Oxidants .....	96
6.5 Concluding Remarks .....	97
7. Chapter 7: Impact of Chloride on Resorcinol Oxidation by Electro-Activated Sulfate .....	98
7.1 Introduction .....	99
7.2 Materials and Methods .....	100
7.2.1 Experimental Setup.....	100
7.2.2 Chemical Analysis .....	101
7.3 Results and Discussion.....	101
7.3.1 Effect of chloride addition on the electrooxidation of resorcinol.....	101
7.3.2 Effect of chloride addition on TOC removal.....	103
7.3.3 Effect of chloride addition on the formation of chlorinated organics .....	104
7.3.4 Effect of chloride addition on the formation of chlorate and perchlorate .....	105
7.3.5 Effect of sulfate addition on chloride-based electrooxidation of resorcinol .....	109
7.3.6 Impact of chloride on the electrooxidation of resorcinol at neutral pH.....	110
7.4 Concluding Remarks .....	111
8. Chapter 8: Conclusions and Implications .....	112
Bibliography of References .....	122

## List of Tables

Table 2.1 The major characteristics and drawback of electrochemical advanced oxidation processes (EAOPs) (Jüttner <i>et al.</i> 2000, Anglada <i>et al.</i> 2009, Sirés and Brillas 2012) .....	33
Table 2.2 The oxidation potential (V vs SHE) for oxygen evolution of different electrode materials in acidic media, as well as their trend of the adsorption type and anodic oxidation power (Chen 2004, Comninellis <i>et al.</i> 2008, Anglada <i>et al.</i> 2009, Comninellis and Chen 2010). .....	35
Table 3.1 The recalcitrant organic compounds investigated in this study along with their molar masses, octanol-water partitioning coefficient (log Kow), pK <sub>a</sub> , and chemical structure. (The values are reported from the EPI-Suite v4.11 software).....	46
Table 3.2 Conditions of liquid chromatography (LC) separation method with the details of the employed gradient .....	47
Table 3.3 The optimized compound-dependent mass spectrometry (MS) parameters: declustering potential (DP), collision energy (CE) and cell exit potential (CXP) for each compound and each transition of the negative and positive mode .....	48
Table 4.1 Apparent rate constants (h <sup>-1</sup> ) for oxidation of target organic contaminants in Na <sub>2</sub> SO <sub>4</sub> and NaNO <sub>3</sub> anolytes (pH 2; 9.0 mS cm <sup>-1</sup> ; and 200 A m <sup>-2</sup> ). .....	60
Table 4.2 Apparent rate constants (h <sup>-1</sup> ) for chemical oxidation of the seven target organic contaminants with non-activated K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> or H <sub>2</sub> O <sub>2</sub> prepared in Na <sub>2</sub> SO <sub>4</sub> solutions (pH 2, 9.0 mS cm <sup>-1</sup> , 40 mM) in the absence of any applied electric current.....	63
Table 4.3 Bimolecular rate constants ( <i>k</i> , M <sup>-1</sup> s <sup>-1</sup> ) for oxidation of target organic contaminants with homogeneously generated <sup>•</sup> OH and SO <sub>4</sub> <sup>•-</sup> radicals. ....	66
Table 4.4 Electric energy consumption per order (E <sub>E0</sub> ), expressed as electric energy, kWh m <sup>-3</sup> , to reduce the concentration of the organic contaminant via electrooxidation in Na <sub>2</sub> SO <sub>4</sub> and NaNO <sub>3</sub> anolytes (pH 2; 9.0 mS cm <sup>-1</sup> ; and 200 A m <sup>-2</sup> ) by one order of magnitude in a unit volume of treated solution.....	70
Table 5.1 Apparent rate constants ( <i>k</i> , h <sup>-1</sup> ) for oxidation of diatrizoate at different anolyte concentrations of NaNO <sub>3</sub> and Na <sub>2</sub> SO <sub>4</sub> prepared at similar conductivity values (pH 2; 500 mL anolyte volume; and 200 A m <sup>-2</sup> ) .....	76
Table 6.1 Removal percentages (%) of electrochemical oxidation of 10 μM diatrizoate in 1.56 mM anolyte, comparing the three anolytes (nitrate, persulfate, and sulfate) prepared as 500 mL with pH 2, and 4.75 ± 0.3 mS cm <sup>-1</sup> and operated with an electric current density of 100 A m <sup>-2</sup> .....	91
Table 6.2 Electric energy consumption per order (E <sub>E0</sub> ), expressed as electric energy, kWh m <sup>-3</sup> , to decrease the diatrizoate concentration in Na <sub>2</sub> SO <sub>4</sub> by one order of magnitude in a unit volume of treated solution for the different current application scenarios .....	96

Table 7.1 Apparent first-order rate constants ( $\pm$ error at 95% confidence level) for electrooxidation of resorcinol ( $k_{RES}$ , $h^{-1}$ ) in $Na_2SO_4$ and $NaNO_3$ anolytes at pH 2 and 9 $mS\ cm^{-1}$ in the presence of 0 – 40 mM NaCl.....	102
Table 7.2 Apparent rate constants ( $\pm$ error at 95% confidence level) for the TOC removal ( $k_{TOC}$ , $h^{-1}$ ) in the electrooxidation of resorcinol in $Na_2SO_4$ and $NaNO_3$ anolytes at pH 2 and 9 $mS\ cm^{-1}$ in the presence of 0 – 40 mM NaCl.....	104
Table 7.3 Estimated ionic mobility ( $u_i$ ) of $Cl^-$ , $NO_3^-$ , $SO_4^{2-}$ , and $HSO_4^-$ ions in dilute solution using the Nernst–Einstein relationship.....	108
Table 7.4 Apparent rate constants ( $h^{-1}$ ) of chloride oxidation in $Na_2SO_4$ versus $NaNO_3$ anolyte, and in the presence of 5, 10, 20, and 40 mM NaCl at pH 2, except where mentioned pH 7 (10 mM NaCl).....	108
Table 7.5 Reaction rate constants ( $h^{-1}$ ) for the removal of TOC and resorcinol, along with the formation of AOCl ( $mgCl\ L^{-1}$ ), at different sulfate concentrations (0, 5, 10, and 20 mM) (pH 2; 200 $A\ m^{-2}$ ; and 10mM $Cl^-$ ).....	109
Table 7.6 Apparent rate constants ( $h^{-1}$ ) for TOC and resorcinol removal ( $\pm$ error at 95% confidence level), in $Na_2SO_4$ and $NaNO_3$ anolytes at pH 7 and 9 $mS\ cm^{-1}$ in the presence of 10 mM NaCl as well as the formed concentrations of AOCl, $ClO_3^-$ , and $ClO_4^-$ (in $mgCl\ L^{-1}$ ), measured after 2.4 $Ah\ L^{-1}$ of supplied specific electrical charge in the resorcinol electrooxidation .....	110

## List of Figures

Figure 2.1 The different pathways of electrochemical oxidation in active and non-active electrodes in the anodic compartment, as well as the oxygen evolution side reactions and the poisoning effect (fouling) on the anode surface. ....	37
Figure 3.1 Schematic diagram of the utilized reactor with its two-compartment electrochemical system, using stainless steel as the cathode and boron doped diamond as the anode .....	44
Figure 3.2: Absorbance measured at 460 nm using the metavanadate method for 1 – 60 mM solution of hydrogen peroxide in the absence of any persulfate .....	50
Figure 3.3 Absorbance measured at 460 nm using the metavanadate method for 1 – 60 mM solution of persulfate in the presence of 0.6 mM hydrogen peroxide .....	51
Figure 3.4 Absorbance measured at 460 nm using the ferrous/thiocyanate method for 1 – 60 mM solutions of hydrogen peroxide (◆) or persulfate (▲).....	51
Figure 3.5 Absorbance measured at 460 nm using the ferrous/thiocyanate method for 0.6 mM solution of hydrogen peroxide with the addition of 1 – 60 mM persulfate concentrations.....	52
Figure 4.1 Disappearance of diatrizoate in electrooxidation in NaNO <sub>3</sub> (▲), NaClO <sub>4</sub> (◆), and Na <sub>2</sub> SO <sub>4</sub> (●) analytes of same initial pH and conductivity (pH 2, 9.0 mS cm <sup>-1</sup> ), at 200 A m <sup>-2</sup> of applied current density .....	58
Figure 4.2 Electrochemical generation of the oxidants: persulfate ions (●) and hydrogen peroxide (◆) in electrooxidation in Na <sub>2</sub> SO <sub>4</sub> anolyte (40 mM, pH 2, 9.0 mS cm <sup>-1</sup> ) at 200 A m <sup>-2</sup> .....	62
Figure 4.3 Disappearance of diatrizoate during electrooxidation in Na <sub>2</sub> SO <sub>4</sub> anolyte (40 mM, pH 2, 9.0 mS cm <sup>-1</sup> ) in the presence of 100 μM methanol (◆) or t-butanol (◇), with an applied current density of 200 A m <sup>-2</sup> .....	68
Figure 4.4 Disappearance of nitrobenzene during electrochemical oxidation in 60 mM NaNO <sub>3</sub> (◆) and 40 mM Na <sub>2</sub> SO <sub>4</sub> (●) analytes at similar operating parameters (pH 2, 9.0 mS cm <sup>-1</sup> , and 200 A m <sup>-2</sup> ).....	69
Figure 5.1 The apparent electrooxidation rate constants (h <sup>-1</sup> ) of diatrizoate in 60 mM NaNO <sub>3</sub> and 40 mM Na <sub>2</sub> SO <sub>4</sub> anolyte at different applied anodic current densities (pH 2; 9.0 mS cm <sup>-1</sup> ; 500 mL anolyte volume) .....	78

Figure 5.2 The apparent electrooxidation rate constants ( $h^{-1}$ ) of diatrizoate in sulfate at different solution volumes of 0.25, 0.5 1.0 and 2.0 L (pH 2; 9.0 $mS\ cm^{-1}$ ; and 200 $A\ m^{-2}$ ) .....	81
Figure 6.1 The procedure for the different modes of intermittent electric current application tested with the electro-chemical oxidation of diatrizoate, where the electric current was applied intermittently every $x$ min and stopped for $y$ min in a cyclic pattern. Sampling points are marked with dotted arrows .....	88
Figure 6.2 The procedure for the off-line oxidation of diatrizoate by pre-oxidized sulfate anolyte (0.5 L; pH 2; and 4.5 $mS\ cm^{-1}$ ). Sampling points are marked with dotted arrows. ....	89
Figure 6.3 The additional removal (%) of the delayed quenching during the sulfate-based electrochemical oxidation of carbamazepine in three samples (t-1, t-2, and t-3), as a function of resting time (min) in order to explore the extent of prolonged oxidation (40 $mM\ SO_4^{2-}$ ; pH 2; and 9.0 $mS\ cm^{-1}$ ; 200 $A\ m^{-2}$ ; and 0.5 L).....	90
Figure 6.4 Diatrizoate removal (%) during the electrochemical oxidation and the delayed quenching, in nitrate (top), persulfate (middle), and sulfate (bottom) anolyte. The grey fraction signifies the removal % in instant-quench samples and the white fraction signifies the removal % of diatrizoate in delayed-quench samples. The error bars represent the standard deviations of duplicate measurements.....	92
Figure 6.5 Diatrizoate removal (%) during the sulfate-based electrochemical oxidation using different intermittent electric current modes. The grey fraction signifies the removal % during applying the electric current, and the white fraction signifies the additional removal occurring during the resting time when the current is stopped .....	94
Figure 7.1 Formation of adsorbable organic chlorine (AOCl, in $mgCl^{-1}\ L^{-1}$ ), after 2.4 $Ah\ L^{-1}$ of specific electrical charge supplied in the electrooxidation of resorcinol in $Na_2SO_4$ and $NaNO_3$ anolytes (pH 2 and 9 $mS\ cm^{-1}$ ) in the presence of 5 – 40 $mM\ NaCl$ .....	105
Figure 7.2 Concentrations of chlorate (A) and perchlorate (B) (in $mgCl^{-1}\ L^{-1}$ ), after 2.4 $Ah\ L^{-1}$ of specific electrical charge supplied in the electrooxidation of resorcinol in $Na_2SO_4$ and $NaNO_3$ anolytes (pH 2 and 9 $mS\ cm^{-1}$ ) in the presence of 5 – 40 $mM\ NaCl$ .....	106

## List of Abbreviations

AOPs	Advanced Oxidation Processes
EAOPs	Electrochemical Advanced Oxidation Processes
CEM	Cation exchange membrane
SHE	Standard Hydrogen Electrode
BDD	Boron Doped Diamond
UV	Ultraviolet radiation
ICM	Iodinated Contrast Media
NOM	Natural Organic Matter
$\cdot\text{OH}$	Hydroxyl radicals
Fe	Iron
$\text{H}_2\text{O}_2$	Hydrogen peroxide
$\text{O}_2\cdot^-$	Superoxide radical
$\text{O}_3$	Ozone
PS,	Peroxydisulfate ( $\text{S}_2\text{O}_8^{2-}$ )
PMS	Peroxymonosulfate
Pt	Platinum
$\text{SO}_4\cdot^-$	Sulfate radical
$\text{NO}_3^-$	Nitrate ion
$\text{SO}_4^{2-}$	Sulfate ion
$\text{Cl}^-$	Chloride ion
$\text{ClO}_3^-$	Chlorate ion
$\text{ClO}_4^-$	Perchlorate ion
$\text{S}_2\text{O}_8^{2-}$	Persulfate ion
CBZ	Carbamazepine
DEET	Diethyl-meta-toluamide
DTR	Diatrizoate Dihydrate
IPM	Iopromide
TBP	Tribromophenol
TCN	Triclosan
TCP	Triclorpyr



## Chapter 1: Introduction

### 1.1. Background

Water is the most precious resource for the living beings' survival, but the availability of fresh water for prompt use is very scarce, and the water contamination is becoming an international concern, threatening the quality of life for all living beings (Brillas *et al.* 2009). Water contamination has been largely attributed to the leaching of natural organic matter, metals, and salts into surface and ground waters, yet the discharge of the synthetic organic matter into the water bodies is considered a major contributor to water contamination (Snyder *et al.* 2003). Such organic contaminants include endocrine-disrupting compounds, pharmaceuticals and personal care products (PPCPs), pesticides and herbicides, as well as other industrial chemicals such as phenolic compounds, anilines, and other benzenic and hetero-aromatic derivatives. These organic contaminants are being extensively released into natural water and wastewater channels, raising a pervasive concern amongst the health regulatory groups and the public, even at low concentration (trace) levels (Ternes 1998, Christian G. Daughton 2001, Kümmerer 2001, Gerecke *et al.* 2002, Kolpin *et al.* 2002, Ternes *et al.* 2002, Snyder *et al.* 2003, Carballa *et al.* 2004, Daughton 2004, Westerhoff *et al.* 2005, Khetan and Collins 2007, Kümmerer 2009, Stephen *et al.* 2011). The main sources of these contaminants are anthropogenic activities, such as industrial (European-Commission 1996, Real *et al.* 2009), agricultural (Hirsch *et al.* 1999, Chiron *et al.* 2000), hospital (Gartiser *et al.* 1996, Pauwels and Verstraete 2006), and household use (Ternes and Hirsch 2000, Barceló 2003, Kümmerer 2004).

Some of these chemical contaminants are biodegradable, hence they are substantially removed in dedicated wastewater treatment facilities (where existing) and in natural water bodies and soils by microbial and enzymatic degradation. Some are also decomposed chemically without microbial influence. Yet, a significant number of these contaminants are resistant to microbial attacks and highly stable to sunlight irradiation. These persistent contaminants have been discovered at low concentrations of typically micrograms per liter all around the world in both natural systems such as lakes (Bevans 1996, Boulanger *et al.* 2005), streams (Kolpin *et al.* 2002), rivers (Schmidt *et al.* 2003), groundwater (Sacher *et al.* 2001), as well as seawater (Weigel *et al.* 2002), and engineered systems such as treated drinking water (Seitz *et al.* 2006), and treated sewage effluents (Nasu *et al.* 2001). This ubiquitousness of trace organic contaminants triggered a great scientific, regulatory, and public

concern for the removal of trace organic contaminants from the aquatic environment, due to their potential carcinogenic, mutagenic, toxic, and bactericidal characteristics, causing potential perilous health effects on human beings.

Numerous water treatment technologies have aimed to reduce the accumulation of these pollutants in the aquatic environment, but reported incomplete, inefficient, or unfavoured transformation of the trace organic contaminants (Stephen *et al.* 2011). Conventional chemical, biological, and physical treatment technologies are incapable of efficiently degrading these persistent organic contaminants (Marrot *et al.* 2006). Therefore, developing simple, safe, efficient, and cost-effective technologies for trace contaminants removal is still considered a major current need and interest for researchers in the field.

Advanced oxidation processes (AOPs) have attracted wide attention due to their *in-situ* generation of highly reactive radicals, principally hydroxyl radicals ( $\cdot\text{OH}$ ), capable of oxidizing organic compounds in water treatment processes (Glaze *et al.* 1987, Brillas *et al.* 2009, Matilainen and Sillanpää 2010). Besides  $\cdot\text{OH}$ -based processes, other AOPs employing persulfate or peroxymonosulfate can generate sulfate radicals ( $\text{SO}_4^{\cdot-}$ ), which are also strong oxidants with a redox potential  $E^\circ(\text{SO}_4^{\cdot-}/\text{SO}_4^{2-}) = 2.5\text{--}3.1$  V vs Standard Hydrogen Electrode (SHE), (Neta *et al.* 1988, Zhang *et al.* 2014) similar to the redox potential of hydroxyl radicals at acidic pH,  $E^\circ(\cdot\text{OH}/\text{H}_2\text{O}) = 2.4\text{--}2.8$  V, (Buxton *et al.* 1988, Wardman 1989). Both radicals have been reported to react with many pharmaceuticals at comparable oxidation rates (Neta *et al.* 1977, Buxton *et al.* 1988, Rickman and Mezyk 2010, Matta *et al.* 2011). Nonetheless, the major drawbacks of AOPs can be attributed to the large amounts of chemicals needed to perform the oxidation, as well as the high energy costs required for UV irradiation and ozone generation (Malato *et al.* 2009).

The electrochemical advanced oxidation processes (EAOPs) such as anodic oxidation (AO), have shown great capabilities in mimicking the performance of traditional AOPs and even surpassing them in water treatment (Chen 2004, Anglada *et al.* 2009, Brillas *et al.* 2009, Kapalka *et al.* 2010). The anodic oxidation is defined as a process in which an electric current is supplied to the electrochemical reactor to trigger chemical reactions that generate *in-situ* reactive species (e.g.,  $\cdot\text{OH}$  and superoxide radicals) on the anode, capable of driving oxidation reactions (Zhao and Li 2006, Garrido *et al.* 2007, Ahad and Slater 2008, Tsitonaki *et al.* 2010). The ability of these electrochemical processes to generate *in-situ* oxidizing species such as  $\cdot\text{OH}$  radicals from the feed water without the specific addition of chemicals, promotes these processes over chemical AOPs in the water treatment fields such as pharmaceuticals removal (Garrido *et al.* 2007), decontamination of dyes (Costa *et al.* 2009)

as well as phenol destruction (Iniesta *et al.* 2001, Wang *et al.* 2009). Non-active anode materials such as boron-doped diamond (BDD) anodes are reported to possess high electrocatalytic activity towards oxidation due to their high oxygen evolution overpotential, rendering them capable of generating weakly adsorbed  $\cdot\text{OH}$  radicals (Comninellis 1994, Chen *et al.* 2003). Besides  $\cdot\text{OH}$ , these powerful BDD anodes can also produce peroxy species such as ozone and hydrogen peroxide as well as percarbonate, perphosphate and persulfate in the presence of their corresponding ions (Cañizares *et al.* 2009, Panizza and Cerisola 2009, Meas *et al.* 2011). However, despite the extensive work published on electrochemical generation of  $\cdot\text{OH}$  radicals and their strong oxidation power in mineralizing organic contaminants in EAOPs, there is very little work conducted on the potential electrochemical contribution of these peroxy species or their intermediate species such as  $\text{SO}_4^{\cdot-}$  radicals to the oxidation of the organic contaminants in these processes.

## 1.2. Research Motivation

Although persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) formation at BDD anode is reported to occur via oxidation of sulfate ions to  $\text{SO}_4^{\cdot-}$  and recombination of two  $\text{SO}_4^{\cdot-}$  to yield persulfate (Serrano *et al.* 2002, Cañizares *et al.* 2009, Davis *et al.* 2014), sulfate electrolytes have been generally considered inert and the BDD electrooxidation mechanisms in the presence of sulfate ions have typically been interpreted by the action of  $\cdot\text{OH}$  not  $\text{SO}_4^{\cdot-}$  (Brillas *et al.* 2009, Panizza and Cerisola 2009, Sirés *et al.* 2014). To date, there is no spectroscopic evidence of the electrochemically formed  $\cdot\text{OH}$ ,  $\text{SO}_4^{\cdot-}$ , or other inorganic radicals generated at a BDD anode (Marselli *et al.* 2003, Bejan *et al.* 2012), but a limited number of studies have suggested that inorganic radicals generated at the anode (e.g.,  $\text{PO}_4^{\cdot-}$ ,  $\text{SO}_4^{\cdot-}$ ,  $\text{Cl}_2^{\cdot-}$ ) may be contributing to a minor additional electrooxidation of organic contaminants (Costa *et al.* 2009, Park *et al.* 2009, Bagastyo *et al.* 2013).

Taking into consideration that  $\text{S}_2\text{O}_8^{2-}$  is viewed to have slow oxidation kinetics with organic compounds in the absence of an activator, electrogenerated  $\text{S}_2\text{O}_8^{2-}$  is expected to potentially contribute only to a minor extent to the bulk oxidation. However,  $\text{SO}_4^{\cdot-}$  radicals, produced as intermediates in the persulfate electrogeneration, are strong oxidants that have shown substantial capabilities in oxidizing persistent organic contaminants. Thus, the electrolysis of sulfate ions to sulfate radical species ( $\text{HSO}_4^{\cdot}$ ,  $\text{SO}_4^{\cdot-}$ ) may have a significant effect on the oxidation kinetics and degradation pathways of contaminants in electrochemical treatment of wastewater. Given that sulfate ions can be present in municipal and industrial wastewater at significant concentrations of several hundred milligrams up to grams per liter level (United-Nations-Environment-Programme 1990,

Tchobanoglous *et al.* 2002, Sgroi *et al.* 2014), it is important to elucidate the role of sulfate ions in electrooxidation processes employing non-active electrodes such as BDD.

Therefore, the objective of this study was to investigate the role of sulfate ions in the electrochemical oxidation of contaminants at BDD anodes by (i) elucidating the potential participation of electrogenerated sulfate-based oxidizing species in electrochemical oxidation of persistent organic contaminants such as pharmaceuticals and pesticides, while (ii) exploring the effect of operating conditions governing the process such as anolyte concentration and volume as well as applied current, and (iii) studying the impact of the presence of the chloride ions on these sulfate-based EAOPs, especially on the formation of organic and inorganic chlorinated by-products.

### 1.3. Research Objectives

This PhD project aimed to investigate the role of the ubiquitous sulfate ions in the higher electrooxidation rates of persistent organics observed in electrochemical treatment of contaminated water at BDD anodes. In this objective, the target was to elucidate the potential participation of electrogenerated sulfate radical species in electrooxidation of persistent organic contaminants, by comparing different anolyte types as well as testing several persistent organic compounds. Probe compounds were also investigated to provide further evidence for the electro-formation of sulfate-based oxidizing agents.

The project also studied the influence of the operating conditions governing these sulfate-enhanced electrochemical oxidation systems. The removal rates of a model compound, diatrizoate, were explored at different operating conditions such as the concentration/conductivity of the anolyte as well as the anodic current density and the volume of the anolyte solutions. The characteristics of these oxidants and their potential extended reactive life-time was also explored in this work, by applying intermittent electric current as an option to achieve energy savings.

Finally, the effect of the presence of chloride ions was also examined, in sulfate and nitrate-based anolyte systems for the electrochemical treatment of resorcinol as a surrogate compound of natural organic matter (NOM). The potential inhibition effect exerted by chloride on sulfate-based removal and mineralization of resorcinol was examined. The effect of sulfate presence on the formation of organic chlorinated compounds as well as the inorganic chlorate and perchlorate by-products were also studied.

Therefore, the main research objectives of the thesis are to:

- I. Investigate the role of sulfate ions in the degradation of persistent organics in electrochemical oxidation at a BDD anode. (Chapter 4)
- II. Investigate the effect of the operating parameters of the sulfate-based electrooxidation processes using BDD anodes. (Chapter 5)
- III. Explore the prolonged oxidation of persistent organics via long-life oxidants produced in the sulfate-based electrochemical systems at BDD anode. (Chapter 6)
- IV. Assess the effect of the presence of chloride ions on the performance of sulfate-based electrochemical systems. (Chapter 7)

## Chapter 2: Literature Review

### 2.1 Occurrence of Trace Organic Contaminants in the Environment

Surface and groundwater bodies, as well as wastewaters discharged by households and hospitals, are reported to contain substantial amounts of persistent chemicals and microbial agents such as herbicides, fire retardants, X-ray contrast agents, disinfectants, antibiotics, and pharmaceuticals (Kümmerer 2001). Low efficiencies in the removal of these trace organic compounds have been reported in the major water and wastewater treatment technologies such as coagulation/flocculation, activated sludge and membrane bioreactors (MBRs), despite their promising capabilities in producing high quality effluents (Tadkaew *et al.* 2011). These organic compounds are inefficiently removed due to their high resistance and have been detected in most effluents of wastewater treatment plants (Pauwels and Verstraete 2006).

Some major persistent trace organic compounds include pesticides and herbicides such as atrazine, 2, 4-dichlorophenoxyacetic acid (2, 4-D), dichlorprop, metolachlor, triclopyr, and the insect repellent N,N-Diethyl-meta-toluamide (DEET) (Brillas *et al.* 2000, Anipsitakis and Dionysiou 2003, Bandala *et al.* 2007, Borràs *et al.* 2010, Tay *et al.* 2013). Other persistent trace organic compounds are pharmaceutically active compounds such as carbamazepine, chloramphenicol, phenytoin, hydrochlorothiazide, triclosan, diclofenac, and sulfamethoxazole (Matta *et al.* 2011, Nfodzo and Choi 2011). Although pharmaceuticals such as ibuprofen and acetaminophen are easily removed due to their high biodegradability and thus are not considered persistent, they are frequently being detected in water bodies and systems due to their high usages above the capacities of the treatment plants. Other pharmaceuticals include the iodinated X-ray contrast media such as diatrizoate, iopromide, iopamidole, and iomeprol used in test scans and are largely detected in wastewaters discharged from hospitals (Kalsch 1999).

Atrazine, 2,4-D, and DEET are widely used pesticides for mitigating the growth of grasses and weeds in farms such as corn and sugar cane (Brillas *et al.* 2000, Borràs *et al.* 2010, Tay *et al.* 2013). Atrazine is considered the most used herbicide world-wide and is described as a potential danger for public health for being an endocrine disrupting compound (Fan *et al.* 2007). In conventional wastewater treatment plants, the removal of atrazine using MBR plants ranged from <10% removal (from 24 ng L<sup>-1</sup> input) (Bernhard *et al.* 2006) to 10 – 40% removal (from 10 ng L<sup>-1</sup> input) (Bouju *et al.* 2008).

Another widely used selective herbicide is 2,4-D which has been widely applied to control broad-leaved weeds and inhibit methano-trophic bacteria in gardens and farming due to its low cost and good selectivity (Brillas *et al.* 2000). This herbicide is described as moderately toxic because it may cause nervous system damage as well as liver and kidney problems on short-term and long-term exposure to more than 100 ppb (Bandala *et al.* 2007). It has been widely detected in surface and groundwater due to low soil sorption and high potential of leachability, where this well-known endocrine disrupter is characterized by low biodegradability and low decomposition at levels above 1.0 ppm (Brillas *et al.* 2000). In conventional water treatments using coagulation and chlorine oxidation, removal of 2,4-D is incomplete, whereas potassium permanganate and activated carbon treatment show effective removal (Aly and Faust 1965). On the other hand, in biological treatment processes, the 2,4-D removal is reported to be complete (> 99% in activated sludge treatments), but its main degradation product is a relatively persistent compound, 2,4-dichlorophenol, which is a toxic compound to humans and freshwater aquatic life at high concentrations (Petrović *et al.* 2003).

Moreover, an active ingredient in the production of insect repellent is DEET. It is widely used to block the insect's chemoreceptors sensing lactic acid and carbon dioxide (CO<sub>2</sub>), and because of this extensive use, it has been widely detected in streams, drinking water, and sewage effluents (Tay *et al.* 2013). In activated sludge treatments, DEET is very poorly removed, whereas its removal in MBR plants ranged between 0% and 50% (Bernhard *et al.* 2006), where it was suggested that DEET removal is dependent on sludge retention time (Kim *et al.* 2007).

A large number of pharmaceuticals have been reported to be present in surface and groundwater, as well as sewage treatment plant effluents, including carbamazepine (anti-convulsant), ibuprofen (anti-inflammatory), and triclosan (antibiotic). They are poorly removed in coagulation and flocculation processes used typically in drinking water treatment systems, but are relatively significantly removed (>70% removal) in membrane treatment systems such as nano-filtration and reverse osmosis (Snyder *et al.* 2003). Some pharmaceutical compounds are characterized by low biodegradability; while others such as anti-inflammatory and anti-biotic drugs are reported to be highly removed through biological treatments (Snyder *et al.* 2003).

Carbamazepine is an anticonvulsant and anti-epileptic drug used primarily in mood-stabilizing and controlling seizures (Zhang *et al.* 2008). It has been widely identified in groundwater at concentrations reaching 610 n g L<sup>-1</sup>, where carbamazepine as well as primidone, which is another antiepileptic drug, persisted in groundwater even after a travel time of 6 years (Drewes *et al.* 2002). It is one of the most dominant drugs in rivers, streams, and sewage treatment plants (STP) effluents,

reaching concentrations up to  $6.3 \mu\text{g L}^{-1}$  (Ternes 1998), in even well-treated domestic effluents such as nitrification/de-nitrification plants as well as plants involving microfiltration (Drewes *et al.* 2002). This pharmaceutical passes untransformed through the CAS treatment systems (Radjenović *et al.* 2009), and has been observed to be recalcitrant with quite low biodegradability (Hai *et al.* 2011).

Ibuprofen is third highest consumed pharmaceutical worldwide being an anti-inflammatory drug for the treatment of fever, muscle aches, and menstrual cramps (Skoumal *et al.* 2009). For that, it has been widely detected, especially in sewage and rivers, reaching concentrations up to  $85 \mu\text{g L}^{-1}$  (Farré *et al.* 2001), due to its low absorption and metabolism in the human body (Behera *et al.* 2012). Ibuprofen affects the growth of duck weed *Lemna minor* and exhibits toxicity to some microorganisms in the aquatic environment such as *Daphnia magna* reproduction. It is reported to be highly removed (>90%) in CAS, but the removal is dependent on the retention time in STPs, where less than 30% removal of ibuprofen was observed with shorter solids (< 5 days) and hydraulic (< 9 hours) retention times (Nakada *et al.* 2006). Its high removal is due to its high biodegradability but its principal metabolites, hydroxy- and carboxy-ibuprofen, are not both similarly removed, as hydroxy-ibuprofen is persistent (Heberer 2002). Moreover, its high initial concentration, often above the removal capacity of wastewater treatment plants, makes it a target organic pollutant.

Triclosan is an antibacterial pharmaceutically active compound largely used in toothpastes, soaps, cosmetics, and other personal care products (Nfodzo and Choi 2011). The potential estrogenic effects of triclosan and its toxicity to some aquatic organisms raised public and regulatory concern (Nfodzo and Choi 2011, Song *et al.* 2012). Due to the wide use of this antibacterial, it has been very widely detected at concentrations reaching to  $21.9 \mu\text{g L}^{-1}$  (Sabaliunas *et al.* 2003). Triclosan removal in wastewater treatment plants is reported to largely vary from 10% to 95% depending on the treatment used. For instance, its removal depends on the oxygen levels and thus it is highly removed in activated sludge and MBR plants (>90%) where aeration is involved and when hydraulic retention times exceeding 15 hours (Thompson *et al.* 2005, Tadkaew *et al.* 2011).

X-ray contrast media such as diatrizoate and iopromide, which are tri-iodated benzene derivatives, are the most intensively used chemicals in hospitals for producing an enhanced image of the soft tissues (Moreau *et al.* 1989). Their world-wide annual consumption was estimated to be around 3,500 tons (Putschew *et al.* 2000) with 130 tons per year in Germany only (Steger-Hartmann *et al.* 1999). They have been detected in substantial quantities in hospital wastewater (Gartiser *et al.* 1996, Pauwels and Verstraete 2006), municipal wastewater (Oleksy-Frenzel *et al.* 2000), as well as in groundwater (Sacher *et al.* 2001), surface waters (Ternes and Hirsch 2000), and sewage treatment plants effluents



(Wischnack *et al.* 1998) with concentrations exceeding  $1.0 \text{ mg L}^{-1}$  (Velo-Gala *et al.* 2013). Diatrizoate, for instance, has been reported to be a very persistent iodinated contrast media showing no or minimal degradation with activated sludge (Kalsch 1999, Haiß and Kümmerer 2006) or retention in soil filters (Tondera *et al.* 2013). Removal of diatrizoate was studied using membranes (Gur-Reznik *et al.* 2011), coagulation/flocculation (Seitz *et al.* 2006), as well as activated carbon (Velo-Gala *et al.* 2013) without any significant removal.

## 2.2 Advanced Oxidation Processes (AOPs) for Removal of Organic Compounds

The biological treatment technologies, such as activated sludge processes, are incapable of efficiently degrading persistent organic contaminants such as pesticides, dyes, diatrizoate, aniline, carbamazepine, and several phenolic compounds (Marrot *et al.* 2006). Chemical oxidation techniques such as ozonation and advanced oxidation processes (e.g., using Fenton reagent) have been studied for degrading pharmaceuticals and contrast media, reporting high removal capabilities (Huber *et al.* 2003, Wadley and Waite 2004).

Advanced oxidation processes are chemical oxidation techniques that are characterized by *in-situ* generation of highly reactive radicals, principally  $\cdot\text{OH}$  radicals, in order to oxidize organic and inorganic compounds in water treatment processes (Glaze *et al.* 1987). These technologies have attracted wide attention due to their promising ability and efficiency in the destruction and removal of trace organic contaminants (Matilainen and Sillanpää 2010). The main characteristic of the AOPs is that they do not collect or transfer pollutants into another phase but effectively degrade and possibly mineralize them, while operating near ambient conditions of temperature and pressure (Matilainen and Sillanpää 2010).

The oxidation ability of AOPs in the removal of recalcitrant and natural organic matter (NOM) is not sufficient to promote AOPs as independent “stand-alone” technologies (Brillas *et al.* 2009). AOPs are reported to be relatively inefficient to treat contaminated water with very high concentrations of organic matter ( $> 5,000 \text{ mg L}^{-1}$ ), as most of such organic matter would be typically biodegradable, and cheaper to treat via the conventional processes. They are only applied when conventional oxidation treatments are not effective in removal of persistent organic pollutants. Thus, the need for coupling AOPs with conventional wastewater treatment technologies is inevitable (Pera-Titus *et al.* 2004).

### 2.2.1 Hydroxyl Radicals-based Advanced Oxidation Processes

The major oxygen-containing intermediates produced in AOPs are hydroxyl radicals, which are reported to be among the most powerful oxidants (Matilainen and Sillanpää 2010). With an oxidation potential of 2.38 – 2.80 V vs SHE (Parsons 2004), hydroxyl radicals are described to be non-selective reactive oxidants with a wide range of organic pollutants.

One of the most efficient AOPs is Fenton reagent, which consists of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) activated with ferrous ions (Fe<sup>2+</sup>). Fenton reaction shows that hydroxyl radicals can be generated by the reaction of Fe<sup>2+</sup> with H<sub>2</sub>O<sub>2</sub> while producing ferric ion (Fe<sup>3+</sup>) and hydroxide (**Eq. 2.1**).



The major drawback of the Fenton process is that it is very pH-dependant and therefore requires large amounts of acids to control pH and maintain it ideally below pH 3. Besides pH, the removal rate is controlled by various operating parameters such as dosage of H<sub>2</sub>O<sub>2</sub> and ferrous ions. Experimental results show that high initial concentrations of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup>, as well as low initial pH are the optimal conditions. Hence, another drawback is the addition of large amounts of chemicals required, especially of iron salts, and these chemicals contribute to the formation of waste sludge that needs to be further treated.

Ozonation has been reported to successfully oxidize many persistent organic contaminants directly or via the formation of hydroxyl radicals (Huber *et al.* 2003, Huber *et al.* 2005). Ozone can be combined with TiO<sub>2</sub> in the presence of hydrogen peroxide (O<sub>3</sub> / H<sub>2</sub>O<sub>2</sub> / TiO<sub>2</sub>) or UV (O<sub>3</sub> / UV / TiO<sub>2</sub>) where both have proven to cause substantial generation of  $\cdot\text{OH}$  radicals (Matilainen and Sillanpää 2010). However, in dark heterogeneous catalysis, both O<sub>3</sub>/TiO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/TiO<sub>2</sub> showed lower oxidation with lower oxidation synergy observed in O<sub>3</sub>/TiO<sub>2</sub> (Mosteo *et al.* 2009). Nevertheless, ozonation is a selective process, where ibuprofen in ozonation is highly persistent because of the absence of any functional groups in ibuprofen to react with ozone (i.e., its low kinetics with ozone ( $k = 9.1 \text{ M s}^{-1}$ )). On the other side, although DEET and ozone both are electron-withdrawing, DEET is highly removed in wastewater treatments incorporating ozone (Westerhoff *et al.* 2005). This suggests that ozone is causing the removal of DEET via hydroxyl radicals intermediates not via direct oxidation. This was supported by Zhang and Lemley (2006) showing an effective removal using anodic Fenton treatment as well. Nonetheless, the removal of diatrizoate was studied using ozonation (Ternes *et al.* 2003, Huber *et al.* 2005), Fenton and photo-Fenton techniques (Real *et al.* 2009), as

well as several other oxidative (Sugihara *et al.* 2013) and reductive techniques (Zwiener *et al.* 2009, Mu *et al.* 2010) including sequential reduction and oxidation process (Radjenovic *et al.* 2013). In almost all studies, diatrizoate was slightly removed with no complete mineralization observed, where the reported by-products were of higher toxicity compared to the original compound itself.

### 2.2.2 Sulfate Radicals-based Advanced Oxidation Processes

Hydroxyl radicals are not the only strong oxidizing agents that can be employed although  $\cdot\text{OH}$ -based AOPs are considered to be the most widespread. Sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) are also very strong oxidizing agents that are characterized by an oxidation potential of  $E^\circ = 2.5 - 3.1$  V vs SHE (Zhao *et al.* 2010), compared to  $\cdot\text{OH}$  ( $E^\circ = 2.4 - 2.8$  V vs SHE). The high efficiency of the  $\text{SO}_4^{\cdot-}$  in mineralizing organic pollutants has drawn a lot of attention recently in the areas of water treatment and in situ chemical oxidation (ISCO) for remediating soil and groundwater (Xiang-Rong Xu 2012). Sulfate radicals have been reported to be effective in the destruction of a wide range of organic compounds present in subsurface soils and groundwater, such as polychlorinated biphenyls (PCBs) (Anipsitakis and Dionysiou 2004); polycyclic aromatic hydrocarbons (PAHs) (Liang and Bruell 2008); as well as volatile organic compounds (VOCs) (Block *et al.* 2004), and non-VOCs (Liang *et al.* 2003).

Pesticides and herbicides such as atrazine and 2,4-D have been reported to be significantly oxidized by sulfate radicals (Deng *et al.* 2012). Its oxidizing capability to degrade 2,4-D as well as its major by-product, 2,4-dichlorophenol (2,4-DCP), is considered a superiority over conventional AOPs because 2,4-DCP is a carcinogenic and toxic contaminant that is not removed in conventional AOPs (Anipsitakis and Dionysiou 2004). Moreover, its oxidation capabilities were also reported in the removal of many pharmaceuticals such as anti-bacterial agents (e.g. triclosan), antibiotics, and other drugs such as acetaminophen, carbamazepine, and sulfamethazole (Nfodzo and Choi 2011).

$\text{SO}_4^{\cdot-}$  radicals are described to be a more selective oxidizing agent than  $\cdot\text{OH}$  radicals because most reactions of  $\text{SO}_4^{\cdot-}$  with organic pollutants involve electron transfer, whereas the non-selective  $\cdot\text{OH}$  radicals also react with organics by hydrogen abstraction or addition (Zemel and Fessenden 1978, Khursan *et al.* 2008, Matta *et al.* 2011). This selectivity was observed in the degradation of atenolol (Murugananthan *et al.* 2011), orange II (Chen and Chen 2006), as well as 2,4-DCP, atrazine, and naphthalene (Anipsitakis and Dionysiou 2003). In the latter work for instance, Anipsitakis and Dionysiou (2003) studied the removal of the three compounds, 2,4-DCP, atrazine, and naphthalene, using sulfate radicals or hydroxyl radicals at similar pH values and molar concentrations, and their results showed that 2,4-DCP and atrazine are more degraded with  $\text{SO}_4^{\cdot-}$  radicals compared to  $\cdot\text{OH}$

radicals, but not naphthalene which was not degraded by  $\text{SO}_4^{\bullet-}$  radicals. This indicates that  $\text{SO}_4^{\bullet-}$  radicals can be more effective than  $\bullet\text{OH}$  radicals depending on the structure of the target contaminant where they showed affinity towards atenolol, 2,4-DCP, and atrazine, whereas no role was observed in the oxidation of orange II and naphthalene.

Generation of sulfate radicals in most of these reported AOPs is accomplished through the chemical activation of peroxydisulfate ion, also known shortly as persulfate ( $\text{S}_2\text{O}_8^{2-}$ ), or peroxymonosulfate (PMS), with both: its mono-anion form ( $\text{HSO}_5^-$ , pH of 6 to 8), and its di-anion form ( $\text{SO}_5^{2-}$ , pH  $\geq 11$ ) (Guan *et al.* 2011, Zhang *et al.* 2014).

Persulfate (PS) is the most recent form of oxidizing agents employed in the field of environmental applications, where mineralization of organic contaminants is required for cyanide removal, dye oxidation, fibre whitening, and many other industrial applications (Serrano *et al.* 2002). Persulfate anion ( $\text{S}_2\text{O}_8^{2-}$ ) with its potential of  $E^\circ = 2.01\text{V}$  is a stronger oxidant than hydrogen peroxide ( $E^\circ = 1.76\text{V}$ ) and surpasses several strong oxidants for its easy storage and transport as well as high stability and solubility at ambient temperature, which promotes its use for remediating contaminated soils and groundwater because of its stability during travel time (Xiang-Rong Xu 2012).

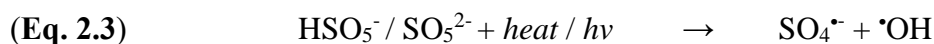
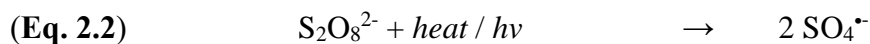
However, at ambient temperature and pH, the oxidation kinetics of persulfate are relatively slow with most organic compounds compared to  $\bullet\text{OH}$  and  $\text{SO}_4^{\bullet-}$  radicals (Latimer 1952, Brillas *et al.* 2009). Therefore, the need for activation steps to transform the  $\text{S}_2\text{O}_8^{2-}$  ions into the more powerful oxidizing agent  $\text{SO}_4^{\bullet-}$  radicals ( $E^\circ = 2.5 - 3.1\text{V}$  vs SHE) is essential to accelerate its oxidation performance in environmental applications.

The production of sulfate radicals requires the activation of persulfate to induce its decomposition into sulfate radicals as well as other reactive intermediates under certain conditions, where every persulfate anion produces one or two  $\text{SO}_4^{\bullet-}$  radicals depending on the activation conditions. Heat, high pH, UV radiation, as well as the addition of transition metals or  $\text{H}_2\text{O}_2$  are the most commonly used activation factors (Zhao *et al.* 2010).

The term *activated persulfate* usually denotes the sum of several reactive intermediate species generated from the activation of persulfate, with  $\text{SO}_4^{\bullet-}$  radicals and  $\bullet\text{OH}$  radicals being the major generated intermediates (Tsitonaki *et al.* 2010).

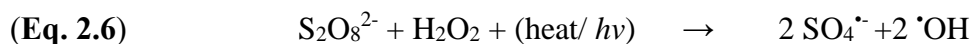
### 2.2.2.1 Thermal activation and UV-light activation of PS and PMS

Persulfate can be activated to decompose into sulfate radicals by heat, and such thermal activation has been reported at temperatures ranging from 35°C to 130°C (Xiang-Rong Xu 2012). In addition, peroxymonosulfate produces both radicals,  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  when the system is heated. The degradation efficiency order between PS and PMS is dependent on the structure of the oxidant being investigated (Antoniou *et al.* 2010, Yang *et al.* 2010). Thermally activated persulfate was reported with high efficiencies in oxidizing organic compounds such as chlorinated ethenes, trichloroethanes, BTEX, as well as several volatile organic carbons, VOCs (Xiang-Rong Xu 2012). In addition, the generation of sulfate radicals can also take place by the activation of persulfate or peroxymonosulfate via irradiating the system with UV radiation, mostly of wavelengths below 270 nm (Zhao and Li 2006, Li *et al.* 2008, Criquet and Leitner 2009, Guan *et al.* 2011). Yet, the thermal activation and UV-activation is very cost-intensive, requiring high energy input and not applicable for *in-situ* chemical oxidation of chemicals in natural systems and soils.



### 2.2.2.2 Alkaline activation (high pH)

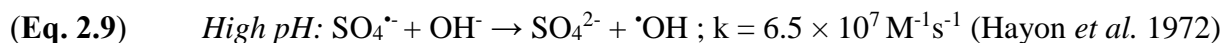
Under acidic pH, the decomposition of  $\text{S}_2\text{O}_8^{2-}$  into  $\text{HSO}_5^-$  and  $\text{H}_2\text{O}_2$  also occurs, where these two oxidants are more reactive with some organic contaminants and are kinetically faster than persulfate. When high pH is combined with heat or UV radiation, both radicals can be generated:  $\text{SO}_4^{\cdot-}$  radicals are produced from PS and PMS, while  $\text{H}_2\text{O}_2$  gets activated and breaks down into two  $\cdot\text{OH}$  radicals where both radicals contribute significantly to the higher organics oxidation.



Nonetheless, as pH increases, the activation of persulfate becomes more effective and the production of radicals increases. The buffering capacity (i.e., mole ratio of pH modifier to persulfate) should be taken into consideration as it plays an important role in the activation efficiency (Block *et al.* 2004). The mechanism of this alkaline activation of persulfate into sulfate free radicals was proposed by Furman *et al.* (2010).



Once the  $\text{SO}_4^{\bullet-}$  radicals are generated, a large chain of reactions is initiated with strong kinetic competition. On one side,  $\text{SO}_4^{\bullet-}$  radicals contribute to the formation of  $\bullet\text{OH}$  radicals, where this radical inter-conversion is very pH-dependent, and the  $\bullet\text{OH}$  formation increases substantially at high pH. On another side occurring simultaneously,  $\text{SO}_4^{\bullet-}$  radicals initiate rapid oxidation reactions of organic contaminants existing in the aqueous solution (Liang *et al.* 2003). Moreover, the  $\bullet\text{OH}$  radicals also contribute to the rapid oxidation reactions of organic contaminants. Therefore, a strong kinetic competition takes place between (i) the  $\bullet\text{OH}$  formation via  $\text{SO}_4^{\bullet-}$  radicals, (ii) the oxidation of organic contaminants via  $\text{SO}_4^{\bullet-}$  radicals, and (iii) the oxidation of organic contaminants via  $\bullet\text{OH}$  radicals.



Hence, the major factors controlling this competition are the pH and the nature of organic contaminants. Under acidic and neutral pH conditions, the degradation of the organic contaminants occurs predominantly via  $\text{SO}_4^{\bullet-}$  radicals, which are more dominant in the aqueous solution. This is mainly because the reaction rate constant of conversion of  $\text{SO}_4^{\bullet-}$  radicals into  $\bullet\text{OH}$  radicals is only  $2 \times 10^{-3} \text{ s}^{-1}$  which is small compared to reaction rates of  $\text{SO}_4^{\bullet-}$  with organic contaminants such as phenolic compounds (Norman *et al.* 1970). In addition, under alkaline conditions, the transformation of  $\text{SO}_4^{\bullet-}$  into  $\bullet\text{OH}$  is very high with a reaction rate constant of  $6.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , and thus  $\bullet\text{OH}$  radicals are more dominant for organic oxidation at high pH.

### 2.2.2.3 Transition metal activation

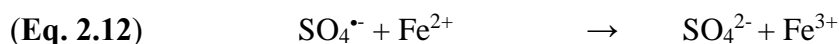
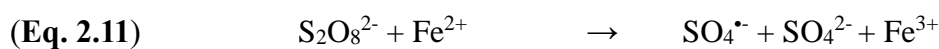
Sulfate radicals can be also generated from the decomposition of persulfate in the presence of transition metal activators such as iron, cobalt, silver, copper, manganese, and cerium at room temperatures (Huie and Clifton 1990, Watts and Teel 2006, Ahad and Slater 2008, Tsitonaki *et al.* 2010, Matta *et al.* 2011, Rivas *et al.* 2012). Ferrous ion ( $\text{Fe}^{2+}$ ) and cobalt ion ( $\text{Co}^{2+}$ ) are the most widely studied metal activators, with the former being used most.



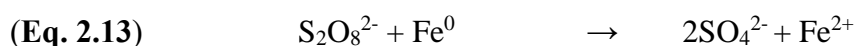
Higher removal of organic contaminants such as triclosan, sulfamethoxazole, and acetaminophen was reported in PMS/Fe ions compared to PS/Fe (Nfodzo and Choi 2011). However, substituting  $\text{Fe}^{2+}$  with  $\text{Co}^{2+}$  when employing  $\text{HSO}_5^-$  showed even higher removal of triclosan and sulfamethoxazole, as well as DEET (Tay *et al.* 2013), with both oxidants, where the optimum ratio was observed with concentration ratio 1:5:5 for triclosan: PMS:  $\text{Co}^{2+}$  (Nfodzo and Choi 2011, Nfodzo and Choi 2011).

The stoichiometric ratio of PS (or PMS) and metallic ions plays an important role (Zhao *et al.* 2010, Nfodzo and Choi 2011, Rivas *et al.* 2012). For instance, in the case of ferrous ion catalysis of persulfate, excess  $\text{Fe}^{2+}$  scavenges  $\text{SO}_4^{\bullet-}$  radicals and produces the undesired  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$ . Therefore, to avoid the combined loss of metal activator and scavenging of the  $\text{SO}_4^{\bullet-}$  radicals, ferrous ions should be added in small amounts and in a slow, gradual mode if possible (Huie and Clifton 1990, Watts and Teel 2006, Ahad and Slater 2008).

Moreover, pH is limited to the acidic values (i.e.,  $\text{pH} < 3$ ) when working with ferrous ions, due to the precipitation of iron hydroxide ( $\text{Fe}(\text{OH})_3$ ) or hydrous ferric oxide ( $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ) at higher pH (Liang *et al.* 2009), and thus maintaining an acidic pH is required (Liang *et al.* 2009, Ahmad *et al.* 2011).



Zhao *et al.*, (Zhao *et al.* 2010) and Tsitonaki *et al.* (Tsitonaki *et al.* 2010) investigated the production of the sulfate radicals in the presence of zero-valent iron (ZVI) at ambient temperature in ZVI-PS system and observed promising removal rates of organic contaminants. The zero valent iron is already a solid so its usage eliminates the concern associated with the iron precipitation and provides a larger pH window for the iron activation of persulfate.



#### 2.2.2.4 Integrated activation systems

Coupling of persulfate UV photolysis with thermal activation or other activators such as high pH and/or transition metals have been reported to increase the activation efficiency (Xiang-Rong Xu 2012). When working in a combined system of high pH and /UV, the  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  generated from peroxymonosulfate increases as pH increases in the range of 8 – 10. However,  $\text{SO}_4^{\bullet-}$  concentration

decreases and  $\cdot\text{OH}$  concentration increases if the oxidation kinetics of the organic compound with the sulfate radical are low, especially with pH above 10 (Guan et al. 2011). Therefore, in these integrated systems, and when  $\text{SO}_4^{\cdot-}$  is stronger oxidant than  $\cdot\text{OH}$ , depending on the organic contaminants targeted in the oxidation process, it is essential to minimize the conversion reaction of  $\text{SO}_4^{\cdot-}$  into  $\cdot\text{OH}$ , in order to maintain higher degradation of the organic pollutants via maintaining the high concentrations of the stronger oxidant. For instance, the superiority of  $\text{SO}_4^{\cdot-}$  over  $\cdot\text{OH}$  for carbamazepine degradation was validated by Matta *et al.* (2011) who compared  $\text{SO}_4^{\cdot-}$  generated from PMS/ $\text{Co}^{2+}$  to  $\cdot\text{OH}$  generated from Fenton's reagent ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ), proving the former to be more efficient. This comparison promotes peroxymonosulfate as a better option than  $\text{H}_2\text{O}_2$  due to its higher effectiveness in mineralization of organic pollutants, although it is not as environmentally friendly and as cheap compared to  $\text{H}_2\text{O}_2$ , and not easier to transport compared to  $\text{H}_2\text{O}_2$ .

### 2.3 Electrochemical processes for wastewater treatment

The electrochemical advanced oxidation processes (EAOPs) such as anodic oxidation (AO), have shown great capabilities in mimicking the performance of traditional AOPs and even surpassing them in water treatment (Chen 2004, Anglada *et al.* 2009, Brillas *et al.* 2009, Kapalka *et al.* 2010). The electrochemical advanced oxidation processes are defined as processes in which an electric current is supplied to the electrochemical reactor to trigger chemical reactions that generate *in-situ* reactive species (e.g., hydroxyl radicals, superoxide radicals) to drive oxidation and reduction (redox) reactions (Zhao and Li 2006, Garrido *et al.* 2007, Ahad and Slater 2008, Tsitonaki *et al.* 2010). The remarkable ability of these non-selective electrochemical processes to generate *in-situ* oxidizing species such as  $\cdot\text{OH}$  radicals from the feed water and/or electrolytes without the extensive addition of chemicals, provides these processes an advantage over conventional AOPs in the water treatment field, such as pharmaceuticals removal (Garrido *et al.* 2007, Yu *et al.* 2014), decontamination of dyes (Costa *et al.* 2009, Brillas and Martínez-Huitle 2015) as well as phenol destruction (Iniesta *et al.* 2001, Wang *et al.* 2009).

The advancement in the electricity production from solar and wind energy further endorses the EAOPs implementation because of the easy availability and accessibility of electric power generated from such energy resources in isolated locations and without the need to periodic chemicals transportation. The principal advantages and disadvantages of EAOPs for environmental applications compared to conventional AOPs are summarized in **Table 2.1** (Jüttner *et al.* 2000, Anglada *et al.* 2009, Sirés and Brillas 2012).



**Table 2.1** The major characteristics and drawback of electrochemical advanced oxidation processes (EAOPs) (Jüttner *et al.* 2000, Anglada *et al.* 2009, Sirés and Brillas 2012)

EAOPs Characteristics	EAOPs Drawbacks
(i) <b>Relative environmental compatibility and minimal use of chemicals:</b> - its main reagent is the electron which is a clean reagent, generating reactive species <i>in-situ</i> .	(i) Mass transfer limitations: - its efficiency depends on the reactor design and size of electrode surface area.
(ii) <b>Versatility, robustness and easy handling:</b> - it is a simple operation and requires quite basic equipment. - it is highly controllable with operational parameters easily modified to minimise side reactions and to suit different contaminants and wastewater characteristics. - it can be terminated easily by cutting off the power and restarted quickly after fixing the operational issue.	(ii) Potential electrode fouling: - the formed by-products may accumulate on the electrode surface causing an anode passivation and/or cathode scaling - this fouling can cause loss of activity, lowered durability, and shortening of the long-term stability of electrode material
(iii) <b>Safety and high energy efficiency:</b> - it operates at ambient conditions of pressure and temperature - its operational parameters are easily modified to reduce power losses.	(iii) Potential high operating cost: - it requires adding electrolytes + regulating pH if conductance is low, and high energy input for heavily polluted water.
(iv) <b>Amenability to automation:</b> - its data acquisition, and process automation are easily controlled by the current and potential.	(iv) Batch mode operation: - it usually works only in batch mode to achieve high removal percentages.
(v) <b>Compatibility and compact design:</b> - it can be easily scaled up and combined with existing treatment plants or applied in isolated communities to chemically and pathogenically treat water sources.	(v) Formation of by-products: - the potential production of more bio-recalcitrant and/or toxic by-products, especially where high chlorine content is employed.

### 2.3.1 Mechanisms of electrochemical oxidation and importance of electrode material

The electrochemical oxidation reactions of the organic pollutants are reported to occur via different mechanisms, taking place either on the electrode surface, in the bulk solution, or simultaneously co-occurring in both (Rao and Venkatarangaiah 2014). The direct electrochemical oxidation, also known as “anodic oxidation”, denotes the oxidation process taking place directly at or very close to the anode, whereas the indirect electrochemical oxidation refers to the electrochemical reactions occurring in the bulk solution. The electrode material is an important factor directing the mechanism, where high catalytic activity towards organic pollutant degradation and low activity towards oxygen evolution are the major desired electrode characteristics in electrochemical oxidation of organic compounds (Chen 2004, Anglada *et al.* 2009).

Electrodes are classified into two categories, active or non-active electrodes, depending on the interaction between the electrode and  $\cdot\text{OH}$  radicals (Martinez-Huitle and Ferro 2006). This electrode nature dictates the value of the oxygen overpotential which is defined as the difference between the thermodynamic value for oxygen production and the voltage at which oxygen evolution starts to take place at this electrode (Chen 2004).

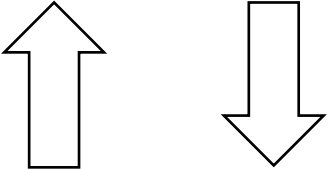
The active electrodes are characterized by strong electrode-hydroxyl radical interaction, which signifies a low oxidation power anode (i.e., low overpotential for oxygen evolution). Examples of active electrodes are stainless steel,  $\text{IrO}_2$ , Pt,  $\text{RuO}_2$ , which are characterized by low concentration of active sites on the anode surface and high concentration of oxygen-vacancies in their oxide lattice (i.e., higher oxidation states are available for  $\text{MO}_{x+1}$ ). Most of these active electrodes are characterized by low oxygen overpotential (**Table 2.2**), and have been reported to be ineffective for anodic oxidation of organic compounds at high current densities (Anglada *et al.* 2009).

In non-active electrodes, the electrode- $\cdot\text{OH}$  interactions are relatively weak, and these are therefore described as poor catalysts for  $\text{O}_2$  generation because they possess a high overpotential for oxygen evolution. Among the most common non-active electrodes are  $\text{PbO}_2$ ,  $\text{SnO}_2$  and most importantly boron doped diamond (BDD). The BDD electrodes are typically non-active electrodes with a weak  $\text{M}-\cdot\text{OH}$  interaction, where the major merit of BDD electrodes is that they possess a very high oxidation potential compared to other electrode materials (2.2 – 2.7 V vs. SHE, depending on the base material, Si or Ti).

This high oxidation potential combined with being very conductive materials and hence yielding high current efficiencies, promotes the outstanding performance of BDD for the fast and complete oxidation of organic contaminants. These non-active electrodes are preferred over active electrodes in the field of electrochemical wastewater treatments because they are capable of completely oxidizing and mineralizing organic compounds while generating less  $\text{O}_2$ , and thus enhancing the anodic process efficiency attributed to higher current efficiency for oxidation of organic pollutants, and minimizing energy losses.

The active electrode promotes the formation of the chemically-adsorbed active oxygen, leading to the partial oxidation of organic pollutants. In contrast, the formation of the physically-adsorbed active oxygen is dictated by the non-active electrode, leading ultimately to the complete oxidation and mineralization of organic pollutants into  $\text{CO}_2$ .

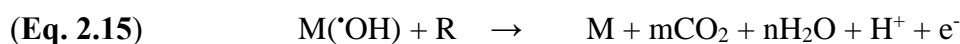
**Table 2.2** The oxidation potential (V vs SHE) for oxygen evolution of different electrode materials in acidic media, as well as their trend of the adsorption type and anodic oxidation power (Chen 2004, Comninellis *et al.* 2008, Anglada *et al.* 2009, Comninellis and Chen 2010).

Electrode Material	Oxidation Potential, V vs SHE	Trend of Adsorption Type and Oxidation power
Si/BDD, Ti/BDD, DiaChem	2.2 – 2.7	<p>More physically adsorbed active oxygen &amp; higher anodic oxidation power</p>  <p>More chemically adsorbed active oxygen &amp; lower anodic oxidation power</p>
Pb – Sn (93:7)	2.5	
TiO <sub>2</sub> (Ebonex ®)	2.2	
SnO <sub>2</sub> – Sb <sub>2</sub> O <sub>5</sub>	1.9 – 2.2	
PbO <sub>2</sub>	1.8 – 2.0	
Graphite	1.7	
IrO <sub>2</sub> –Ta <sub>2</sub> O <sub>5</sub> , RuO <sub>2</sub>	1.4 – 1.8	
Pt	1.3 – 1.6	

### 2.3.1.1 Physisorbed active oxygen and chemisorbed active oxygen

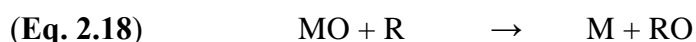
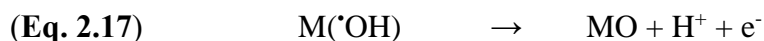
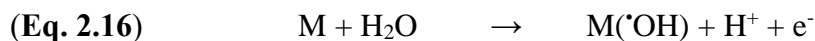
The first stage in the electro-oxidation of pollutants occurs via the generation of the “active oxygen” transferred from water molecules to the surface of the electrode, denoted as (M), to form physically-adsorbed  $\cdot\text{OH}$  radicals, denoted as  $\text{M}(\cdot\text{OH})$ , which is defined as a higher oxide anode. The reactivity of the  $\text{M}(\cdot\text{OH})$  intermediate depends on the electrode nature being active or non-active, where the electrode nature plays a major role in determining the extent of the oxidation of the pollutants.

When the electrode is non-active, the interaction between the electrode and  $\cdot\text{OH}$  is weak, and further interaction beyond  $\text{M}(\cdot\text{OH})$  is unfavored. Thus, direct mineralization of the organic pollutants takes place via the direct attack of  $\text{M}(\cdot\text{OH})$  on the organic matter (R) to oxidize it completely into  $\text{CO}_2$ .



If the electrode is active, the electrode- $\cdot\text{OH}$  interaction is strong and thus the overpotential for oxygen evolution is low. Thus, after the formation of the first higher oxide anode,  $\text{M}(\cdot\text{OH})$ , the strong interaction between the electrode and  $\cdot\text{OH}$  encourages the further oxidation of  $\text{M}(\cdot\text{OH})$  into a higher oxidation oxide anode,  $\text{MO}$ . The chemisorbed active oxygen is defined as oxygen in the oxide lattice,  $\text{MO}_{x+1}$ , where the physisorbed active oxygen,  $\text{M}(\cdot\text{OH})$ , is oxidized into a higher oxide anode,  $\text{MO}$ .

The chemisorbed active oxygen, MO, reacts with the organic species to transform it into an oxidation product (RO). It is noted that MO acts as a mediator and reacts in a selective manner, leading to partial oxidation of the reactants. The accumulation of the by-products leads to a ‘poisoning effect’ on the electrode surface.



Both physisorbed and chemisorbed active oxygen reactions are in competition with oxygen evolution side reactions which cause both active oxygen species, MO and M( $\cdot$ OH), to decompose. Evolution of oxygen ( $\text{O}_2$ ) is considered unfavored limiting reaction because it decreases the efficiency of anodic process and results in energy loss. The different pathways of electrochemical oxidation in both active and non-active electrodes as well as the oxygen evolution side reactions of both cases and the poisoning effect of the active electrode cases are illustrated in **Figure 2.1**.

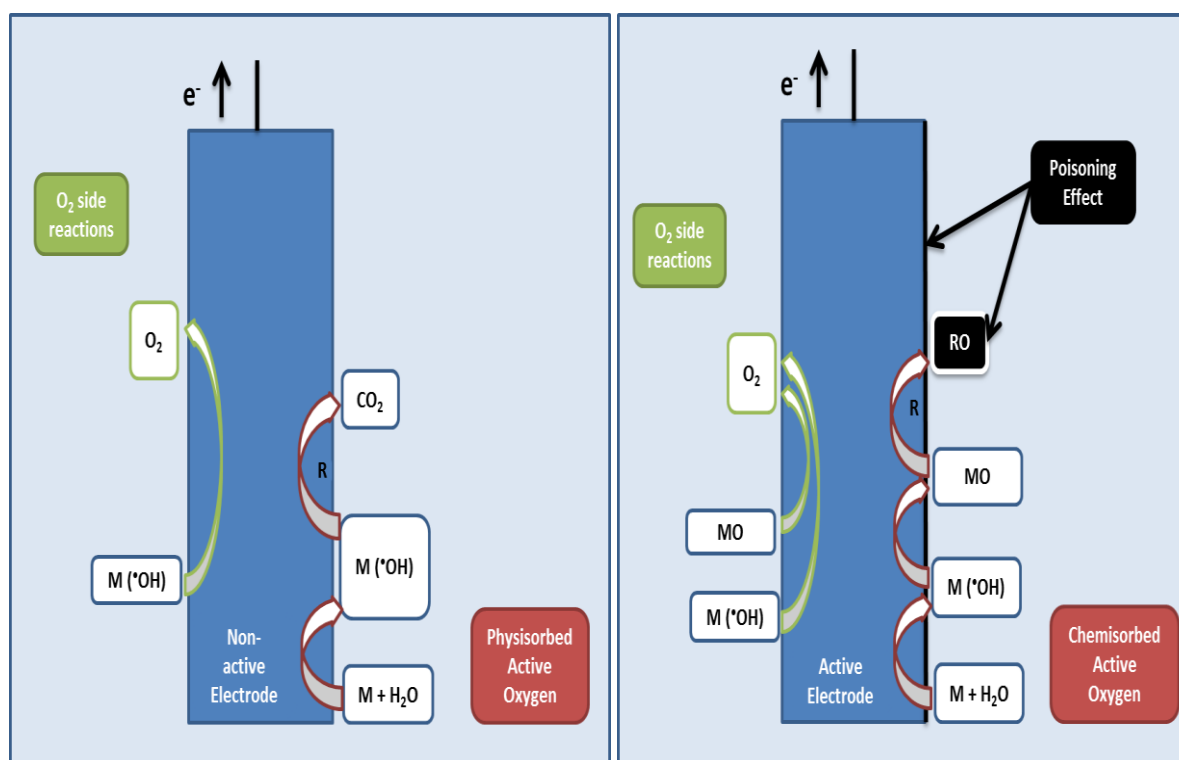
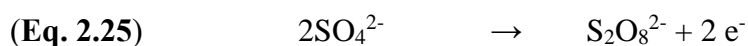
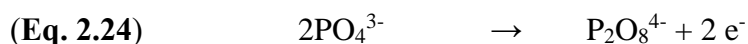
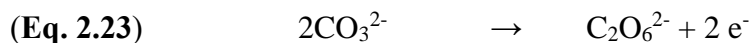


### 2.3.1.1 Other indirect electrochemical oxidation besides $\cdot\text{OH}$

Besides  $\cdot\text{OH}$ , the indirect electrochemical oxidation takes place in the bulk of the solution, mainly in the vicinity of the electrode surface, by different mediated oxidation reactions, triggered through various electrochemically generated oxidants (Anglada *et al.* 2009). Anodes characterized with high overpotential for oxygen evolution reaction (OER) can generate stable *in-situ* generated chemical oxidants such as ozone, persulphate, percarbonate, and perphosphate, which play an important role in mediating the transfer of the electrons from the electrode surface and the organic compounds. As explained earlier, ozone is a strong oxidant widely used in water disinfection and can be generated electrochemically via anodic oxidation (Seitz *et al.* 2006). Its high oxidation potential allows intense oxidation of organic pollutants while disintegrating into oxygen molecules.



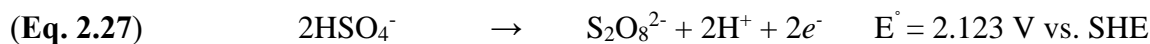
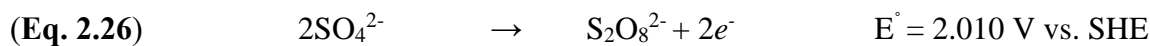
Percarbonate ( $C_2O_6^{2-}$ ), perphosphate ( $P_2O_8^{4-}$ ) and persulphate ( $S_2O_8^{2-}$ ) are also powerful mediators in the indirect oxidation of organics, where persulfate is considered the next-generation AOP due to the formation of the very strong oxidizing sulphate radical ( $SO_4^{\cdot-}$ ), receiving growing attention recently in the field of remediation of organically and inorganically contaminated groundwater as well as soils.



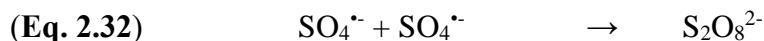
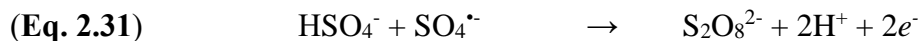
**Figure 2.1** The different pathways of electrochemical oxidation in active and non-active electrodes in the anodic compartment, as well as the oxygen evolution side reactions and the poisoning effect (fouling) on the anode surface.

## 2.4 Electrochemical Formation of Persulfate

Peroxydisulfuric acid ( $H_2S_2O_8$ ) or peroxydisulfate ( $S_2O_8^{2-}$ ) can be prepared electrochemically from sulfate anions on electrodes, characterized by high overpotential for oxygen evolution reaction such as BDD electrodes (Serrano *et al.* 2002, Khamis *et al.* 2010). The mechanism for the preparation of the persulfate has been explained to occur through direct oxidation on the BDD anode where it involves the oxidation of both species of sulfate,  $HSO_4^-$  and  $SO_4^{2-}$ .



Recent studies incorporated the  $\text{SO}_4^{\cdot-}$  radicals in the formation process, along with the contribution of the electrochemically generated hydroxyl radicals in the formation of the persulfate (Serrano *et al.* 2002, Khamis *et al.* 2010, Davis *et al.* 2014, Davis *et al.* 2014). To date, there is no spectroscopic evidence of electrochemical formation of  $\cdot\text{OH}$  or  $\text{SO}_4^{\cdot-}$  at a BDD anode (Marselli *et al.* 2003, Bejan *et al.* 2012). Yet, the  $\cdot\text{OH}$  radical readily formed at BDD anodes has been proposed to react with  $\text{HSO}_4^-$  and  $\text{H}_2\text{SO}_4$ , leading to  $\text{S}_2\text{O}_8^{2-}$  formation (Caro 1898, Palme 1920, Kolthoff and Miller 1951).



Khamis *et al.* (2010) could not prove the existence of free  $\text{SO}_4^{\cdot-}$  radicals via their spectroscopic study, but suggested the formation of the intermediate, surface-adsorbed BDD( $\text{SO}_4^{\cdot-}$ ) radicals, which reacts with sulfate ions  $\text{SO}_4^{2-}$  to produce  $\text{S}_2\text{O}_8^{2-}$  and denied any production of free sulfate radicals. Moreover, Davis *et al.* (2014) reported that persulfate can be electro-generated via two pathways, (i) oxidation of sulfate ions into  $\text{SO}_4^{\cdot-}$  radicals which occurs on BDD surface even before the water oxidation (**Eq. 2.33 – 2.36**), and (ii) indirect oxidation of sulfate ions via  $\cdot\text{OH}$  radicals to form sulfate radicals (**Eq. 2.29 – 2.30**). These sulfate radicals would consequently undergo subsequent oxidation of sulfate ions (**Eq. 2.31**) or recombination (**Eq. 2.32**) to form persulfate. In their DFT model, Davis *et al.* (2014) determined that the most favorable energetic pathway for the formation of persulfate is via sulfate radical recombination (i.e., oxidation of sulfate ions to sulfate radicals).



Therefore, since this sulfate radical formed as an intermediate in the persulfate formation is a strong oxidant itself, it can act as an oxidizing agent to react with organic compounds as a side reaction to persulfate formation. However, despite all these extensive mechanistic studies, electrogenerated

persulfate has been considered to contribute only to a minor extent to bulk oxidation since persulfate has slow oxidation kinetics with organic compounds in the absence of an activator. Sulfate electrolytes have been generally considered inert, and thus BDD electrooxidation mechanisms in the presence of sulfate have typically been interpreted by the action of  $\cdot\text{OH}$  not  $\text{SO}_4^{\cdot-}$  (Brillas *et al.* 2009, Panizza and Cerisola 2009, Sirés *et al.* 2014).

Hence, it is important to investigate the possible contribution of the sulfate-based oxidizing agents that are potentially electro-generated in BDD-based electrochemical oxidation systems employing electrolytic solutions that contain sulfate ions, and elucidate their role in the oxidation of persistent organic chemicals and under various operating conditions.

## 2.5 Concluding Summary and Thesis Objectives

There has been increasing interest in recent years in electrooxidation to remove persistent organic contaminants from wastewater (Oturán 2014), especially using BDD anodes. This is because a BDD anode has high electrocatalytic activity towards organic oxidation via generating  $\cdot\text{OH}$  radicals, which are capable of oxidizing organic contaminants (Comninellis 1994, Chen *et al.* 2003). Most literature on electrochemical advanced oxidation processes focuses on the efficiency of the oxidation of numerous organic contaminants via hydroxyl radicals and examines the different possible methods of interaction between these oxidants and the investigated organic compounds. However, despite the published knowledge on the persulfate electro-formation from sulfate ions via the participation of sulfate radicals, there are no extensive studies focusing on the possible contribution of these electro-generated sulfate radicals to the electrochemical oxidation of the organic contaminants.

Since persulfate has slow oxidation kinetics with organic compounds in the absence of an activator, electrogenerated persulfate has been considered to contribute only to a minor extent to the bulk oxidation, and BDD electrooxidation mechanisms in the presence of sulfate have typically been interpreted by the action of  $\cdot\text{OH}$  not  $\text{SO}_4^{\cdot-}$  radicals (Brillas *et al.* 2009, Panizza and Cerisola 2009, Sirés *et al.* 2014). However,  $\text{SO}_4^{\cdot-}$  are strong oxidants with similar redox potential as  $\cdot\text{OH}$  radicals, and both radicals have been reported to react with many pharmaceuticals at comparable oxidation rates (Neta *et al.* 1977, Buxton *et al.* 1988, Rickman and Mezyk 2010, Matta *et al.* 2011). Thus, electrolysis of sulfate ions to sulfate radical species ( $\text{HSO}_4^{\cdot}$ ,  $\text{SO}_4^{\cdot-}$ ) may have a significant effect on the oxidation kinetics and degradation pathways of contaminants in electrochemical treatment of wastewater. Given that sulfate can be present in municipal and industrial wastewaters at significant

concentrations of several hundred mg L<sup>-1</sup> up to g L<sup>-1</sup> level (United-Nations-Environment-Programme 1990, Tchobanoglous *et al.* 2002, Sgroi *et al.* 2014), it is important to elucidate the role of sulfate ions in the electrooxidation processes at BDD anodes.

Therefore, the objective of this PhD project is to address the potential electrochemical oxidation of organic contaminants in the presence of sulfate ions via *in-situ* produced sulfate-based oxidizing species. The presence of such sulfate-based oxidants would demonstrate that the sulfate solutions used as electrolytes in electrochemical systems, might not be inert in the electrooxidation processes, contrary to what is assumed in literature. The evidence of the presence of these *in-situ* produced sulfate reactive oxidizing species, most likely to be SO<sub>4</sub><sup>•-</sup> radicals, would also contribute to further understanding of the mechanism for the electrochemical degradation of persistent organic compounds at BDD anodes, using SO<sub>4</sub><sup>2-</sup> ions as electrolytes. Hence, this study aimed to investigate the role of sulfate ions in the electrochemical oxidation of contaminants at BDD anodes by:

- (i) Elucidating the potential participation of electrogenerated sulfate-based oxidizing species in electrochemical oxidation of persistent organic contaminants such as pharmaceuticals and pesticides,
- (ii) Exploring the effect of operating conditions governing the sulfate-based electrooxidation process such as anolyte concentration/conductivity and volume, as well as applied current density, besides examining the reactive life-time of these sulfate-based oxidants, and
- (iii) Studying the impact of the chloride ions on the sulfate-based electrooxidation process, and on the formation of organic and inorganic chlorinated by-products.

Chapter 4 of this work investigated the role of the sulfate ions in the higher electrooxidation rates of persistent organics observed in electrochemical treatment of contaminated water at BDD anodes. The aim was to elucidate the potential participation of electrogenerated sulfate reactive oxidizing species in electrooxidation of persistent organic contaminants, by comparing different anolyte types as well as testing several persistent organic compounds. Probe compounds were also investigated to provide further evidence for the electro-formation of sulfate-based oxidizing agents.

Chapter 5 studied the influence of the operating conditions governing the generation and contribution of the electro-chemically generated sulfate-based oxidants in the removal of a model compound, diatrizoate. The main operating parameters investigated in this study were the concentration/conductivity of the anolyte as well as the anodic current density and the volume of the anolyte solutions.



The characteristics of these oxidants and their potential extended reactive life-time were explored in Chapter 6. By applying intermittent electric current, the ongoing reaction of these longer-lived oxidants in the bulk liquid could be utilised as an option to reduce energy consumption. Delayed on-bench quenching with methanol was also tested to further confirm the longevity of the sulfate-based oxidizing agents and to identify some of the governing parameters in more detail.

In Chapter 7, the effect of the presence of chloride ions was examined in different electrolyte solutions. Using sulfate and nitrate (as an inert control) electrolytes, prepared with the addition of varying concentrations of chloride, the electrochemical treatment of resorcinol, as a surrogate of natural organic matter, was studied. The potential inhibition effect exerted by chloride on sulfate-based removal and mineralization of resorcinol was examined. Furthermore, the effect of sulfate on the formation of organic chlorinated by-products as well as inorganic by-products such as chlorate and perchlorate was also studied.

## **Chapter 3: Major Research Methodology**

This chapter presents the major research approach for this study including the materials and methods, covering all the results chapters. It includes a detailed description of the Reactor Design and Specifications (Section 3.1) as well as Chemicals and Reagents (Section 3.2). This chapter also describes the all the Chemical Analyses (Section 3.3) used in this study, including Liquid Chromatography - Mass Spectrometry (Section 3.3.1), High Performance Liquid Chromatography (Section 3.3.2), Ion Chromatography (Section 3.3.3) and Adsorbable Organic Chlorides (Section 3.3.4). It also details the procedure for the quantification of persulfate and hydrogen peroxide (Section 3.3.5). Sampling Procedure and Data Analysis (Section 3.4) are defined as well in this chapter, in addition to the Energy Consumption Estimation (Section 3.5).

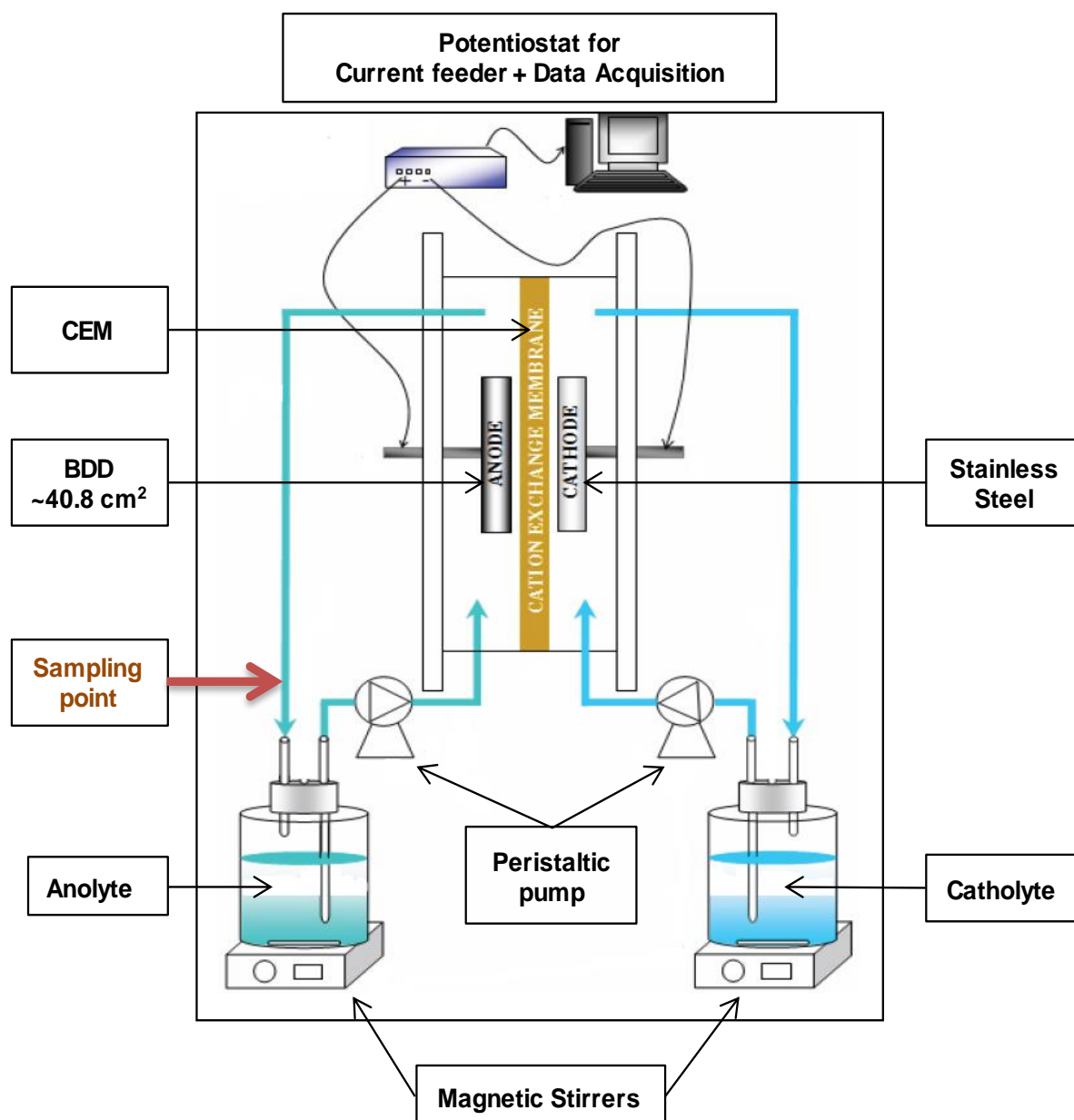
### 3.1 Reactor Design and Specifications

The experiments were performed in a laboratory-scale plate-and-frame electrolytic cell, divided by a cation exchange membrane (CEM). The CEM (Ultrex CMI-7000, Membranes International, Ringwood, NJ, U.S.A.) was introduced into the cell configuration to divide the solution into anode half-cell (anolyte) and cathode half-cell (catholyte), where only the cations diffusion is permissible and the anions diffusion is halted. This modified configuration enables the separate investigation of the oxidation reaction mechanisms and avoids the reduction of the oxidized species at the cathode. The inter-electrode distance between the two electrodes was 3.5 cm, and the dimensions of the anodic or cathodic compartment were  $20 \times 5 \times 2$  cm, and thus the net volume of the anodic and cathodic compartment was 200 mL each. A schematic diagram of the utilized reactor with its two-compartment electrochemical system is shown in **Figure 3.1** (noting that reactor dimensions in the figure are not up to scale).

Working electrode was DIACHEM® BDD (polycrystalline,  $5\mu\text{m}$  thick, 1000–4000 ppm boron doping on monocrystalline niobium plate from one side only) purchased from Condias (Itzehoe, Germany), and stainless steel was used as the counter electrode. The BDD electrode dimensions were  $4.8 \times 8.5$  cm with a thickness of around 2 mm, and the stainless steel electrode had roughly the same surface area of  $\sim 40\text{ cm}^2$ .

When the anodic compartment is filled with the anolyte solution in the absence of any flow, the fraction of the volume in the region above the anode is 60 mL and that below the anode is 55 mL as per the reactor configuration. The anolyte volume surrounding the anode is 85 mL, with 75 ml being between the BDD anode surface and the cation exchange membrane (i.e., active surface of the BDD anode), thus leaving only 10 mL of the anolyte volume on the other side of the BDD anode (i.e., the inactive niobium layer).

Prior to the experiments, the BDD electrode was polarized anodically for 2 h in 0.1 M  $\text{H}_2\text{SO}_4$  at constant anodic potential of 3.0 V vs Standard Hydrogen Electrode (SHE). The reference electrode was a 3M Ag/AgCl (+0.210 V vs SHE), supplied by BASi (West Lafayette, IN, U.S.A.), which was placed in the proximity of the working electrode. Chronopotentiometric electrolysis experiments were conducted using a VSP potentiostat/ galvanostat, using an external booster channel (BioLogic, Claix, France).



**Figure 3.1** Schematic diagram of the utilized reactor with its two-compartment electrochemical system, using stainless steel as the cathode and boron doped diamond as the anode

All electrochemical oxidation experiments were conducted at room temperature ( $23 \pm 2$  °C) in batch mode with anodic and cathodic flow rates of  $200 \text{ mL min}^{-1}$ . The change in temperature was found in the preliminary experiments to be insignificant as the system was vented, and thus temperature was not an influencing factor in this study. Anodic glassware used in chemical and electrochemical oxidation experiments were protected from light to halt any possible degradation occurring to effect of light. During most experiments, no pH control was conducted unless pH effect was being examined. In all cases, no buffer solutions were employed to avoid any possible contribution of the buffer constituents. The anodic reactions took place in the acidic range because of the acidic nature of the electrolytic solution and because the pH dropped very quickly in the anodic department due to

the oxygen evolution reaction which produce  $H^+$  along with  $O_2$ . The anode chamber contained the target organic compounds dissolved in the electrolyte solution (sodium sulfate, nitrate, or perchlorate) prepared at different characteristics (concentration, conductivity, and pH). The cathodic chamber in all experiments contained the same electrolyte solution as the anolyte solution, with the same characteristics, but without any organic compounds.

## 3.2 Chemicals and Reagents

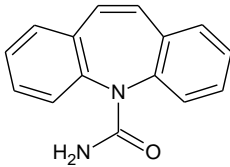
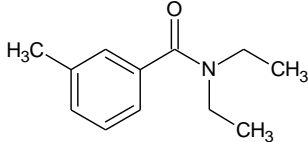
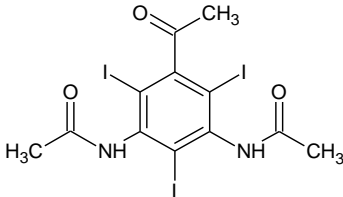
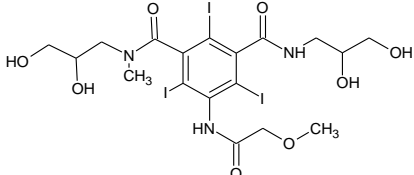
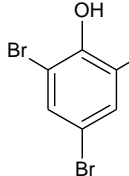
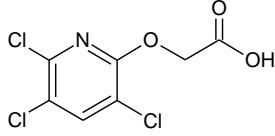
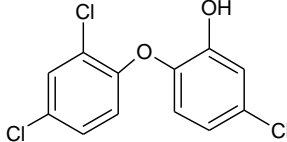
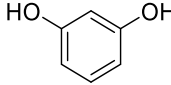
The target organic compounds investigated in this work were diatrizoate, carbamazepine, N,N-diethyl-meta-toluamide (DEET), iopromide, tribromophenol, triclosan. **Table 3.1** presents the seven persistent organic compounds along with their molar masses, octanol-water partitioning coefficient ( $\log K_{ow}$ ),  $pK_a$ , as well as their chemical structures. Analytical standards for these target organic compounds as well as nitrobenzene and resorcinol were purchased from Sigma-Aldrich (Steinheim, Germany). Sodium sulfate ( $Na_2SO_4$ ), sodium chloride ( $NaCl$ ), hydrogen peroxide ( $H_2O_2$ ), *tert*-butanol, were also purchased from Sigma-Aldrich (Steinheim, Germany). Sodium nitrate ( $NaNO_3$ ), sodium perchlorate ( $NaClO_4$ ), potassium chlorate ( $KClO_3$ ), and sodium hydroxide ( $NaOH$ ) were purchased from Chem-Supply (Gillman, Australia). Sulfuric acid ( $H_2SO_4$ , 98%), hydrochloric acid ( $HCl$ , 32%) and solvents for liquid chromatography (acetonitrile, methanol) were purchased from Merck (Darmstadt, Germany). Potassium persulfate ( $K_2S_2O_8$ ), nitric acid ( $HNO_3$ , 69%) and formic acid were purchased from Ajax Finechem (Auckland, New Zealand). Sodium bisulfite ( $NaHSO_3$ ) was purchased from Acros Organics (Geel, Belgium). All solutions were prepared using analytical grade reagents and Milli-Q water.

## 3.3 Chemical Analysis

### 3.3.1 Liquid Chromatography - Mass Spectrometry

The target persistent organic compounds investigated in this study were analysed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) using negative and positive electrospray ionization mode (ESI), on a Shimadzu Prominence ultrafast LC (UFLC) system (Shimadzu, Kyoto, Japan) coupled with a 4000 QTRAP MS equipped with a Turbo Ion Spray Source (Applied Biosystems-Sciex, Foster City, CA, U.S.A.). Diatrizoate, carbamazepine, DEET, and iopromide were detected and quantified using the positive mode; whereas tribromophenol, triclopyr, and triclosan were quantified using the negative mode. The limit of detection was  $1.0 \mu\text{g/L}$  for all compounds. **Table 3.2** displays the conditions of the LC separation method and its gradient for both methods.

**Table 3.1** The recalcitrant organic compounds investigated in this study along with their molar masses, octanol-water partitioning coefficient (log  $K_{ow}$ ),  $pK_a$ , and chemical structure. (The values are reported from the EPI-Suite v4.11 software)

Chemical Name	Molecular formula	Molar mass (g/mol)	Log $K_{ow}$	$pK_a$	Chemical Structure
<b>Carbamazepine</b> (CBZ)	$C_{15}H_{12}N_2O$	236.27	2.25	13.9	
<b>N,N-Diethylmeta-toluamide</b> (DEET)	$C_{12}H_{17}NO$	191.27	2.26	1.95	
<b>[Sodium] Diatrizoate</b> (DTR)	$C_{11}H_9I_3N_2O_4$	613.91	1.37	3.4	
<b>Iopromide</b> (IPM)	$C_{18}H_{24}I_3N_3O_8$	791.11	-2.49	9.9	
<b>Tribromophenol</b> (TBP)	$C_6H_3Br_3O$	330.80	4.18	6.8	
<b>Triclopyr</b> (TCPA)	$C_7H_4Cl_3NO_3$	256.46	2.53	2.7	
<b>Triclosan</b> (TCN)	$C_{12}H_7Cl_3O_2$	289.54	4.66	8.1	
<b>Resorcinol</b> (RES)	$C_6H_6O_2$	110.1	0.80	9.43	

**Table 3.2 Conditions of liquid chromatography (LC) separation method with the details of the employed gradient**

LC Separation Column	Alltima C18 Column (250 × 4.6 mm, particle size 5 μm) from Alltech Associates Inc. (Deerfield, IL, USA)																
Temperature of Operation	40 °C																
Positive Mode																	
Mobile Phase Solutions	<i>Eluent A</i> : Acetonitrile with 0.1% formic acid <i>Eluent B</i> : HPLC grade water with 0.1% formic acid																
Gradient Method	<table border="1"> <thead> <tr> <th><i>Time (min)</i></th> <th><i>Pump B concentration (%)</i></th> </tr> </thead> <tbody> <tr><td>0.50</td><td>5</td></tr> <tr><td>5.00</td><td>60</td></tr> <tr><td>13.00</td><td>90</td></tr> <tr><td>15.00</td><td>100</td></tr> <tr><td>17.00</td><td>100</td></tr> <tr><td>18.00</td><td>5</td></tr> <tr><td>23.00</td><td>5</td></tr> </tbody> </table>	<i>Time (min)</i>	<i>Pump B concentration (%)</i>	0.50	5	5.00	60	13.00	90	15.00	100	17.00	100	18.00	5	23.00	5
<i>Time (min)</i>	<i>Pump B concentration (%)</i>																
0.50	5																
5.00	60																
13.00	90																
15.00	100																
17.00	100																
18.00	5																
23.00	5																
Negative Mode																	
Mobile Phase Solutions	<i>Eluent A</i> : Acetonitrile and methanol (1:1; v/v) <i>Eluent B</i> : HPLC grade water with 1mM ammonium acetate																
Gradient Method	<table border="1"> <thead> <tr> <th><i>Time (min)</i></th> <th><i>Pump B concentration (%)</i></th> </tr> </thead> <tbody> <tr><td>0.50</td><td>95</td></tr> <tr><td>7.00</td><td>10</td></tr> <tr><td>10.00</td><td>10</td></tr> <tr><td>12.00</td><td>0</td></tr> <tr><td>15.00</td><td>0</td></tr> <tr><td>16.00</td><td>95</td></tr> <tr><td>21.00</td><td>95</td></tr> </tbody> </table>	<i>Time (min)</i>	<i>Pump B concentration (%)</i>	0.50	95	7.00	10	10.00	10	12.00	0	15.00	0	16.00	95	21.00	95
<i>Time (min)</i>	<i>Pump B concentration (%)</i>																
0.50	95																
7.00	10																
10.00	10																
12.00	0																
15.00	0																
16.00	95																
21.00	95																

The source-dependent parameters in the mass spectrometer (MS) were as follows: curtain gas (CUR), 30 V; nitrogen collision gas (CAD), high; source temperature (TEM), 700°C; ion source gases GS1 and GS2, 62 V; ion spray voltage, 5500 V, and entrance potential (EP), 10 V. The settings for the compound-dependent parameters of each transition are summarized in **Table 3.3**.

**Table 3.3 The optimized compound-dependent mass spectrometry (MS) parameters: declustering potential (DP), collision energy (CE) and cell exit potential (CXP) for each compound and each transition of the negative and positive mode**

Organic compound	Q1 Mass (Da)	Q3 Mass (Da)	DP	CE	CXP
<b>Carbamazepine</b>	237.2	193.3	61	47	12
	237.2	194.2	61	27	16
<b>DEET</b>	192.2	91.2	61	45	6
	192.2	119.1	61	25	8
<b>Diatrizoate</b>	615	361	80	30	10
	615	233.1	85	33	10
<b>Iopromide</b>	791.88	773.87	120	35	10
	791.88	572.9	125	54	10
<b>Tribromophenol</b>	326.7	79	-90	-72	-10
	328.7	81	-92	-72	-12
<b>Triclopyr</b>	256.01	198	-55	-30	-10
	254.01	196	-55	-30	-10
<b>Triclosan</b>	287	35.4	-40	-35	-7
	289	37.4	-40	-35	-7

### 3.3.2 High Performance Liquid Chromatography

Nitrobenzene and resorcinol were analysed by high performance liquid chromatography (HPLC) equipped with a diode array UV-detector (SPD-M10AVP) purchased from Shimadzu, Japan. An Alltima C<sub>18</sub> column (5 µm; 4.6 × 250 mm) was operated at 35°C, with an isocratic mobile phase of methanol/water to elute the target compounds. Nitrobenzene was eluted using 1:1 methanol/water (v/v) at 1 mL min<sup>-1</sup>, and detected at 254 nm; whereas, 0.125:0.875 methanol/water (v/v) was employed at 0.7 mL min<sup>-1</sup> to elute resorcinol which was detected at 266 nm. The injection volume in both methods was 40 µL.



### 3.3.3 Ion Chromatography

The concentrations of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{ClO}_3^-$ , and  $\text{ClO}_4^-$  were determined by ion chromatography (IC) using Dionex ICS-2100 (Sunnyvale, CA), equipped with a DS6 heated conductivity detector (35°C). A potassium hydroxide (KOH) eluent was applied at flow rate of  $1 \text{ mL min}^{-1}$ , starting with 20 mM KOH for the first 6 minutes, then it was raised to 60 mM over 2 min, kept at 60 mM for 12 min, and then lowered straight to 20 mM and kept at 20 mM for 4 min (total analysis time 24 min). The injection volume was 25  $\mu\text{L}$  and the separation was achieved with a Dionex IonPac AG19 ( $4 \times 50 \text{ mm}$ ) guard and an IonPac AS19 separating column ( $4 \times 250 \text{ mm}$ ), heated to 30°C.

### 3.3.4 Adsorbable Organic Chlorides (AOCI)

The total organic chlorides were determined by measuring the adsorbable organic halide (AOX) using AQF-2100H Shimadzu system (Japan) which involved an automatic quick furnace followed by a gas absorption unit and ending with IC system. The 30 mL samples were acidified with 10  $\mu\text{L}$  of 70% nitric acid, unless already at pH 2. Then 10 mL of the sample was used to flush/purge the system, before concentrating another 10 mL of the sample on two consecutive activated carbon cartridges (40 mg activated carbon per glass column with 2 mm inner diameter; CPI International, California, USA) using the Mitsubishi TX-3AA Adsorption Module. The enriched cartridges were then washed with 10 mL of  $8.2 \text{ g L}^{-1}$  potassium nitrate ( $\text{KNO}_3$ ;  $\geq 99\%$  purity; Sigma-Aldrich, Germany) and 1 mL MilliQ water to remove inorganic halides, followed by drying the cartridge via injecting 5 mL air into the cartridges. Then the enriched activated carbon collected after the Adsorption Module step was combusted into hydrogen chloride gas in the automatic quick furnace AQF-2100 in the presence of oxygen for 4 – 5 min at 1000°C. The produced halide gas was absorbed in the gas adsorption unit GA-210 with 10mL hydrogen peroxide solution (50  $\mu\text{L}$ ) to reduce chloride gas to chloride ions, which were then measured in a Dionex ICS-2100 ion chromatograph (Thermo Fisher Scientific, Australia). The measured concentration of  $\text{Cl}^-$  corresponds to the total adsorbable organic chlorides (AOCI). A Dionex Eluent Generator Cartridge III with 30–75 mM KOH with a flow rate of  $1 \text{ mL min}^{-1}$  was used to elute the  $\text{Cl}^-$  over a Dionex IonPac AS11-HC column and AG11-HC guard column.

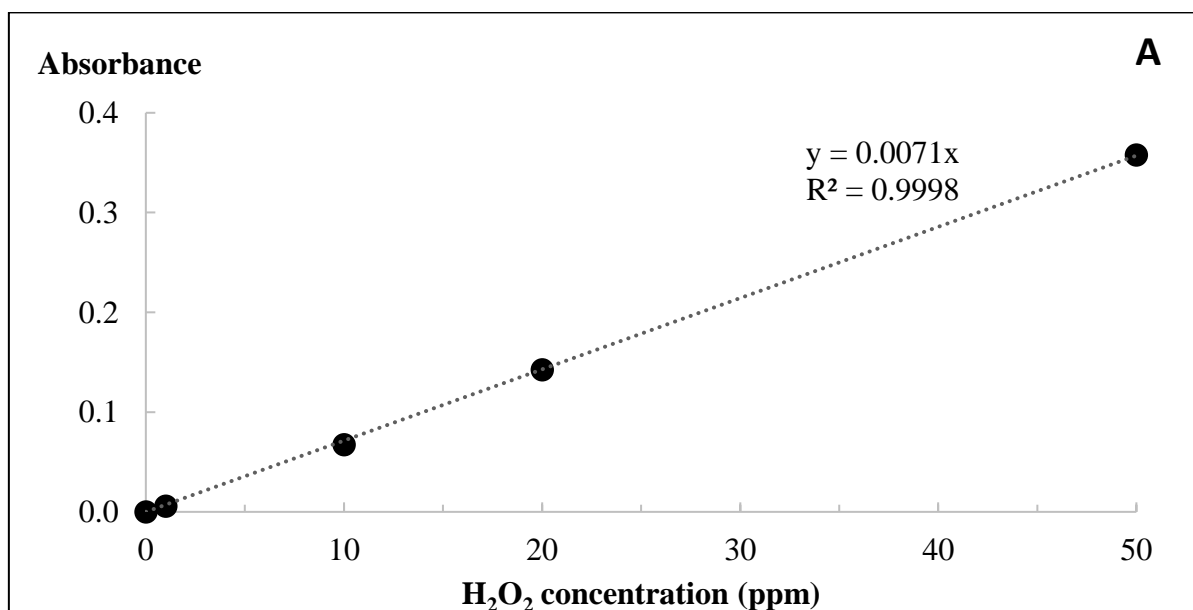
### 3.3.5 Hydrogen Peroxide and Persulfate Quantification

In regard to the potential interferences in the generally applied methods, the chemical analysis of  $\text{H}_2\text{O}_2$  and persulfate  $\text{S}_2\text{O}_8^{2-}$  was conducted using two different methods.

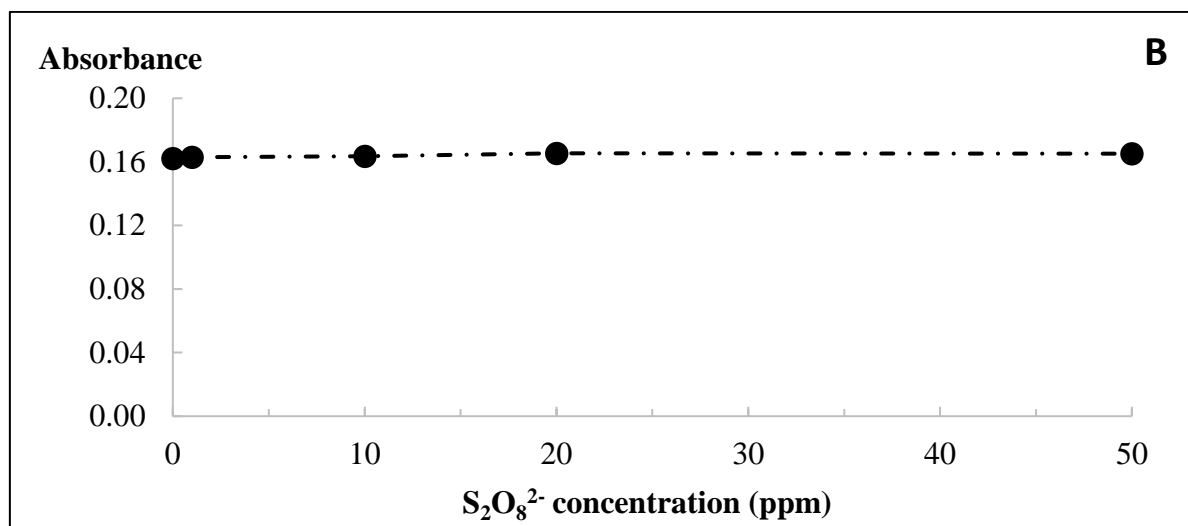
Both  $S_2O_8^{2-}$  and  $H_2O_2$  have been reported to form in electrochemical systems (Saracco *et al.* 2000, Serrano *et al.* 2002). Persulfate has also been described to possibly decompose to hydrogen peroxide in strongly acidic aqueous solutions (Kolthoff and Miller 1951). But both oxidants are expected to react with reducing agents like potassium iodide (Saracco *et al.* 2000, Lin *et al.* 2014) or ferric ions ( $Fe^{2+}$ ) which is a widely known activator for these oxidants to produce their corresponding radicals (Cao *et al.* 2008, Velo-Gala *et al.* 2014). Therefore, it was crucial to develop a quantification method capable of measuring each oxidant while accounting for any potential interference.

Hydrogen peroxide concentration was quantified in this study with ammonium metavanadate (Nogueira *et al.* 2005), yielding a linear regression of  $R^2=0.9998$  for  $H_2O_2$  concentrations of 1 – 60 mM (**Figure 3.2**). This method was tested for different concentrations of  $H_2O_2$  in the presence and absence of persulfate ( $S_2O_8^{2-}$ ), where 1 mL ammonium metavanadate was added to 9 mL of the aqueous sample containing hydrogen peroxide prepared with the corresponding concentration. Further investigation for any possible interferences of  $S_2O_8^{2-}$  in the measurement was conducted by adding different concentrations of  $S_2O_8^{2-}$  (1 – 60 mM) to a fixed concentration of  $H_2O_2$  solution (0.6 mM; 20 mg L<sup>-1</sup>), **Figure 3.3**.

Results show that the ammonium metavanadate method was found to be insensitive to the presence of  $S_2O_8^{2-}$  in the investigated concentration range (i.e., from 1 to 60 mg L<sup>-1</sup>  $S_2O_8^{2-}$ ). Thus, this method was used for the measurement of  $H_2O_2$  concentration in the solution.

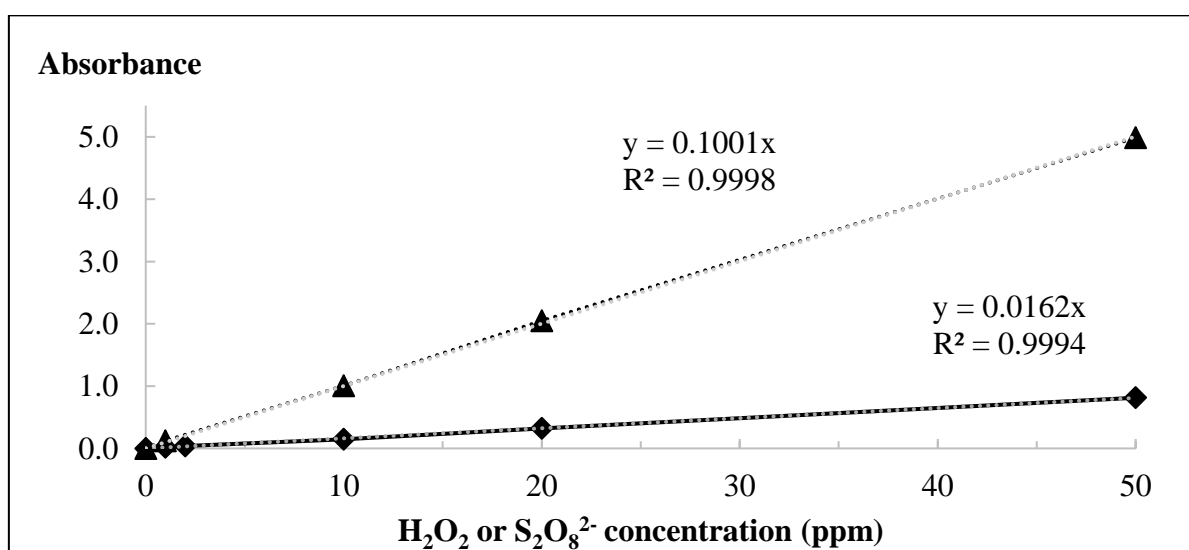


**Figure 3.2: Absorbance measured at 460 nm using the metavanadate method for 1 – 60 mM solution of hydrogen peroxide in the absence of any persulfate**



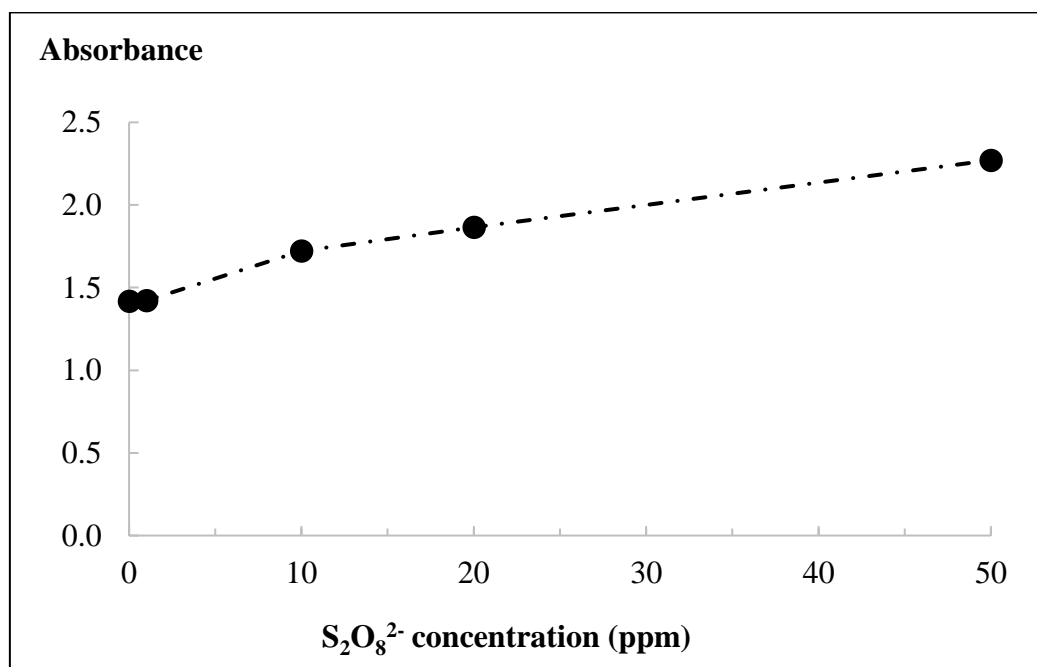
**Figure 3.3** Absorbance measured at 460 nm using the metavanadate method for 1 – 60 mM solution of persulfate in the presence of 0.6 mM hydrogen peroxide

The ferrous/thiocyanate method was used to detect both oxidants by dissolving 0.1 mL of the aqueous sample into 10 mL  $H_2SO_4$  and adding 0.9 mL water and 0.1 mL of 0.4 M ferrous ammonium sulfate then mixed for 40 min before adding 0.2 mL of 0.6M ammonium thiocyanate ( $NH_4SCN$ ) to colour the sample (Huang *et al.* 2002). Results show that persulfate was detected with the ferrous/thiocyanate method, but was found to be susceptible to  $H_2O_2$  interference. The addition of  $H_2O_2$  in the range of  $1.0\text{ mg L}^{-1}$  to  $60\text{ mg L}^{-1}$  without any addition of  $S_2O_8^{2-}$  ions significantly coloured the solution and reported a linear increase in the absorbance, similar to that of  $S_2O_8^{2-}$  without any addition of  $H_2O_2$  (Figure 3.4).



**Figure 3.4** Absorbance measured at 460 nm using the ferrous/thiocyanate method for 1 – 60 mM solutions of hydrogen peroxide (◆) or persulfate (▲)

Moreover, the absorbance values reported for  $\text{H}_2\text{O}_2$  ( $0.6 \text{ mM}$ ;  $20 \text{ mg L}^{-1}$ ) significantly increased from 1.42 to 2.27 as concentration of added  $\text{S}_2\text{O}_8^{2-}$  increased from 0 to  $60 \text{ mg L}^{-1}$  (**Figure 3.5**), signifying that both oxidants were detected. Thus, this method was used for determining a combined concentration of  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$  in the solution.



**Figure 3.5 Absorbance measured at 460 nm using the ferrous/thiocyanate method for 0.6 mM solution of hydrogen peroxide with the addition of 1 – 60 mM persulfate concentrations**

### 3.4 Sampling Procedure and Data Analysis

The kinetic study involved periodic sampling by taking aqueous samples from the analyte solution containing the target organic compound along with the electrolytic ions over a period of up to 8 hours. During periodic sampling, samples were collected and were frozen or immediately quenched with methanol (MeOH) to halt any oxidizing activity of the radicals on the organic contaminants, unless mentioned otherwise. For the analytical quantification, 1.0 ml samples were prepared by quenching an aqueous sample of  $750 \mu\text{L}$  by  $250 \mu\text{L}$  MeOH. The concentrations of the target organic compounds or analytic ions were then measured using LC-MS, HPLC, and/or IC.

For data processing, measured concentrations ( $C$ ) were normalized against the initial concentration ( $C_0$ ) of target organic contaminant. All the concentration ratios values ( $C/C_0$ ) from duplicate or replicate experiments were then fitted with a pseudo-first order kinetic relationship because the concentration of the formed radicals were expected to be in high excess compared to that of the

organic compounds being studied. The best-fit values of a pseudo-first order kinetic decay rate were determined by a nonlinear parameter estimation routine in Aquasim 2.1d (Reichert 1994), and these values were expressed with estimates of error at the 95% confidence level. The confidence limits were calculated using a standard error estimated by Aquasim and an appropriate  $t$ -value for the respective number of degrees of freedom ( $\text{DOF} > 10$ ) of the duplicate experiment. In all results, the values are expressed as the mean of at least two experiments, with their standard deviations.

### 3.5 Energy Consumption Estimation

The energy consumption calculations for the electrochemical oxidation of target persistent organic compounds investigated in this study were based on the average cell voltage. Since the degradation reactions of target contaminants was observed to be of first order kinetics, it was decided to express the consumption of energy input per order of pollutant reduction. Thus, electric energy per order ( $E_{EO}$ ) was used as a more appropriate parameter to estimate energy consumption of the electrochemical system. It primarily estimates the electric energy,  $\text{kWh m}^{-3}$ , consumed to reduce the concentration of the organic contaminant by one order of magnitude in a unit volume of treated solution.

The electric power was calculated from the applied current ( $I$ , A) and the average cell voltage ( $U$ , V) per volume of treated solution ( $V$ , L), then multiplied by the reaction time ( $t$ , h) required to achieve the corresponding order of magnitude of removal as per the following formula (Bolton *et al.* 2001).

$$\text{(Eq. 3.1)} \quad E_{EO} = \frac{U \cdot I \cdot t}{V \cdot \log \frac{C_0}{C}}$$

## Chapter 4: Role of Sulfate Electrolyte in Electrochemical Oxidation of Recalcitrant Organics at Boron-doped Diamond Anodes

This chapter presents the results of investigating the effect of sulfate anolyte in the electrochemical oxidation of contaminants at BDD anodes. It presents the outcomes of the study on the effect of anolyte nature on electrooxidation rates of persistent organic contaminants (Section 4.3.1), as well as the electro-generation of persulfate and its potential role in the diatrizoate electrooxidation (Section 4.3.2). It also elucidates the potential role of electro-generated sulfate radicals in the electrooxidation of diatrizoate (Section 4.3.3) and describes the effect of specific radical quenchers on the electrooxidation of diatrizoate (Section 4.3.4), and the electrooxidation of nitrobenzene in Na<sub>2</sub>SO<sub>4</sub> anolyte (Section 4.3.5). Moreover, the electric energy consumption and potential savings were further reported in this Chapter (Section 4.3.6).

This chapter is an edited version of the following publication:

- Farhat, A., Tait, S., Keller, J., Radjenovic, J. (2015). Removal of Persistent Organic Contaminants by Electrochemically Activated Sulfate. *Environ. Sci. Technol.*, 2015, 49 (24), pp 14326–14333. DOI: 10.1021/acs.est.5b02705.

## 4.1 Introduction

In environmental applications, boron-doped diamond (BDD) anodes have attracted a lot of interest in electrochemical oxidation processes for removing persistent organic contaminants from wastewater, because of their ability to electro-generate hydroxyl radicals ( $\cdot\text{OH}$ ) capable of mineralizing organic contaminants (Chen *et al.* 2003, Oturan 2014). Besides  $\cdot\text{OH}$  as well as ozone and hydrogen peroxide, BDD anodes can also produce peroxy species (e.g.,  $\text{C}_2\text{O}_6^{2-}$ ,  $\text{P}_2\text{O}_8^{4-}$  and  $\text{S}_2\text{O}_8^{2-}$ ) in the presence of their corresponding ions (Saha *et al.* 2003, Cañizares *et al.* 2009, Panizza and Cerisola 2009, Meas *et al.* 2011), where persulfate has been reported to possess slow oxidation kinetics with organic compounds in the absence of an activator. Thus, BDD electrooxidation mechanisms in the presence of sulfate have typically been interpreted by the action of  $\cdot\text{OH}$ , while considering sulfate an inert anolyte (Brillas *et al.* 2009, Panizza and Cerisola 2009, Sirés *et al.* 2014).

However, persulfate formation is considered to occur via oxidation of sulfate ions to sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) and recombination of two  $\text{SO}_4^{\cdot-}$  to yield  $\text{S}_2\text{O}_8^{2-}$  (Serrano *et al.* 2002, Cañizares *et al.* 2009, Davis *et al.* 2014). Yet, as in the case of  $\cdot\text{OH}$  generated at a BDD anode (Marselli *et al.* 2003, Bejan *et al.* 2012), there is no spectroscopic evidence of electrochemically formed  $\text{SO}_4^{\cdot-}$ . The principal pathway for the formation of  $\text{SO}_4^{\cdot-}$  is reported to occur by advanced oxidation processes, where  $\text{SO}_4^{\cdot-}$  are produced via heat, UV, alkaline, or metal-catalyst activation of persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) or peroxymonosulfate ( $\text{HSO}_5^-$ ) (Tsitonaki *et al.* 2010). Sulfate radicals are strong oxidants with a redox potential  $E^\circ(\text{SO}_4^{\cdot-}/\text{SO}_4^{2-}) = 2.5 - 3.1 \text{ V}$  (Neta *et al.* 1988, Zhang *et al.* 2014), which is similar to the redox potential of hydroxyl radicals at acidic pH ( $E^\circ(\cdot\text{OH}/\text{H}_2\text{O}) = 2.7 \text{ V}$ ) (Buxton *et al.* 1988, Wardman 1989).

Both radicals have been reported to react with many pharmaceuticals at comparable oxidation rates (Neta *et al.* 1977, Buxton *et al.* 1988, Rickman and Mezyk 2010, Matta *et al.* 2011). Yet,  $\text{SO}_4^{\cdot-}$  tends to react primarily via electron transfer mechanisms, and  $\cdot\text{OH}$  is more likely to react via addition to unsaturated bonds and H-abstraction (Anipsitakis and Dionysiou 2004). Thus, electrolysis of ‘assumed inert’ sulfate ions to sulfate radical species ( $\text{HSO}_4^{\cdot}$ ,  $\text{SO}_4^{\cdot-}$ ) may have a significant effect on the oxidation kinetics and degradation pathways of contaminants in electrochemical treatment of wastewater, rendering it not an inert anolyte solution. Given that sulfate can be present in municipal and industrial wastewaters at significant concentrations of several hundred  $\text{mg L}^{-1}$  up to  $\text{g L}^{-1}$  level (United-Nations-Environment-Programme 1990, Tchobanoglous *et al.* 2002, Sgroi *et al.* 2014), it is important to elucidate the role of sulfate ions in electrooxidation at a BDD anode.

The objective of this study was to investigate the role of sulfate and persulfate ions in the electrochemical oxidation of contaminants at BDD anodes and elucidate the participation of electrogenerated sulfate radical species in electrooxidation of persistent organic contaminants. We have quantified the rates of electrooxidation of several organic contaminants at BDD anode, including diatrizoate, carbamazepine, N,N-diethyl-meta-toluamide (DEET), iopromide, tribromophenol, triclosan and triclopyr. These contaminants were selected due to their high persistence to chemical oxidation, e.g., by ozone or  $\cdot\text{OH}$ . Experiments are performed in sulfate anolyte, and compared with inert nitrate and perchlorate anolytes. To determine the major participating oxidants, electrooxidation experiments were performed with the iodinated contrast media (ICM), diatrizoate, as a model contaminant, in the presence of the radical scavengers, *tert*-butanol and methanol. In an attempt to further segregate the effects of  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$ , the study also examined electrooxidation of nitrobenzene at a BDD anode, as a typical  $\cdot\text{OH}$  probe compound.

## 4.2 Materials and Methods

### 4.2.1 Experimental Setup

All specifications and operating conditions of the laboratory-scale CEM-divided electrochemical reactor are described in the **Cell Design and Reactor Specifications (Section 3.1)**. To investigate the effect of sulfate-based anolyte in electrooxidation at BDD anode, experiments were performed with an applied current density of  $200 \text{ A m}^{-2}$ , using sodium sulfate anolyte ( $\text{Na}_2\text{SO}_4$ , pH 2,  $9.0 \text{ mS cm}^{-1}$ , 40 mM) and compared with sodium nitrate anolyte ( $\text{NaNO}_3$ , pH 2,  $9.0 \text{ mS cm}^{-1}$ , 60 mM), unless stated otherwise. The experiments were performed with seven persistent organic contaminants: diatrizoate, carbamazepine, DEET, iopromide, tribromophenol, triclosan, and triclopyr, each tested separately with an initial concentration of  $2 \mu\text{M}$ . To confirm the inertness of nitrate ions in electrooxidation at a BDD anode, preliminary experiments compared electrooxidation rates of diatrizoate as a model compound in nitrate (60 mM) and perchlorate anolytes (74 mM) prepared at pH 2 and  $9.0 \text{ mS cm}^{-1}$ .

Persulfate can decompose to hydrogen peroxide in strongly acidic aqueous solutions (Kolthoff and Miller 1951). To determine the maximum amount of  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$  generated at the BDD anode in  $\text{Na}_2\text{SO}_4$  (40 mM, pH 2,  $9.0 \text{ mS cm}^{-1}$ ), chronopotentiometric experiments were performed at the highest applied current density (i.e.,  $200 \text{ A m}^{-2}$ ) without added organic, and the concentrations of  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$  were measured. Then, to investigate the contribution of chemical oxidation of  $\text{S}_2\text{O}_8^{2-}$  to electrooxidation,  $2 \mu\text{M}$  solutions of each persistent organic was prepared in  $\text{Na}_2\text{SO}_4$  (40 mM, pH



2, 9.0 mS cm<sup>-1</sup>), followed by adding K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> to a final concentration of 0.55 mM. The mixture was left to react chemically in the absence of any electric current while periodically collecting samples for the analysis of target organic contaminant.

Diatrizoate was also selected to further study the effect of the addition of radical scavengers, *tert*-butanol or methanol (0.1 mM). This study was conducted in Na<sub>2</sub>SO<sub>4</sub> anolytes (36 mM; pH 2; 9.0 mS cm<sup>-1</sup>) with an applied current density of 200 A m<sup>-2</sup>. Additional experiments at lower sulfate concentration and conductivity were conducted to further investigate the effect of the radical scavengers.

Given the lack of a suitable SO<sub>4</sub><sup>•-</sup> probe compound, electrooxidation experiments were performed with nitrobenzene, a common <sup>•</sup>OH probe compound (Liang and Su 2009), at 200 A m<sup>-2</sup>, in Na<sub>2</sub>SO<sub>4</sub> (35 mM) or NaNO<sub>3</sub> anolytes (54 mM). Due to the poor sensitivity of the employed analytical method, nitrobenzene was added at a higher initial concentration (i.e., 400 μM).

In all experiments, the pH of the Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub> anolytes was adjusted to pH 2.0 ± 0.1 with concentrated H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, respectively. This pH was chosen as both radicals exhibit similar redox potentials at acidic pH, and because the production of protons at the anode did not lead to further lowering of the pH that remained constant in all experiments. The selected pH was above the second pK<sub>a</sub> of sulfuric acid (pK<sub>a</sub> (HSO<sub>4</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup>)= 1.92) (Kotz *et al.* 2011), and thus SO<sub>4</sub><sup>2-</sup> ions were the dominant species in the solution. The conductivity of the anolytes was similar in both Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub> solutions in all experiments, where it was mostly fixed at 9.0 ± 0.5 mS cm<sup>-1</sup>.

#### 4.2.2 Chemical Analysis

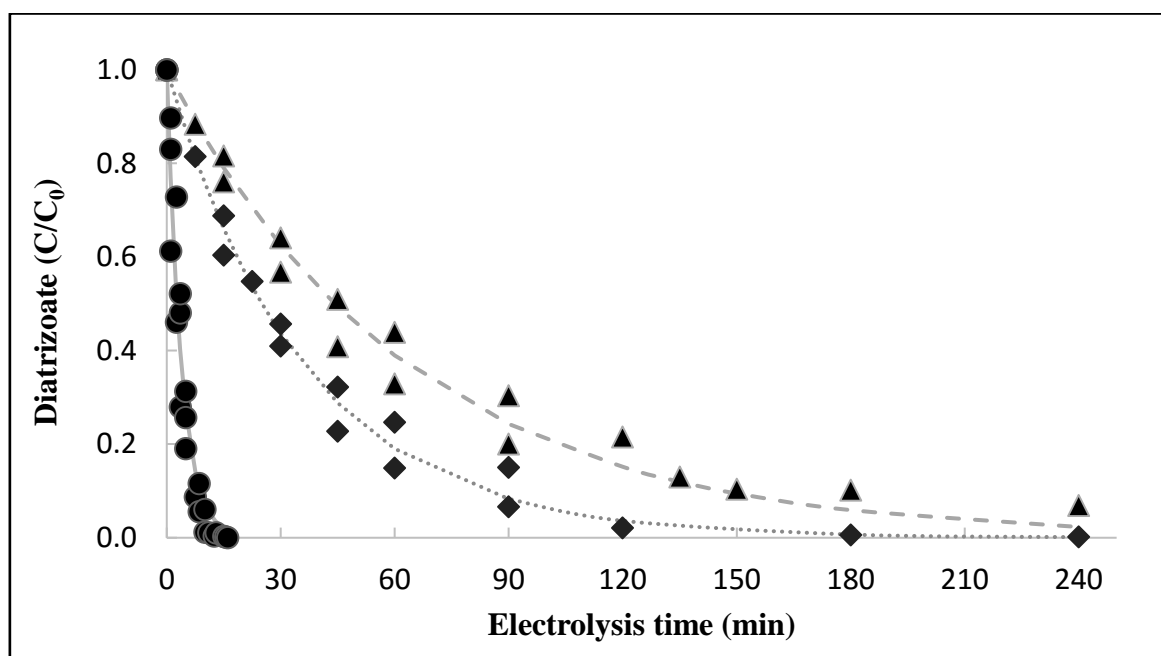
The concentrations of the target organic contaminants were analysed using LC-MS/MS; whereas nitrobenzene concentrations were quantified by using HPLC. Details of the two analytical methods are summarized in **Chemical Analysis Section 3.3.1** and **Section 3.3.2**. In order to measure the concentrations of the electro-generated H<sub>2</sub>O<sub>2</sub> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, the ammonium metavanadate method (Nogueira *et al.* 2005), as well as the ferric/thiocyanate method (Huang *et al.* 2002), were used to overcome the interferences in the quantification of H<sub>2</sub>O<sub>2</sub> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (See **Section 3.3.5** for more details).

Energy consumption was expressed as electric energy per order ( $E_{EO}$ ) as a more appropriate parameter to estimate energy efficiency of the electrochemical system since target contaminants are present at low concentrations. It primarily estimates the electric energy,  $\text{kWh m}^{-3}$ , consumed to reduce the concentration of the organic contaminant by one order of magnitude in a unit volume of treated solution (See **Section 3.5** for more details).

### 4.3 Results and Discussion

#### 4.3.1 Effect of anolyte on electrooxidation rates of persistent organic contaminants

Nitrate and perchlorate ions are known to not react with  $\cdot\text{OH}$  (Pignatello *et al.* 2006). Moreover, both ions are usually considered as inert in electrooxidation at a BDD anode (Sirés *et al.* 2014). In the present work, this was confirmed in preliminary experiments comparing electrooxidation of diatrizoate in  $\text{NaNO}_3$  and  $\text{NaClO}_4$  anolytes (**Figure 4.1**). The apparent rate constants for oxidation of diatrizoate were observed to be  $0.94 \pm 0.07 \text{ h}^{-1}$  and  $1.9 \pm 0.07 \text{ h}^{-1}$  in the nitrate and perchlorate anolytes, respectively. Since both inert electrolytic solutions were similar in their slower removal of DTR as compared to sulfate, it was decided to test only  $\text{NaNO}_3$  as an inert background anolyte for subsequent comparison with  $\text{Na}_2\text{SO}_4$  anolyte because nitrate is more used in literature and is not as toxic as perchlorate, where it is easier to handle in the lab.



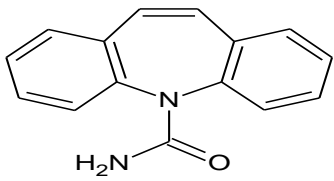
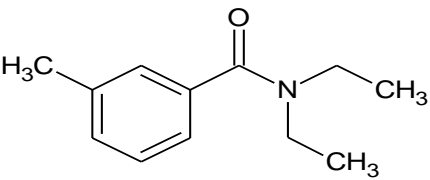
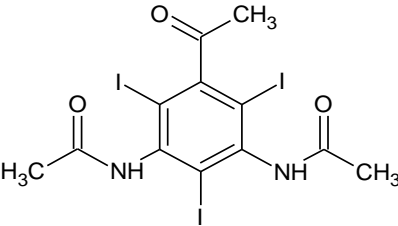
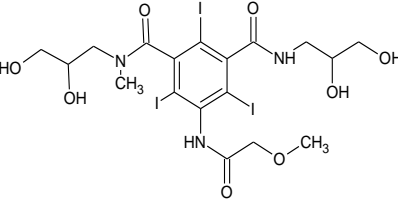
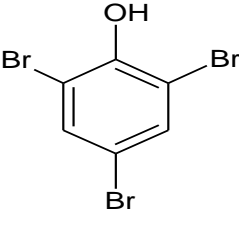
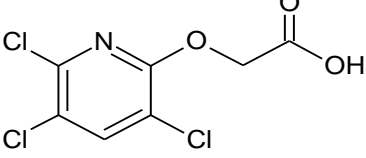
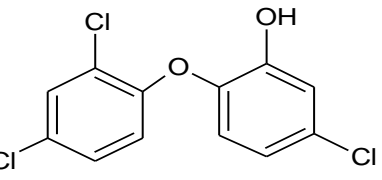
**Figure 4.1** Disappearance of diatrizoate in electrooxidation in  $\text{NaNO}_3$  (▲),  $\text{NaClO}_4$  (◆), and  $\text{Na}_2\text{SO}_4$  (●) anolytes of same initial pH and conductivity (pH 2,  $9.0 \text{ mS cm}^{-1}$ ), at  $200 \text{ A m}^{-2}$  of applied current density

In all the experiments (including with  $\text{NaNO}_3$  and  $\text{NaClO}_4$  anolytes as noted above), the disappearance of each organic contaminants could be described by pseudo-first order rate kinetics. **Table 4.1** summarizes the apparent rate constants for the electrooxidation of target organic contaminants in  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  anolyte of the same initial conductivity and pH (9.0  $\text{mS cm}^{-1}$ , pH 2). The lowest rate constants were observed for the ICM, i.e., iopromide and diatrizoate, in  $\text{NaNO}_3$  anolyte ( $k_{\text{NaNO}_3}$ ,  $\text{h}^{-1}$ ) with  $0.83 \pm 0.15$  and  $0.94 \pm 0.07 \text{ h}^{-1}$ , respectively. ICM have been reported to be recalcitrant in various oxidation processes (Ternes *et al.* 2003, Dickenson *et al.* 2009, Sugihara *et al.* 2013). For example, transformation of diatrizoate and iopromide have been observed to be slow in ozonation (Ternes *et al.* 2003), with some improvement in the presence of UV light (Huber *et al.* 2003), or  $\text{H}_2\text{O}_2$  (Westerhoff *et al.* 2005, Ning and Graham 2008), that induces the formation of  $\cdot\text{OH}$  radicals. Similar to ICM, halogen groups in triclopyr, triclosan and tribromophenol exhibit a negative inductive effect that decreases the electron density at the benzene ring, thus increasing persistence to oxidation. Oxidation of other model contaminants yielded  $k_{\text{NaNO}_3}$  constants of the same order of magnitude (**Table 4.1**). Note that the experimental conditions (i.e., applied current density, anolyte conductivity and pH, and recirculation flow rate) were identical with both  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  anolytes.

Electrooxidation of all the organic contaminants was substantially faster in  $\text{Na}_2\text{SO}_4$  anolyte than in  $\text{NaNO}_3$  anolyte. That is, apparent rate constants were 10 – 15 times higher in sulfate anolyte than in nitrate anolyte. The highest removal rates in sulfate anolyte solutions were reported for triclosan ( $66.0 \pm 8.5 \text{ h}^{-1}$ ), followed by tribromophenol ( $40.9 \pm 3.0 \text{ h}^{-1}$ ) then carbamazepine ( $29.4 \pm 2.1 \text{ h}^{-1}$ ), with the lowest being iopromide ( $11.9 \pm 0.72 \text{ h}^{-1}$ ). Similar trend was observed in the absence of sulfate anions. Electrochemical degradation of tribromophenol reported the highest difference between sulfate and nitrate anolytes with 15 folds, followed by the iodinated compounds, diatrizoate and iopromide, as well as DEET, whereas the lowest was trichlopyr.

Significantly higher electrooxidation rates of target contaminants in the sulfate anolyte may be explained by the: *i*) formation of  $\text{SO}_4^{\cdot-}$  at the anode surface, and/or *ii*) persulfate formation and its acid-catalyzed hydrolysis to hydrogen peroxide, which may activate persulfate to  $\text{SO}_4^{\cdot-}$  (Kolthoff and Miller 1951, Tsitonaki *et al.* 2010).

**Table 4.1** Apparent rate constants ( $h^{-1}$ ) for oxidation of target organic contaminants in  $Na_2SO_4$  and  $NaNO_3$  analytes (pH 2; 9.0  $mS\ cm^{-1}$ ; and 200  $A\ m^{-2}$ ).

Organic compound	Chemical structure	Electrooxidation rate constants	
		$k_{Na_2SO_4}$ ( $h^{-1}$ )	$k_{NaNO_3}$ ( $h^{-1}$ )
Carbamazepine		29.4±2.1	2.4±0.37
DEET		14.4±1.2	1.0±0.13
Diatrizoate		13.7±1.8	0.94±0.07
Iopromide		11.9±0.72	0.83±0.15
Tribromophenol		40.9±3.0	2.7±0.56
Triclopyr		13.6±1.6	1.3±0.11
Triclosan		66.0±8.5	5.4±1.3

### 4.3.2 Persulfate electro-generation and potential role in the electrooxidation

Peroxymonosulfate and hydrogen peroxide are oxidants that are also believed to be generated in the sulfate-based electrochemical process from the persulfate-formation/hydrolysis route, where  $\text{HSO}_5^-$  is reported to be the intermediate in the decomposition of  $\text{S}_2\text{O}_8^{2-}$  into  $\text{H}_2\text{O}_2$  (Michaud *et al.* 2000, Serrano *et al.* 2002, Canizares *et al.* 2003). In these published studies, the produced concentrations were very low, and only small traces of  $\text{HSO}_5^-$  and  $\text{H}_2\text{O}_2$  were detected. Yet, it was not explained whether the  $\text{H}_2\text{O}_2$  was possibly decomposing in the anodic compartment, or it was being insignificantly produced in the first place.

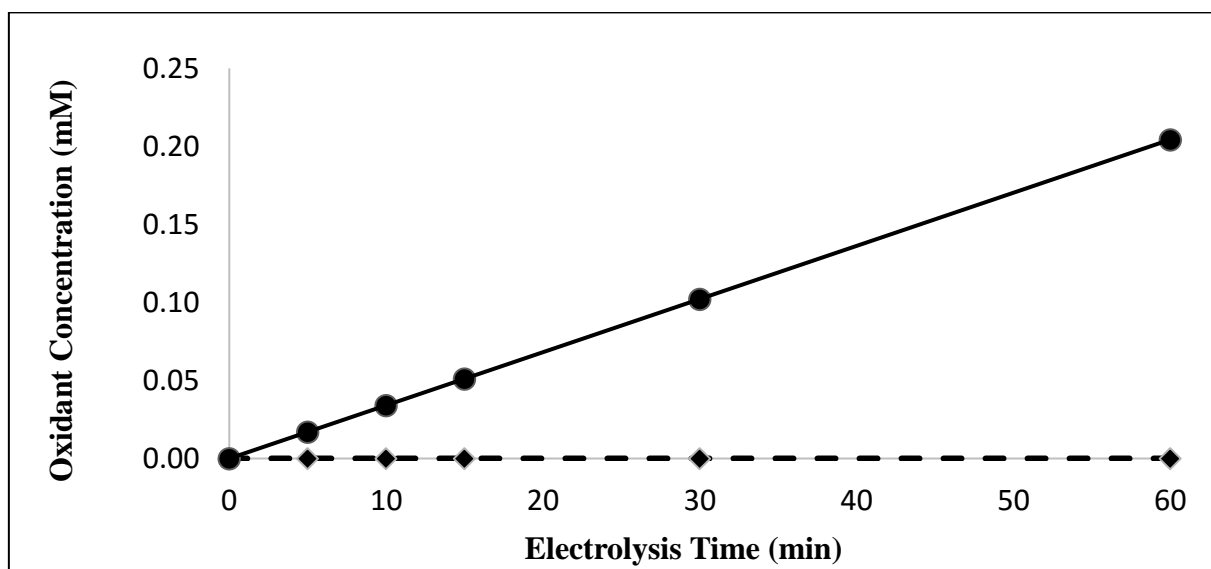
Previously, electrooxidation of coumaric acid at Pt anode was attributed to the formation of persulfate from sulfate ions and its acid-catalyzed hydrolysis to  $\text{H}_2\text{O}_2$ , which decomposes to  $\cdot\text{OH}$  radicals in the presence of dissolved iron (Kolthoff and Miller 1951, Saracco *et al.* 2000). Saracco *et al.* (2000) attributed the coumaric acid removal to the bulk oxidation with  $\text{H}_2\text{O}_2$ , which was quantified at 6 mM after 30 min when 100 mM sodium sulfate was used as electrolyte. However, the authors quantified only  $\text{H}_2\text{O}_2$  without measuring  $\text{S}_2\text{O}_8^{2-}$  in their work, where it is noticed that  $\text{H}_2\text{O}_2$  was measured using the iodimetric titration method which quantifies both  $\text{S}_2\text{O}_8^{2-}$  and  $\text{H}_2\text{O}_2$ , assuming that  $\text{H}_2\text{O}_2$  was being produced in significant amounts, whereas  $\text{S}_2\text{O}_8^{2-}$  would possibly have been the actual peroxide specie being produced (Saracco *et al.* 2000). Moreover,  $\text{H}_2\text{O}_2$  was reported to activate persulfate to generate  $\text{SO}_4^{\cdot-}$  in advanced oxidation processes for applications such as *in-situ* chemical oxidation (ISCO) of groundwater (Tsitonaki *et al.* 2010).



The oxidation powers of pure  $\text{S}_2\text{O}_8^{2-}$  and  $\text{H}_2\text{O}_2$  with the seven surrogate compounds was studied under same operating conditions (40 mM  $\text{Na}_2\text{SO}_4$  electrolyte; pH 2; 9.0 mS  $\text{cm}^{-1}$ ) in chemical oxidation tests without any applied electric current. In order to identify the starting concentrations of  $\text{S}_2\text{O}_8^{2-}$  and  $\text{H}_2\text{O}_2$ , oxidation of sulfate (40 mM) on BDD was run in the absence of any organic compounds, and the concentrations of  $\text{S}_2\text{O}_8^{2-}$  and  $\text{H}_2\text{O}_2$  were quantified. Taking into consideration that all recalcitrant compounds were oxidized completely in only 15 minutes with sulfate electrolytes, the concentrations of persulfate and peroxide were chosen to be more than what would be produced after even 30 minutes.

The results showed no electrochemical formation of  $\text{H}_2\text{O}_2$  ( $< \text{LOD}=1 \text{ mg L}^{-1}$ ) in  $\text{NaNO}_3$  anolyte solution, suggesting that the recombination of two  $\cdot\text{OH}$  radicals into  $\text{H}_2\text{O}_2$  is not significant despite the thermodynamic feasibility. This also indicated that any potential electrochemical formation of  $\text{H}_2\text{O}_2$  in  $\text{Na}_2\text{SO}_4$  anolytes would be generated from the decomposition of the electro-produced persulfate. However, no  $\text{H}_2\text{O}_2$  electrogeneration ( $< \text{LOD}=1 \text{ mg L}^{-1}$ ) was also detected in  $\text{Na}_2\text{SO}_4$  anolyte, which only reported persulfate formation in this work. The measured concentration of electrogenerated persulfate, in the absence of organic contaminants, reached 0.2 mM at the highest applied charge density, i.e., after 60 min of oxidation, during electrooxidation in 40 mM  $\text{Na}_2\text{SO}_4$  anolyte where 0.1 mM  $\text{S}_2\text{O}_8^{2-}$  was formed after 30 min (**Figure 4.2**).

Nonetheless, in order to investigate the oxidation power of  $\text{S}_2\text{O}_8^{2-}$  and  $\text{H}_2\text{O}_2$  with the seven surrogate compounds, higher concentrations of these oxidants were examined in the the chemical oxidation tests in the absence of any electric current. Despite that  $\text{H}_2\text{O}_2$  was not quantified in the sulfate oxidation into persulfate, we accounted for a scenario where  $\text{H}_2\text{O}_2$  might still theoretically be formed in the system, but probably followed by its rapid decomposition, although no known activators were present in the system to activate its decomposition. Thus, the  $\text{H}_2\text{O}_2$  concentration tested with the seven surrogate compounds was selected to be 6.4 mM which is higher than that reported by Saracco *et al.* (2000) after 30 minutes. For persulfate, the experiments were conducted with 0.6 mM  $\text{S}_2\text{O}_8^{2-}$ , which was selected as 6 folds higher than the 0.1 mM persulfate formed after 30 minutes in the absence of any persistent organic compounds.



**Figure 4.2** Electrochemical generation of the oxidants: persulfate ions (●) and hydrogen peroxide (◆) in electrooxidation in  $\text{Na}_2\text{SO}_4$  anolyte (40 mM, pH 2,  $9.0 \text{ mS cm}^{-1}$ ) at  $200 \text{ A m}^{-2}$

Results of the chemical oxidation show that these surrogate compounds reported no or very minimal degradation compared to the electrochemical degradation rates, **Table 4.2**. Given that persulfate has slow oxidation kinetics with organic compounds (Tsitonaki *et al.* 2010), it was unlikely to cause the higher electrooxidation rates in sulfate anolyte without activation by UV, heat, alkaline conditions or metal catalysts. And this was confirmed by chemical oxidation experiments with persulfate that yielded significantly lower rate constants compared to the apparent rate constants obtained in electrooxidation displayed in **Table 4.1**. Only less than 10% removal was observed after 30 minutes with pure  $S_2O_8^{2-}$  or  $H_2O_2$ , corresponding to less than  $0.09\text{ h}^{-1}$  oxidation rates which is more than 240 times slower than the rates of the electrochemical oxidation with sulfate ions (i.e.,  $11.9 - 66.0\text{ h}^{-1}$ ). Addition of both oxidants to diatrizoate, to investigate synergistic effect of these oxidants, similarly reported minimal removal (<10% removal;  $< 0.09\text{ h}^{-1}$ ).

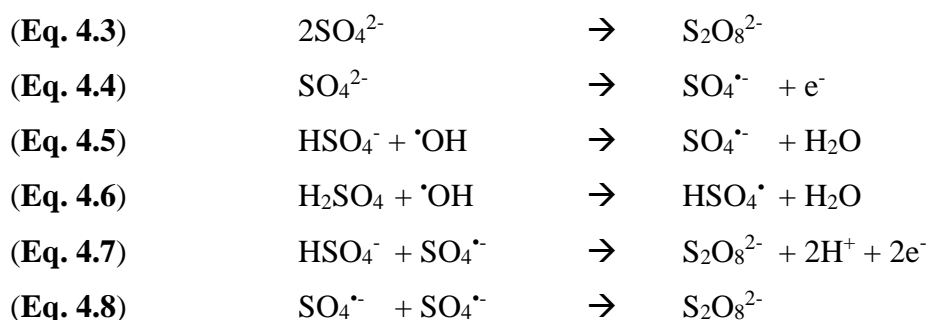
**Table 4.2 Apparent rate constants ( $\text{h}^{-1}$ ) for chemical oxidation of the seven target organic contaminants with non-activated  $K_2S_2O_8$  or  $H_2O_2$  prepared in  $Na_2SO_4$  solutions (pH 2, 9.0 mS  $\text{cm}^{-1}$ , 40 mM) in the absence of any applied electric current**

Target Persistent Organic compound	Oxidation rate constant $k_{S_2SO_8^{2-}}, \text{h}^{-1}$	Oxidation rate constant $k_{H_2O_2}, \text{h}^{-1}$
Carbamazepine	0.026	0.061
DEET	0.010	0.071
Diatrizoate	0.022	0.089
Iopromide	0.043	0.006
Tribromophenol	0.014	0.054
Triclopyr	0.061	0.019
Triclosan	0.005	0.087

Thus, it is unlikely that the higher observed removal rates of the electrooxidation of these surrogate compounds are instigated primarily by pure  $S_2O_8^{2-}$  or  $H_2O_2$ , without the involvement of other strong oxidizing agents such as sulfate radicals that can potentially be produced in such sulfate-based electrochemical systems. Therefore, the activation of the formed persulfate by  $H_2O_2$  was also discarded as possible causes of the enhanced electrooxidation of organic contaminants in  $Na_2SO_4$ . Furthermore, electrochemical oxidation experiments using persulfate as anolyte solution, as will further be described in Chapter 6, showed similar removal as nitrate and further indicated the minimal role that persulfate would potentially play in these processes.

### 4.3.3 Potential role of electro-generated $SO_4^{\cdot-}$ in the electrooxidation of diatrizoate

Even though the mechanism of the formation of persulfate on BDD anodes has been described with a direct oxidation of sulfate ions on the BDD surface (Eq. 4.3), recent studies incorporated  $SO_4^{\cdot-}$  in the formation process (Eq. 4.4 – 4.8) (Serrano *et al.* 2002, Khamis *et al.* 2010, Davis *et al.* 2014, Davis *et al.* 2014). Khamis *et al.* (2010) could not prove the existence of free  $SO_4^{\cdot-}$  radicals via their spectroscopic study, but explained persulfate formation via surface-adsorbed BDD( $SO_4^{\cdot-}$ ) radicals.



In electrooxidation at a BDD anode, sulfate is considered to be oxidized to persulfate in two stages (Serrano *et al.* 2002, Cañizares *et al.* 2009, Davis *et al.* 2014). The first stage is direct with one-electron oxidation of  $SO_4^{2-}$  to  $SO_4^{\cdot-}$  radical which occurs on BDD surface even before the water oxidation (Eq. 4.4), or indirect oxidation of  $H_2SO_4$  or  $HSO_4^-$  via the electrogenerated  $\cdot OH$  to form sulfate radicals (Eq. 4.5 – 4.6). The second stage follows with these sulfate radicals consequently undergoing subsequent oxidation of sulfate ions (Eq. 4.7) or recombination (Eq. 4.8) to form persulfate (Davis *et al.* 2014). According to modelling of persulfate production at a BDD anode using density functional theory (DFT), electrogenerated  $SO_4^{\cdot-}$  may react with active sites at the electrode surface to form chemisorbed intermediates which can then stabilize sulfate radical species (Davis *et al.* 2014). In their DFT model, they determined that the most favorable energetic pathway for the formation of persulfate is via sulfate radical recombination (i.e., oxidation of sulfate ions to  $SO_4^{\cdot-}$ ).



Therefore, since sulfate radical formed as an intermediate in the persulfate formation is a strong oxidant itself, it can act as an oxidizing agent in the presence of organic compound instead of forming persulfate. Similar to anodically formed  $\cdot\text{OH}$  (Bejan *et al.* 2012), and chlorine radical species (e.g.,  $\text{Cl}_2\cdot^-$ ) (Park *et al.* 2009), it is possible that the formed sulfate radicals could contribute to oxidation of persistent organic contaminants. The resulting anode potential ( $E_{\text{AN}}$ ) at  $200 \text{ A m}^{-2}$  was relatively constant at  $2.8 - 3.1 \text{ V}$  and  $3.0 - 3.6 \text{ V}$  vs SHE in both  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  anolytes, respectively. Thus, the formation of both  $\cdot\text{OH}$  and  $\text{SO}_4\cdot^-$  radicals at a BDD anode was thermodynamically possible in these experiments.

Although less is known about the oxidation reaction kinetics of organic contaminants with  $\text{SO}_4\cdot^-$ , reaction rates are generally assumed to be comparable to that of oxidation by  $\cdot\text{OH}$  (Rickman and Mezyk 2010, Tsitonaki *et al.* 2010, Matta *et al.* 2011). Target organic contaminants have similar bimolecular oxidation rates in the order of  $10^8 - 10^9 \text{ M}^{-1} \text{ s}^{-1}$  by homogeneously formed  $\cdot\text{OH}$  and  $\text{SO}_4\cdot^-$  radicals, with  $\cdot\text{OH}$  being in the range of  $10^8 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , and  $\text{SO}_4\cdot^-$  ranging from  $<10^6 \text{ M}^{-1} \text{ s}^{-1}$  (for aromatic compounds with nitro-groups) to  $10^8 - 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (for chloro- substituted and bromo-substituted aromatic compounds), except for iopromide which was reported with only  $1 - 2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  (Chan *et al.* 2010), **Table 4.3**. For instance, the second-order reaction rate constants of carbamazepine with  $\cdot\text{OH}$  radicals ( $8.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Huber *et al.* 2003)) which is slightly higher than with  $\text{SO}_4\cdot^-$  radicals ( $1.92 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Matta *et al.* 2011)). Whereas diatrizoate, which is considered less reactive towards ozonation or  $\cdot\text{OH}$  (Huber *et al.* 2005), has slightly higher rate constant with  $\text{SO}_4\cdot^-$  radicals ( $6.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) compared to  $\cdot\text{OH}$  radicals ( $5.4 - 6.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) (Real *et al.* 2009, Velo-Gala *et al.* 2014)).

However, studies comparing the removal of carbamazepine (Matta *et al.* 2011) and diatrizoate (Velo-Gala *et al.* 2014) with chemically generated  $\cdot\text{OH}$  radicals and  $\text{SO}_4\cdot^-$  radicals show higher removal with  $\text{SO}_4\cdot^-$  radicals despite the similar reactivity rates. The probable differences were explained by the higher concentration of the generated  $\text{SO}_4\cdot^-$  radicals as compared to  $\cdot\text{OH}$  radicals. Kinetics models reported by De Laat *et al.* (2004) and Truong *et al.* (2004) suggest that the concentration of sulfate radicals is much higher than that of  $\cdot\text{OH}$  radicals when they co-exist at pH less than 2. They explain in their models that the distribution of radicals as a function of pH is predominant with  $\text{SO}_4\cdot^-$  radicals in the acidic medium. In their work, the calculated equilibrium concentrations suggest that more hydroxyl radicals react with sulfate ions, producing sulfate radicals under pH 2 when increasing sulfate ions concentration in solution.

**Table 4.3 Bimolecular rate constants ( $k$ ,  $M^{-1} s^{-1}$ ) for oxidation of target organic contaminants with homogeneously generated  $\cdot OH$  and  $SO_4^{\cdot-}$  radicals.**

	$k_{SO_4^{\cdot-}}$ , $M^{-1} s^{-1}$	Ref.	$k_{\cdot OH}$ , $M^{-1} s^{-1}$	Ref.
Carbamazepine	$1.92 \times 10^9$	(Matta <i>et al.</i> 2011)	$8.80 \times 10^9$	(Huber <i>et al.</i> 2003)
DEET	$1.90 \times 10^9$	(Tay <i>et al.</i> 2013)	$5.00 \times 10^9$	(Song <i>et al.</i> 2009)
Diatrizoate	$6.59 \times 10^8$	(Velo-Gala <i>et al.</i> 2014)	$5.40 \times 10^8$	(Real <i>et al.</i> 2009)
Iopromide	$2.00 \times 10^4$	(Chan <i>et al.</i> 2010)	$3.30 \times 10^9$	(Huber <i>et al.</i> 2003)
Tribromophenol	-		-	
Triclopyr	-		$1.20 \times 10^9$	(Armbrust 2000)
Triclosan	-		$9.60 \times 10^6$	(Lee and Von Gunten 2012)

Using the same calculation method as in Matta *et al.* (2011), the concentration of  $SO_4^{\cdot-}$  radicals in the carbamazepine oxidation in sulfate in our system (assuming the oxidation process is completely executed via sulfate radicals without the involvement of persulfate and the co-existing  $\cdot OH$  radicals) is calculated to be  $5.12 \times 10^{-12}$  M, compared to  $\cdot OH$  radicals concentration in the carbamazepine oxidation in nitrate ( $1.13 \times 10^{-13}$  M). Similarly, for diatrizoate,  $SO_4^{\cdot-}$  concentration is two orders of magnitude higher than concentration of  $\cdot OH$  radicals with  $1.12 \times 10^{-11}$  M versus  $3.79 \times 10^{-13}$  M.

Moreover, electrogenerated  $SO_4^{\cdot-}$  may have contributed significantly to electrooxidation due to their continuous regeneration at the anode surface. After reacting with the organic compound,  $SO_4^{\cdot-}$  are reduced to sulfate ions, which are attracted to the positively charged anode and can be oxidized again to reactive sulfate radical species, in the presence of an anodic potential above 2.1 V.

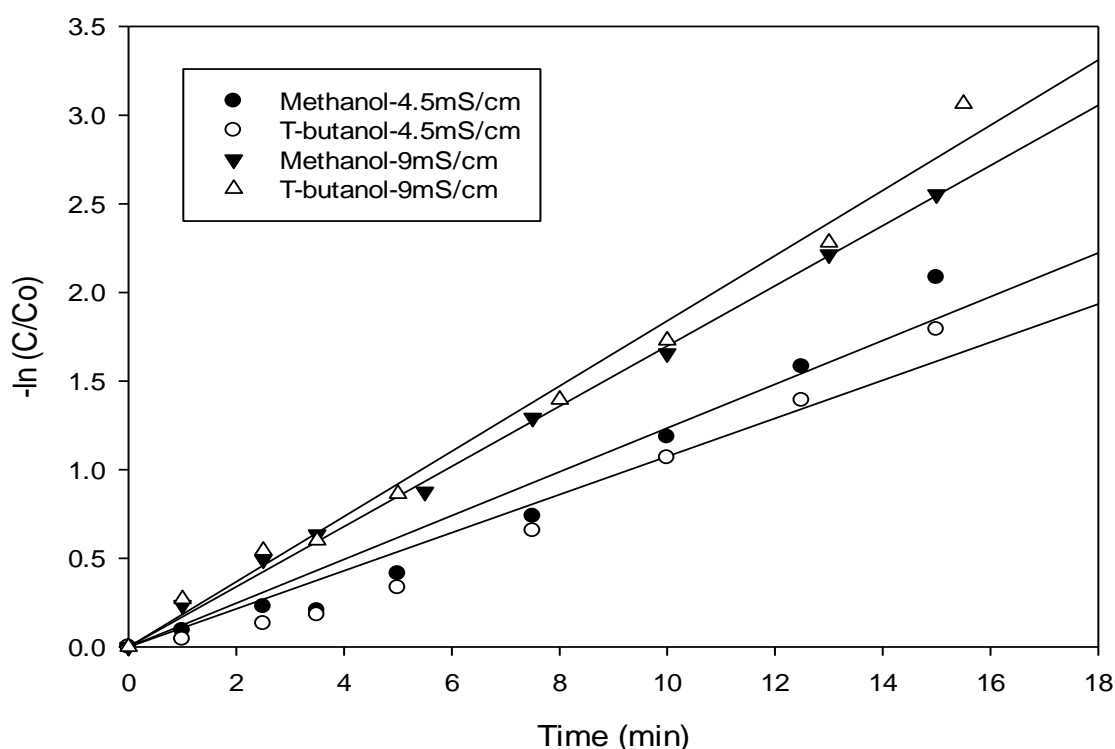
Given that all experiments were performed at pH 2, hydrolysis of potentially formed sulfate radicals to hydroxyl radicals was excluded because it is reported to be insignificant at  $\text{pH} < 9$  (Liang *et al.* 2007, Yang *et al.* 2015). Thus, efficient formation of  $\text{SO}_4^{\cdot-}$  at the BDD anode and their reaction with the organic contaminants simultaneously with the formed  $\cdot\text{OH}$  radicals may have yielded significantly higher electrooxidation rates in sulfate compared to nitrate anolyte. Participation of radical species in electrooxidation was also confirmed in the experiments conducted with the addition of specific radical quenchers, as explained further below.

Electrooxidation rate of iopromide in sulfate anolyte was higher than the one expected based on its reactivity with the homogeneously formed  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  (Huber *et al.* 2003, Chan *et al.* 2010). This further indicates the generation of a higher concentration of the  $\text{SO}_4^{\cdot-}$  radicals as compared to  $\cdot\text{OH}$  radicals. It could also be possible that iopromide may have been partly adsorbed to the anode surface, which would enhance its reactivity with the heterogeneously formed  $\text{SO}_4^{\cdot-}$ , although that was also expected to be similar with  $\cdot\text{OH}$  radicals in  $\text{NaNO}_3$ .

In addition, enhanced electrooxidation at a BDD anode in the presence of sulfate may also be due to the formation of more reactive organic radicals. Homogeneously formed  $\text{SO}_4^{\cdot-}$  are known to react with organic compounds primarily via direct electron transfer (Neta *et al.* 1977, Tsitonaki *et al.* 2010), while  $\cdot\text{OH}$  also reacts via hydrogen abstraction or addition to double bonds (Bossmann *et al.* 1998).

#### 4.3.4 Effect of specific radical quenchers on electrooxidation of diatrizoate

In an attempt to discern the contributions of electrogenerated  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  in sulfate anolyte, electrooxidation of diatrizoate was conducted with the addition of specific alcohol quenchers, methanol and *tert*-butanol. Methanol has relatively similar reactivity with  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  with oxidation rate constants of  $9.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and  $1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively (Buxton *et al.* 1988, Clifton and Huie 1989). However, alcohols with no  $\alpha$ -hydrogen such as *tert*-butanol are known to react much slower with sulfate radicals, the reaction rate with  $\cdot\text{OH}$  ( $3.8 - 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) being approximately 1000 times greater than that with  $\text{SO}_4^{\cdot-}$  ( $4 - 9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) (Buxton *et al.* 1988, Clifton and Huie 1989). Thus, addition of methanol should have a more pronounced effect on the electrooxidation than when *tert*-butanol is added. Nevertheless, similar pseudo-first order electrooxidation rates of diatrizoate were observed for both quenchers in  $\text{Na}_2\text{SO}_4$  anolyte in the presence of 0.1 mM methanol ( $10.2 \pm 0.55 \text{ h}^{-1}$ ) or *tert*-butanol ( $11.2 \pm 0.7 \text{ h}^{-1}$ ), as shown in **Figure 4.3**. When investigating lower concentrations of sulfate ions ( $4.5 \text{ mS cm}^{-1}$ ), similar results were also reproduced.



**Figure 4.3** Disappearance of diatrizoate during electrooxidation in  $\text{Na}_2\text{SO}_4$  anolyte (40 mM, pH 2,  $9.0 \text{ mS cm}^{-1}$ ) in the presence of  $100 \mu\text{M}$  methanol (◆) or *t*-butanol (◇), with an applied current density of  $200 \text{ A m}^{-2}$

This result may indicate that a significant role in the generation of  $\text{SO}_4^{\cdot-}$  at BDD anode was played by the  $\cdot\text{OH}$ . By scavenging the  $\cdot\text{OH}$ , added *tert*-butanol affects the yield of  $\text{SO}_4^{\cdot-}$  (Eq. 4.2 and 4.3). In addition, both alcohols are oxidized at BDD anodes directly or via  $\cdot\text{OH}$  and other reactive oxygen species (Chang *et al.* 2006, Chaenko *et al.* 2011), which will limit their reactivity with  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  radicals. Therefore, addition of specific alcohol quenchers could not elucidate between sulfate and hydroxyl radicals' contributions to electrooxidation of diatrizoate. Nevertheless, the observed decrease in the removal rates in the presence of alcohol quenchers indicates a significant contribution of radical oxidant species to electrooxidation of diatrizoate at BDD anode. The similar results could also be indicating that very high concentrations of sulfate radicals are being produced, and suggesting that higher concentrations of the quenchers are required in order to achieve a clearer differentiation of the radicals. Previous experience with higher concentrations of quenchers has led to the deactivation of the active surface of the BDD anode, and the risk was assessed to be quite high, thus further increase in quencher's concentration was discarded.

### 4.3.5 Electrooxidation of nitrobenzene in Na<sub>2</sub>SO<sub>4</sub> anolyte

Being a specific  $\cdot\text{OH}$  probe compound, nitrobenzene was selected for the differentiation of sulfate radicals and hydroxyl radicals because of its high reactivity with hydroxyl radical ( $k_{\text{HO}\cdot} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) compared to sulfate radical ( $k_{\text{SO}_4^{\cdot-}} \leq 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) (Neta *et al.* 1977, Buxton *et al.* 1988). Therefore, the electrochemical removal rate of nitrobenzene was evaluated in the presence of sulfate and nitrate at pH 2 and 9.0  $\text{mS cm}^{-1}$  (Figure 4.4).

The apparent rate constants for oxidation of nitrobenzene in Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub> anolyte were  $0.55 \pm 0.03 \text{ h}^{-1}$  and  $0.38 \pm 0.02 \text{ h}^{-1}$ , respectively. The results show that sulfate electrolyte reported slightly higher removal rate than nitrate despite the lower reactivity of sulfate radicals. Nevertheless, on the contrary to the target organic contaminants (Table 4.1), electrooxidation of nitrobenzene was not several folds higher in the presence of sulfate in the anolyte.

These results further advocate findings of De Laat *et al.* (2004) that the distribution percentage of radicals in the sulfate-based electrochemical oxidation systems using BDD anodes is largely dominated by sulfate radicals rather than  $\cdot\text{OH}$ . Thus, it attributed the higher removal in sulfate to the formation of much higher concentrations of the electro-generated  $\text{SO}_4^{\cdot-}$  compared to  $\cdot\text{OH}$  in these sulfate-based electrochemical oxidation systems using BDD anodes. The higher concentration of the electro-generated sulfate radicals in such sulfate-based electrochemical oxidation systems employing BDD anodes may compensate for their lower reactivity with the surrogate organic compound present, and their significant contribution to its oxidation.

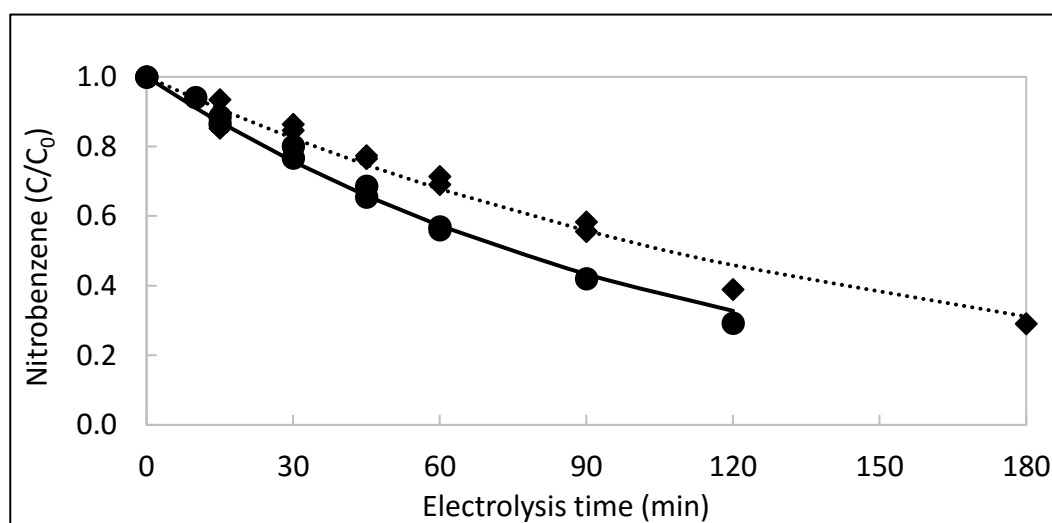


Figure 4.4 Disappearance of nitrobenzene during electrochemical oxidation in 60 mM NaNO<sub>3</sub> (◆) and 40 mM Na<sub>2</sub>SO<sub>4</sub> (●) anolytes at similar operating parameters (pH 2, 9.0  $\text{mS cm}^{-1}$ , and 200  $\text{A m}^{-2}$ )

### 4.3.6 Energy Consumption

The energy consumption of the electrochemical system was estimated as the electric energy per order ( $E_{EO}$ ), kWh m<sup>-3</sup>, required to reduce the concentration of the organic contaminant by one order of magnitude in a unit volume of treated solution, as described in **Chapter 3 (Section 3.5)**.

As shown in **Table 4.1**, electrooxidation of all the organic contaminants being substantially faster in Na<sub>2</sub>SO<sub>4</sub> anolyte than in NaNO<sub>3</sub> anolyte by 10 – 15 folds. This resulted in a drastic decrease in the electrolysis time and a lower electric energy per order ( $E_{EO}$ ) required for the anodic oxidation process (**Table 4.4**). For example, removal of diatrizoate required only 8.5 minutes and 2.44 kWh m<sup>-3</sup> in sulfate anolyte, compared to 180 minutes and an energy consumption of 45.6 kWh m<sup>-3</sup> for the electrooxidation in nitrate anolyte.

The highest energy savings were reported for the sulfate-based electrochemical decomposition of the iodinated compounds, diatrizoate (18.7 folds) and iopromide (12.4 folds), as compared to nitrate, followed by the amidated compounds, DEET (11.5 folds) and carbamazepine (10.4 folds), then the chlorinated compounds, triclosan (9.0 folds) and triclopyr (8.2 folds), with the brominated contaminant, tribromophenol reporting the lowest with only 3.8 folds.

**Table 4.4 Electric energy consumption per order ( $E_{EO}$ ), expressed as electric energy, kWh m<sup>-3</sup>, to reduce the concentration of the organic contaminant via electrooxidation in Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub> anolytes (pH 2; 9.0 mS cm<sup>-1</sup>; and 200 A m<sup>-2</sup>) by one order of magnitude in a unit volume of treated solution.**

Organic compound	Electric energy consumption per order ( $E_{EO}$ ), kWh m <sup>-3</sup>	
	$E_{Na_2SO_4}$	$E_{NaNO_3}$
Carbamazepine	1.26	13.1
DEET	3.07	35.2
Diatrizoate	2.44	45.6
Iopromide	3.09	38.4
Tribromophenol	4.56	17.2
Triclopyr	2.66	21.8
Triclosan	0.92	8.32

#### 4.4 Concluding Remarks

In conclusion, the sulfate-based solutions such as  $\text{Na}_2\text{SO}_4$  have been widely used as supporting electrolytes for electrochemical degradation of contaminants using a BDD anode (Sirés *et al.* 2014). Electrooxidation pathways have been widely explained by the role of  $\cdot\text{OH}$  and other reactive oxygen species, while the participation of sulfate radical species has been largely neglected. Results of this work advocate that sulfate species cannot be considered as inert at high current densities and potentials typically applied in electrochemical treatment using a BDD anode. In this work, the electrooxidation rates of seven persistent organic contaminants were 10 – 15 folds faster in  $\text{Na}_2\text{SO}_4$  anolyte than in  $\text{NaNO}_3$  anolyte suggesting the formation of sulfate-based oxidants. With the slow kinetics of persulfate with these persistent contaminants, sulfate radicals are most likely to be the sulfate-based reactive oxidants in such BDD-based electrochemical systems. Regardless of the nature of the main oxidant species formed in these sulfate-based treatment, electrooxidation kinetics were significantly enhanced compared to sulfate-free electrolytes. Thus, activation of sulfate at BDD electrodes at high anode potential may have significant implications in the treatment of sulfate-containing waters. Therefore, investigating the impact of the operating parameters governing the electrochemical oxidation systems is crucial to further elucidate the characteristics of these oxidizing agents, as will be presented in **Chapter 5**.

## Chapter 5: Effect of Operating Parameters on the Electrooxidation Rates of Diatrizoate

This chapter presents a detailed investigation on the influence of the operating conditions that govern the sulfate-based electrochemical oxidation systems. Such operating conditions include the concentrations and conductivity of the anolyte solution (Section 5.3.1), and the applied current density (Section 5.3.2). It also includes the results of the effect of a combined scenario of low sulfate concentration and low current density on electrochemical oxidation of diatrizoate (Section 5.3.3), as well as the effect of the anolyte volume (Section 5.3.4)

Most of the results of this chapter have also been published in the following publication:

- Farhat, A., Tait, S., Keller, J., Radjenovic, J. (2015). Removal of Persistent Organic Contaminants by Electrochemically Activated Sulfate. *Environ. Sci. Technol.*, 2015, 49 (24), pp 14326–14333. DOI: 10.1021/acs.est.5b02705.



## 5.1 Introduction

In the previous chapter, the roles of sulfate and persulfate ions in the electrochemical oxidation of contaminants at BDD anodes were elucidated, suggesting the participation of electrogenerated sulfate radical species in electrooxidation of persistent organic contaminants. Investigating different operating conditions governing the electrochemical generation of these species thus becomes of importance, in order to explore a potential saturation effect or a possible limited range of the high sulfate performance.

Therefore, the electrolyte solution concentration/conductivity, applied current density, as well as other operating conditions such as anolyte volume were studied with both electrolytes, sulfate and nitrate, to identify the influence of these factors on the oxidation rate of the investigated organic contaminant, which was continued to be chosen as diatrizoate because of the high persistence of this organic contaminant reported.

The electrolytic concentration is a primary factor influencing the production of the radicals and thus the extent of the destruction of the persistent organic compounds. Although it is expected that the higher concentrations would induce higher production of radicals and higher oxidation rates, it is important to examine if the oxidation rates at high concentrations would stop increasing after a certain concentration threshold of sulfate and nitrate, and if these two anolytes would produce a similar removal rate after a certain saturation stage.

The effect of applied current density is also crucial for the energy consumption economical study, besides its significance for the radical production and the extent of oxidation reactions. Anodic potential above the oxidation potential of sulfate radicals (i.e., 2.8 – 3.1 V) are required to be achieved under all tested current densities. It is expected that the higher applied current density will lead to a higher radical production as well as higher organic oxidation.

The effect of the electrolyte solution volume treated in the electrochemical system was also investigated in order to examine if the mass transfer limitations inside the reactor affect the oxidation of organic compounds by sulfate and hydroxyl radicals. This would also anticipate for a possible effect of the higher ratio of 'active volume' -to- the total volume of the electrolyte solution, where the active volume can be defined as the portion of the solution volume being actively in contact with the anode surface and within the double layer embracing it.

## 5.2 Materials and Methods

To investigate the effect of operating conditions in electrooxidation at BDD anode, experiments were performed using sodium  $\text{Na}_2\text{SO}_4$  anolyte and compared with  $\text{NaNO}_3$  anolyte at different operating conditions. The electrochemical oxidation experiments were performed using diatrizoate as a model compound with an initial concentration of  $2 \mu\text{M}$  using the CEM-divided electrochemical reactor as described in the **Cell Design and Reactor Specifications (Section 3.1)**.

Sulfate concentrations of 5, 15 and 40 mM were examined to explore the effect of anolyte concentration, and compared to different concentrations of nitrate anolyte (8, 18, and 60 mM). Concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  were used to adjust the pH of the sulfate and nitrate anolytes to  $\text{pH } 2.0 \pm 0.1$ , respectively. Thus, the solutions of nitrate and sulfate were prepared by adding a combination of nitric acid and sodium nitrate salt for the nitrate anolyte solution, and sulfuric acid and sodium sulfate salt for the sulfate anolyte solution. Higher concentrations of nitrate were used because it was decided that the two anolyte systems were to be prepared with similar conductivity values, and for that, more nitrate was required in order to achieve similar conductivities. The conductivity of the anolytes was  $9.0 \pm 1.0 \text{ mS cm}^{-1}$  in the 40 mM  $\text{Na}_2\text{SO}_4$  and 60 mM  $\text{NaNO}_3$  solutions, whereas it was  $4.3 \pm 1.0 \text{ mS cm}^{-1}$  (5 and 15 mM sulfate as well as 8 and 18 mM nitrate).

The two anolytes were not compared at similar concentrations, but were rather compared at the same initial conductivity and pH value in order to minimize their effect on the activity of the anode surface, and the electrochemical activity and speciation of the surrogate compounds. Electrolyte conductivity is believed to affect the distribution of electrode potential and thus the activity of its surface. Therefore, it was chosen as the fixed parameter over the electrolyte concentration in order to alleviate the inhomogeneous distribution of potential across the anode surface (Sonoyama and Sakata 1999).

In all of these electrochemical oxidation experiments investigating the effect of the anolyte concentration, the applied current density was fixed at  $200 \text{ A m}^{-2}$  in both  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  anolyte, and the volume of the anolyte and catholyte solutions was 500 mL each.

The effect of the applied current density was explored by testing the diatrizoate electrooxidation at 100, 150, and  $200 \text{ A m}^{-2}$  in both anolytes. These experiments were conducted at fixed concentrations of  $\text{SO}_4^{2-}$  anolyte (40 mM) and  $\text{NO}_3^-$  anolyte (60 mM) at pH 2 and with 500 mL anolyte volume. Both anolytes concentrations and pH values corresponded to a fixed conductivity of  $9.0 \pm 0.5 \text{ mS cm}^{-1}$ .

Furthermore, the effect of volume of the anolyte solution was also studied in this work with four different volumes (250, 500, 1000, and 2000 mL) being compared in sulfate and nitrate anolytes. The same applied current density of  $200 \text{ A m}^{-2}$  was employed in all these experiments, while comparing fixed concentrations of sulfate anolyte (40 mM) and nitrate anolyte (60 mM) at same pH value of 2.

One further experiment using lower sulfate concentration was conducted with 1.56 mM sulfate ( $150 \text{ mg L}^{-1}$ ), which is in the order of typical sulfate concentrations in municipal wastewater, although sulfate has also been detected in many surface and ground waters at concentrations of up to 630 and 230  $\text{mg L}^{-1}$ , respectively (United-Nations-Environment-Programme 1990, Tchobanoglous *et al.* 2002, Sgroi *et al.* 2014). To prevent further addition of sulfate in the case of 1.56 mM  $\text{Na}_2\text{SO}_4$  anolyte, pH was adjusted to pH 2 with concentrated  $\text{HNO}_3$ . The conductivity of this prepared solution was within the  $4.3 \pm 1.0 \text{ mS cm}^{-1}$  range as in the previous experiments, and an applied current density of  $100 \text{ A m}^{-2}$  was employed in this test.

The flowrate was not changed throughout all the experiments of this thesis because it is expected to create a higher or lower turbulence inside the anodic chambers if changed, and thus leading to different mixing patterns of the anolyte solution inside the reactor.

## 5.3 Results and Discussion

### 5.3.1 Effect of anolyte concentration and conductivity on diatrizoate electrooxidation

When comparing relatively equivalent concentrations of sulfate and nitrate, the results show that diatrizoate is completely oxidized at a higher rate in the systems employing sulfate electrolytes, where the reaction rates plots were fit to pseudo-first order models. With sulfate concentrations of 5 mM, diatrizoate is removed 6 times faster than in similar nitrate concentrations (8.51 mM), **Table 5.1**. Increasing the sulfate concentration to 15 mM, the apparent rate constants for oxidation of diatrizoate were 10 times higher than the rate constants in  $\text{NO}_3^-$  anolyte (18 mM) at the same conductivity and pH.

When taking into consideration the ionic strength of both electrolytic solutions, sodium sulfate has a higher ionic strength than sodium nitrate with a factor of 3. Therefore, correcting for the concentrations of these solutions requires incorporating this factor, which leads to the comparison of 5.0 mM  $\text{SO}_4^{2-}$  solution and 18 mM  $\text{NO}_3^-$  solution (which is even more than 3 times higher). The comparison still shows that  $\text{SO}_4^{2-}$  solution with the corrected concentration yielded 4.2 folds higher

diatrizoate removal rate than  $\text{NO}_3^-$ . Even nitrate concentration of 60 mM, being 12 times higher than the  $\text{SO}_4^{2-}$  (5.0 mM), yielded lower apparent removal rate constant by several folds even though the  $\text{NO}_3^-$  solution was prepared at a higher conductivity ( $9.0 \text{ mS cm}^{-1}$ ) compared to that of the 5.0 mM  $\text{SO}_4^{2-}$  ( $4.5 \text{ mS cm}^{-1}$ ).

**Table 5.1 Apparent rate constants ( $k$ ,  $\text{h}^{-1}$ ) for oxidation of diatrizoate at different anolyte concentrations of  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  prepared at similar conductivity values (pH 2; 500 mL anolyte volume; and  $200 \text{ A m}^{-2}$ )**

$\text{NaNO}_3$ (mM)	$\text{Na}_2\text{SO}_4$ (mM)	$k$ ( $\text{h}^{-1}$ )
8.5	-	$0.75 \pm 0.04$
18	-	$1.06 \pm 0.09$
60	-	$0.94 \pm 0.07$
-	5.0	$4.49 \pm 0.71$
-	15	$10.4 \pm 0.86$
-	40	$13.7 \pm 1.82$

The effect of conductivity on electrooxidation kinetics was noted to be minor, as the rate constants obtained for  $\text{NaNO}_3$  anolytes of different molarities were very similar. During nitrate experiments tested at  $9.0 \text{ mS cm}^{-1}$ , it was observed that the conductivity increased from  $9.0$  to  $\sim 18 \text{ mS cm}^{-1}$  over 3 hours which is the time needed to completely remove diatrizoate in nitrate. And despite this high conductivity, no acceleration in the diatrizoate removal rate was observed, and the linearity pattern of diatrizoate removal was not affected, which further advocates the insignificant effect of conductivity. It is noted that in sulfate, conductivity was measured to only increase from a starting value of  $9.0 \text{ mS cm}^{-1}$  to a maximum value of  $11 \text{ mS cm}^{-1}$  in 15 minutes which was enough to oxidize diatrizoate completely.

Increasing degradation rates of diatrizoate at higher sulfate concentrations further explicates the higher concentration of sulfate radicals suggested in the previous chapter (**Sections 4.3.3 – 4.3.5**). The anolyte composition and nature of electroactive species can affect the exchange current density of electrochemical reactions, where, for example, the presence of specifically adsorbed ions such as fluoride ions inside the inner Helmholtz layer of an electrode/electrolyte interface may catalyse the oxygen evolution reaction (OER) at the anode surface (Hwang *et al.* 2014). Whereas, the presence of chloride anions can affect the rates of electrochemical reaction, through electrostatic effects and shielding of the anode surface, hindering the OER (Ferro *et al.* 2000).

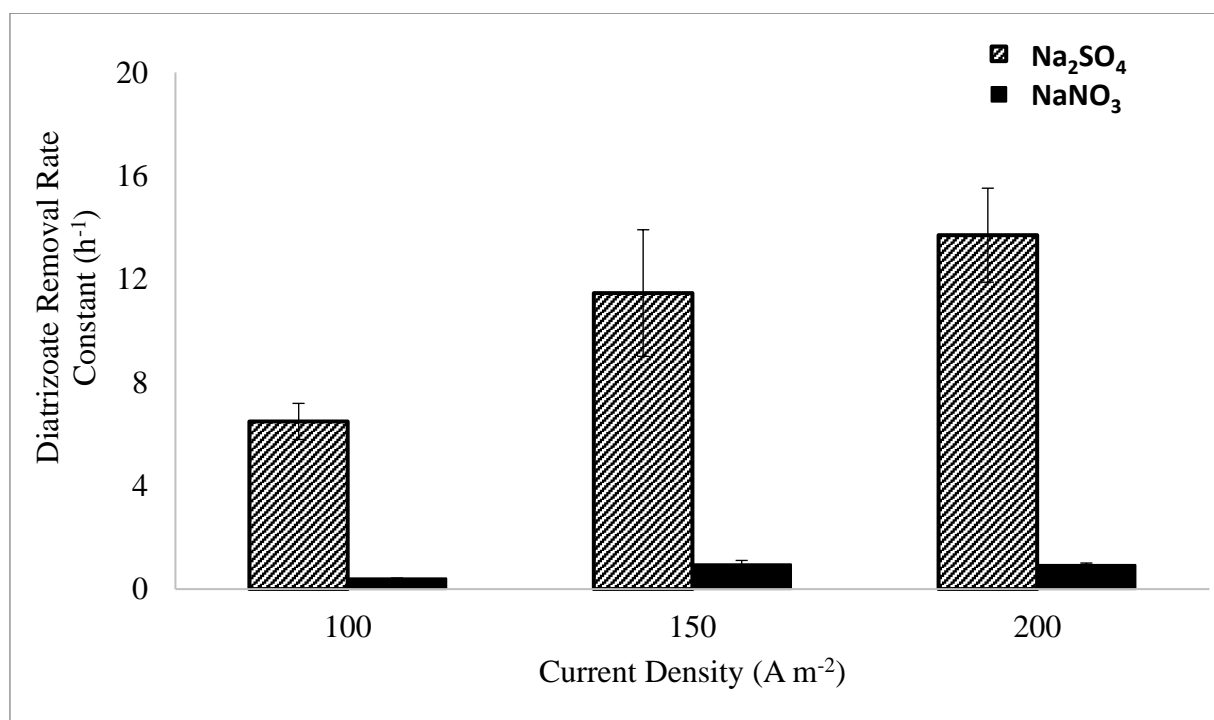
The sulfate ions in anodic oxidations has been described to adsorb on the anode surface, which reduces the anode active sites for  $\cdot\text{OH}$  radicals formation and increases the formation of  $\text{SO}_4\cdot^-$  patches (Smit and Hoogland 1971, Smit and Hoogland 1971). The high sulfate adsorption was reported on various electrode materials such as platinum and bismuth by (Smit and Hoogland 1971, Samec *et al.* 1997, Jäger *et al.* 2008). Sulfate oxidation into persulfate is considered another side reaction occurring besides OER, and thus, it is most likely expected to be in competition with the oxygen evolution for the active sites on the BDD surface. Therefore, increasing the concentration of sulfate would lead to higher sulfate adsorption on the anode. Higher sulfate adsorption will reduce the active sites for  $\cdot\text{OH}$  radicals formation and increase the formation of adsorbed sulfate patches, on which  $\text{S}_2\text{O}_8^{2-}$  is produced, leading to OER inhibition (Smit and Hoogland 1971, Smit and Hoogland 1971, de Souza *et al.* 2013). Moreover, the increased current density is also expected to cause faster oxidation of sulfate ions mainly because it potentially causes alleviation in the mass transfer limitations, and thus accelerates the anode surface oxidation of sulfate ions, which increases the formation of persulfate (Davis *et al.* 2014).

Therefore, the presence of sulfate in the anolyte appeared to be the single most determinant factor for the measured rate constants. This superiority with even very low sulfate concentration suggests that even the possibility of a potential generation of higher concentrations of  $\cdot\text{OH}$  radicals in sulfate than nitrate is unlikely to occur. The oxidizing species that are electro-generated in the sulfate electrolytes are most likely to be different in nature and certainly have stronger oxidation potential compared to the nitrate electrolytes which electro-generate only  $\cdot\text{OH}$  radicals in these BDD-based electrochemical systems. This advocates that sulfate electrolyte is not inert but actually reactive, and suggests that the oxidizing species formed are sulfate-based oxidizing species, possibly sulfate radicals. These radicals are generated in addition to  $\cdot\text{OH}$  radicals in these sulfate-based BDD-EAOPs, and are characterized by a strong oxidizing capabilities.

### 5.3.2 Effect of applied current density on electrooxidation rates of diatrizoate

Since the oxidation of the aromatic organic contaminants is affected by the current density of the electrochemical system, lower current densities were investigated to assess if this superiority of sulfate can still be observed at lower current densities. The results of diatrizoate removal at various current densities (100, 150, and 200 A m<sup>-2</sup>) for both electrolytes are shown in **Figure 5.1**.

As expected, the decrease in current density yielded lower electrooxidation rates in NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> anolytes, which is similar to what was observed by Davis *et al.* (2014). Yet, electrooxidation rate was still 12 – 16 times higher in the latter case compared to nitrate. The results demonstrated that the lowest current density (100 A m<sup>-2</sup>) led to 16-fold faster diatrizoate removal rates in sulfate electrolyte (6.49 ± 0.70 h<sup>-1</sup>) compared to nitrate (0.41 ± 0.02 h<sup>-1</sup>). When comparing higher current densities (150 and 200 A m<sup>-2</sup>), the ratio was still 12 – 15 folds higher in sulfate. With its lowest reaction rate constant (6.49 ± 0.70 h<sup>-1</sup>), the sulfate electrolyte still yielded 7-fold faster removal rates than the nitrate case employing the highest current density of 200 A m<sup>-2</sup> (0.94 ± 0.07 h<sup>-1</sup>). This indicated that the current density is likely to be another factor affecting the electro-generation of these sulfate-based oxidizing species, and further demonstrated that sulfate anolytes generate sulfate-based oxidizing agents characterized by strong oxidizing power.



**Figure 5.1** The apparent electrooxidation rate constants (h<sup>-1</sup>) of diatrizoate in 60 mM NaNO<sub>3</sub> and 40 mM Na<sub>2</sub>SO<sub>4</sub> anolyte at different applied anodic current densities (pH 2; 9.0 mS cm<sup>-1</sup>; 500 mL anolyte volume)

At all applied current densities, the resulting anode potential was in the range of 2.8 – 3.1 V and 3.0 – 3.6 V in NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> anolytes, respectively. At lower applied currents, charge transfer limitations were expected to become more pronounced, leading to slower electrooxidation of diatrizoate. However, given that the anode potential was above the thermodynamic potentials for SO<sub>4</sub><sup>•-</sup> and <sup>•</sup>OH in both anolytes, both species could have participated in electrooxidation.

Investigating the effect of current density in the nitrate cases, where the removal rate constants of diatrizoate were very similar when comparing 4.5 to 9.0 mS cm<sup>-1</sup> or 150 to 200 A m<sup>-2</sup>, unlike with sulfate, it can be suggested that increasing the current density above a certain threshold might be possibly instigating a “shielding effect”, probably due to higher oxygen gas evolution reaction occurring as a consequence of such increase. In BDD-based electrochemical oxidation systems operating at a potential above 2.3 V vs. SHE, the surface reaction starts with the adsorption of the hydroxyl radical on the BDD surface through the formation of complex BDD(<sup>•</sup>OH) from water discharge. These formed <sup>•</sup>OH radicals will react with the organic or inorganic compounds present in the solution, and the side reaction occurring would be the reaction of <sup>•</sup>OH radicals leading to oxygen evolution.

Increase of current density in nitrate would probably lead to an increase in the concentration of BDD(<sup>•</sup>OH) formed, triggering the increase in the evolution of the oxygen gas. This is mainly because the mass transfer limitations restrict the access of organic molecules to reach the BDD electrode in order to react with the formed <sup>•</sup>OH radicals. In the case of sulfate, it is most likely that the sulfate ions are adsorbed to the BDD electrode where they react with BDD(<sup>•</sup>OH) to form another complex, BDD(SO<sub>4</sub><sup>•-</sup>), which competes with BDD(<sup>•</sup>OH) for more active sites on BDD surface. This is expected to reduce the oxygen formation at the anode surface because of the lower formation of BDD(<sup>•</sup>OH) compared to nitrate. Thus, in a sulfate-based electrochemical oxidation systems using BDD, increasing the current density would increase the formation of this BDD(SO<sub>4</sub><sup>•-</sup>) and potentially reduce the concentration of BDD(<sup>•</sup>OH), therefore leading to higher diatrizoate oxidation.

Therefore, higher oxidation of the organic compounds reported at increased sulfate concentrations and current densities can be explained due to higher formation of SO<sub>4</sub><sup>•-</sup> radicals which are the main intermediates in the formation of persulfate. An increase in sulfate concentration or current density will enhance the oxidation of sulfate ions leading to higher formation of SO<sub>4</sub><sup>•-</sup> radicals which are strong oxidants and are capable of degrading organic compounds, hence increasing oxidation rates. On the other side, increasing the anolyte concentration or current density in the case of nitrate will mostly lead to higher OER without considerably increasing the oxidation rates.

### 5.3.3 Effect of combined low sulfate concentration and current on diatrizoate removal

The removal rates of diatrizoate were further investigated at much lower sulfate concentration within the range detected in water systems using higher concentration of diatrizoate, and applying the lower scenario of applied current density to explore the effectiveness of sulfate system at low operating conditions. Thus, the electrochemical removal of 10  $\mu\text{M}$  diatrizoate was tested using 150  $\text{mg L}^{-1}$  of sulfate concentration (1.56 mM), and compared to a nitrate anolyte with the similar concentration and conductivity, while employing an applied current density of 100  $\text{A m}^{-2}$ .

Results show that even such low  $\text{Na}_2\text{SO}_4$  concentration of 1.56 mM was observed to yield a high removal rate constant of  $1.48 \pm 0.152 \text{ h}^{-1}$ , which is still substantially higher than that of 1.56 mM nitrate ( $0.354 \pm 0.0155 \text{ h}^{-1}$ ) and also higher than all those removal rate constants observed in all previous  $\text{NaNO}_3$  anolyte concentrations (i.e.,  $k_{\text{NaNO}_3} = 0.75 - 1.06 \text{ h}^{-1}$ ), including the highest tested nitrate concentration of 60 mM. This scenario of low operating conditions further confirms the formation of sulfate-based oxidizing agents, that are different in nature and stronger in oxidation power than the conventionally reported  $\cdot\text{OH}$  radicals.

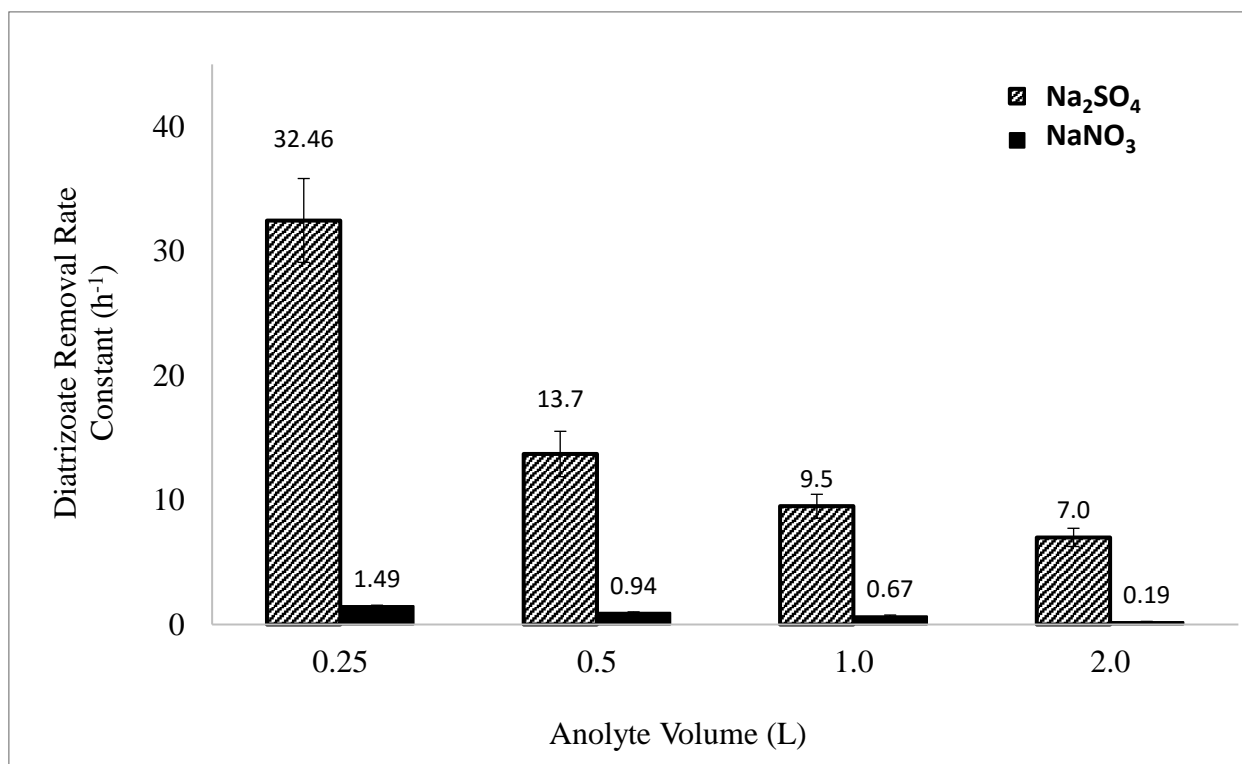
Since sulfate concentration of 1.56 mM ( $150 \text{ mg L}^{-1}$ ) is in the order of typical sulfate concentrations in municipal wastewater, this electrochemical activation of sulfate ions at BDD anodes may have significant implications in the treatment of sulfate-containing waters, especially that sulfate has also been detected in many surface and ground waters at concentrations of up to 630 and 230  $\text{mg L}^{-1}$ , respectively, (Tchobanoglous *et al.* 2002, Sgroi *et al.* 2014).

### 5.3.4 Effect of anolyte volume on diatrizoate removal rates

To assess the effect of active volume ratio, the volume of the anolyte solution was varied for the electrooxidation of diatrizoate. The mass transfer limitations would potentially be a controlling factor which significantly affects the rate of the oxidation reaction, especially in the absence of any adjustments on the flow rate of the influent. The results of diatrizoate electrooxidation with 40 mM sulfate solutions of four different volumes (0.25, 0.5, 1.0, and 2.0 L) are displayed in **Figure 5.2**.

The results show that as the volume of the solution increased from 0.25 L up to 2.0 L, the rate of diatrizoate removal decreased by more than 5 folds in sulfate anolyte solutions from  $32.46 \pm 3.37 \text{ h}^{-1}$  to  $7.00 \pm 0.73 \text{ h}^{-1}$ . In the case of nitrate anolyte, the differences in the oxidation rates at different solution volumes followed the same trend where diatrizoate removal rate decreased as the anolyte volume was increased from  $1.49 \text{ h}^{-1}$  (0.25 L) to only  $0.19 \text{ h}^{-1}$  (2.0 L).





**Figure 5.2** The apparent electrooxidation rate constants ( $\text{h}^{-1}$ ) of diatrizoate in sulfate at different solution volumes of 0.25, 0.5 1.0 and 2.0 L (pH 2;  $9.0 \text{ mS cm}^{-1}$ ; and  $200 \text{ A m}^{-2}$ )

The anolyte volume is 200 mL, where the active volume in the vicinity of the anode surface is approximately 75 mL as per the reactor configuration. So, the ratio of the active volume to the total anolyte volume is expected to play a significant role in determining the removal rates of diatrizoate (at the fixed flow rate of  $200 \text{ mL min}^{-1}$ ). The hydraulic residence time for all solution volumes in the anodic compartment is similar at fixed flow rate, but since the inflow solution is being recirculated indefinitely after being exposed to the BDD anode surface, the exposure time of the anolyte containing the organic compound to the active BDD anode surface is the dominant factor when the anolyte volume is varied. Therefore, as the ratio of the active volume to the total anolyte volume increases (i.e., at lower anolyte volumes), higher diatrizoate removal rates are expected because of the larger exposure time of the anolyte containing the organic compound to the active BDD anode surface.

The removal rate constant of diatrizoate was reduced by relatively around 2 folds as the anolyte volume increase from 0.25 L ( $32.46 \pm 3.37 \text{ h}^{-1}$ ) to 0.5 L ( $13.7 \pm 1.8 \text{ h}^{-1}$ ). However, increasing the anolyte volume from 0.5 L to 1.0 L and then to 2.0 L induced removal rate constants that were not proportional to the 2-fold reduction in the anolyte volume, but higher than expected.

This suggests that the oxidation reaction of diatrizoate was not only occurring via sulfate radicals in the vicinity of the electrode but might also be potentially taking place in the bulk solution. Assuming sulfate radicals have a very short life-time of microseconds similar to other electro-chemically generated radicals, sulfate-based ‘longer lifetime’ oxidizing species can possibly be also generated, besides  $\text{SO}_4^{\cdot-}$  radicals, where these oxidants can travel into the bulk of the solution after being electrogenerated and further contribute to the overall diatrizoate oxidation process (Burns *et al.* 2012). Without corrections for flow rates, in larger volumes, these sulfate-based long-life oxidizing species have to travel more in the bulk solution to be able to react with diatrizoate; whereas, the traveling distance would certainly be shorter in the small volumes, and thus the oxidation would be faster, as presented in **Figure 5.2**. The possible electro-generation of sulfate-based ‘longer lifetime’ oxidizing species will be further discussed in **Chapter 6**.

#### 5.4 Concluding Remarks

The superiority of sulfate-based electrochemical systems using BDD anodes was investigated over a wide range of various operating conditions, where results indicated higher removal rates than nitrate in all the examined cases. The removal rate of diatrizoate was faster at the lowest concentration of sulfate (5 mM) compared to the rate measured with a 12-fold higher concentration of nitrate. Even when the applied current density was halved to  $100 \text{ A m}^{-2}$ , sulfate anolyte yielded a significantly higher electrochemical oxidation rate than nitrate.

Even the lowest investigated sulfate concentration of 1.56 mM (i.e.,  $\sim 150 \text{ mg L}^{-1}$ ), reported up to 4 times higher apparent rate constants for diatrizoate degradation in a sulfate-based anolyte, compared to the inert nitrate electrolyte of the same concentration and was still higher than the rate achieved with the highest nitrate concentration studied in this work (i.e. 60 mM). Since sulfate concentrations have been detected in many surface and ground waters at concentrations up to  $630 \text{ mg L}^{-1}$ , this activation of sulfate at BDD electrodes polarized at a sufficiently high anode potential may have significant implications in the treatment of sulfate-containing wastewaters.

The results from testing different volumes fell within the same scheme, where 2.0 L of diatrizoate were treated by sulfate faster than 0.25 L of diatrizoate being treated in the absence of sulfate. This suggested that the reaction of diatrizoate oxidation was not only occurring via  $\text{SO}_4^{\cdot-}$  radicals in the vicinity of the electrode but might also be potentially taking place in the bulk of the anolyte solution.

The potential electro-generation of sulfate-based oxidizing species characterized by a ‘longer lifetime’ is worth investigating, and will be further discussed in **Chapter 6**.

## **Chapter 6: Long-life Oxidizing Species in Sulfate-based Electrochemical Systems**

Chapter 6 explores the potential extended reactive life time of the sulfate-based oxidizing agents in electrochemical systems. Early on during experimental work of the thesis, it became apparent that these oxidizing agents may have oxidising capacity beyond when the applied current is stopped. This chapter examines the extended reactive life time of oxidizing agents by delayed quenching experiments (Section 6.3.1), and pulse electric current applications (Section 6.3.2). It also studies the effect of off-line diatrizoate oxidation without applied current by pre-oxidized sulfate anolyte (Section 6.3.3). An extended working lifetime could be greatly advantageous from an applications perspective, because it may allow alternative operational strategies with current on-off cycling to conserve energy.

## 6.1 Introduction

The previous chapter focused on the influence of the operating conditions such as the concentrations and conductivity of anolyte solutions, as well as the applied current density and the anolyte volume on the electrochemical oxidation of diatrizoate in Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub> anolytes. Besides the results of anolyte volume effect, in the final sets of experiments in Chapter 5, an unfamiliar but noteworthy phenomenon was observed. Several replicate experiments of the 1.56 mM sulfate yielded ‘largely different’ removal rates despite repetitions, with the lowest removal rate being  $1.48 \pm 0.152 \text{ h}^{-1}$ , and the highest being  $> 4.5 \text{ h}^{-1}$  (above that which was observed in 5 mM sulfate concentration). Although in all our sampling procedure, ~ 1.0 ml samples were collected from the electrochemical reactor then quenched with 250  $\mu\text{L}$  methanol, it was observed that a delay of several minutes in the quenching procedure might possibly alter the results of the concentrations of the target organic compounds measured using LC-MS. A plausible analytical method could not be found, except that quenching agent was added to samples after different times following the sampling event.

The preliminary observations suggested that the oxidation reaction did not actually stop after the sample was taken out of the reactor (i.e. in the absence of electrical current). These findings suggested that these sulfate-based electrochemical systems might be possibly capable of producing long-life oxidizing agents that are strong enough to further degrade diatrizoate to a substantial extent. This was contrary to the common assumption that the oxidation reaction of chemical compounds stops when the electric current is not applied anymore (except where chlorine is formed).

The possibility of the formation of long-life sulfate-based oxidizing species was only reported from disinfection studies using ‘chlorine-free’ sulfate-based electrochemical systems, carried by Bergmann group (Bergmann and Rollin 2007, Bergmann *et al.* 2009) and few other authors (Gusmão *et al.* 2010, Li *et al.* 2010, Gómez-López *et al.* 2013). In their work, a sulfate solution was electrolyzed in the absence of any chloride or organic matter, and then added to a solution containing microorganism such as *E. coli*, resulting in significant disinfection of the microbial solution, where the extent of this sulfate-based electrochemical disinfection reached up to 50% in some cases (Gusmão *et al.* 2010).

Thus, the objectives of this Chapter 6 were to explore the possibility of formation of long-life sulfate-based oxidizing agents and their ability to oxidize chemicals even after the applied current is stopped. The extended reactive life-time of such oxidants could be of significant importance from an applications perspective as it may induce large potential savings in the electric energy consumption resulting from alternative operational strategies.

## 6.2 Materials and Methods

The CEM-divided electrochemical reactor described in the **Cell Design and Reactor Specifications (Section 3.1)** was used. The preliminary experiments involved the electrochemical oxidation of 2  $\mu\text{M}$  carbamazepine using 40 mM sulfate prepared with pH 2 and 9.0  $\text{mS cm}^{-1}$ , and operated with 200  $\text{A m}^{-2}$ . These experiments were performed using the delayed quenching approach further described below in **Section 6.2.1**.

In order to assess the occurrence of the phenomenon of the extended reactive lifetime of the sulfate-based oxidants in another compound having different structure than carbamazepine, the electrochemical oxidation of 10  $\mu\text{M}$  diatrizoate was performed in 3 different anolyte solutions. Sodium sulfate, nitrate, or persulfate solutions of 500 mL were prepared at salt concentrations of 1.56 mM (pH 2 and  $4.75 \pm 0.3 \text{ mS cm}^{-1}$ ). All anolyte solutions were prepared by first adjusting pH to 2 using nitric acid, then adding 1.56 mM of the corresponding salt ion, thus yielding relatively similar solution conductivity. Note that the total concentration of nitrate was higher than that of sulfate and persulfate because of adding nitric acid. The applied current density in this study was 100  $\text{A m}^{-2}$ .

### 6.2.1 Delayed Quenching Experiments

Control experiments were conducted by periodically taking two oxidized samples for every specific time  $t$ . One sample was immediately quenched using methanol without any delays and within less than 5 seconds of the actual sampling. The other sample was left on the bench at room temperature without quenching or freezing for a certain time (e.g., 30 minutes), then the same quenching procedure was applied. The concentrations of the instant-quenching samples were then compared with those of the ‘on-bench *delayed-quenching*’. The purpose of these experiments was to exclude any effect of the actual anode surface in terms of if the oxidizing agents are possibly adsorbed on the anode surface and are able to oxidize the organic compound even without any applied current (i.e., after the current is stopped).

In the preliminary experiments testing carbamazepine, samples were collected from the reactor at 3 different time points (Sample  $t-1$ , Sample  $t-2$ , and Sample  $t-3$ ). At every sampling time,  $t$ , 6 samples were collected, then quenched with methanol after a delay of 0, 10, 20, 30, 40, 60, or 90 min. This test was mainly conducted to explore the extent of the reactive life-time of the additional oxidation reaction occurring in these systems.

After conducting the preliminary experiments, electrooxidation of diatrizoate control experiments were conducted along with the delayed quenching experiments. However, the resting time on the bench in the delayed quenching step was defined to be 30 min in these tests.

### 6.2.2 Pulse Electric Current Experiments

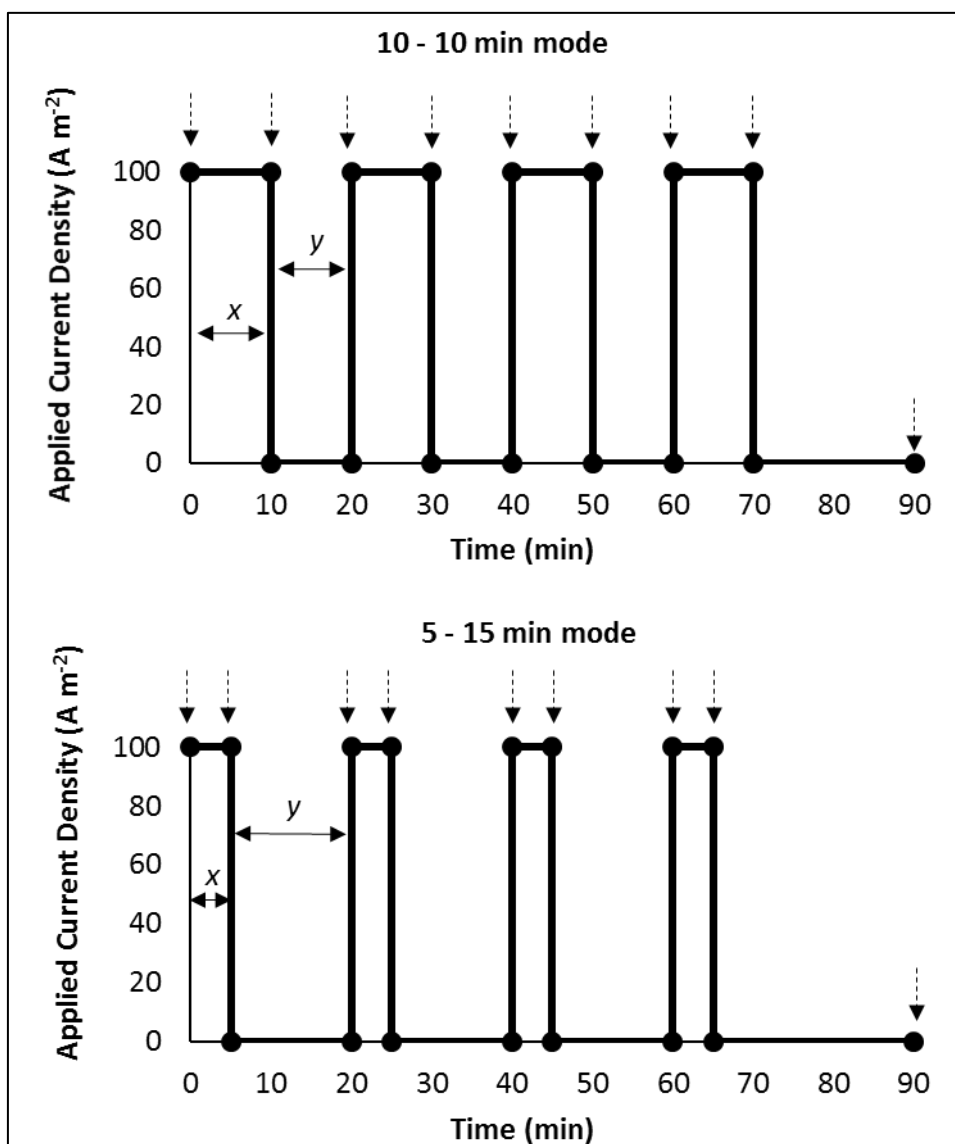
A second set of experiments were performed at similar conditions to the *delayed-quenching* experiments, but with an intermittent current mode instead of a continuous current. The intermittent mode was designed to apply the electric current for  $x$  minutes (e.g., 5 minutes) followed by no current for  $y$  minutes (e.g., 15 minutes), then applying the current again for  $x$  minutes and stopping it for  $y$  minutes in a cyclic mode for up to 80 minutes. In all experiments, the samples were left after the 80 minutes for an extra 10 min designated as an extra resting time. To keep the reactor mixed, the circulation of anolyte continued during the no-current period.

The samples were periodically collected for analysis at the end of electrolysis time (i.e.,  $x$ ) and resting time (i.e.,  $y$ ), and immediately quenched with methanol. The first ‘electrooxidation time – resting time’ mode was a 10 – 10 min scenario, which was then compared to a 5 – 15 min scenario. This procedure of both scenarios is illustrated in **Figure 6.1**.

Results of the first two modes were then further compared to 1 – 19 min and 1 – 9 min, where electrooxidation time in the latter two studies was reduced to 1 min, to investigate the effect of introducing a spiked current. In these later experiments, the current was first applied for 5 min then stopping for 15 min to activate the system, followed by spiking a current for 1 min then stopping for 19 min or 9 min. Samples were not collected after electrolysis time and were taken only after resting time (i.e., every 10 or 20 min without including any sampling after the spike minute itself).

### 6.2.3 Off-line Diatrizoate Oxidation Experiments

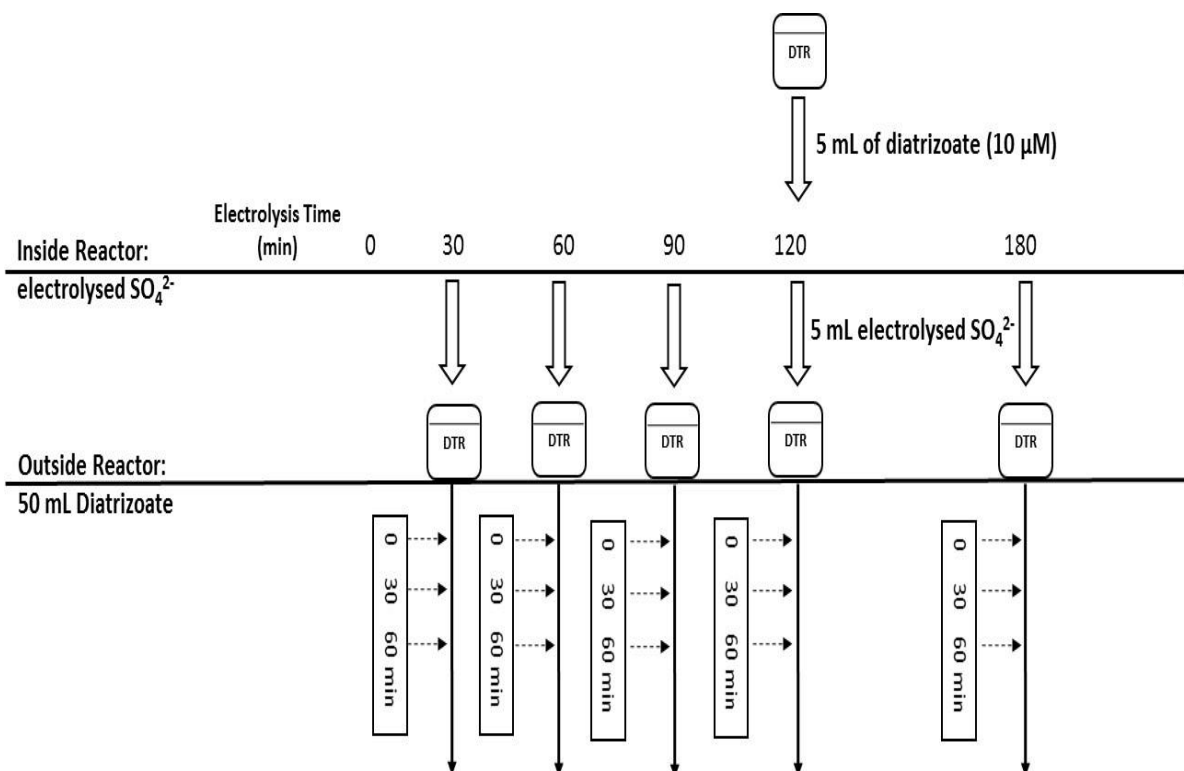
To study the potential possibility of catalysis by the by-products of the contaminant being oxidized, a new approach was tested by electrolyzing a pure sulfate solution without any organic matter inside the reactor, and then adding an aliquot of the electrolysed sulfate onto a diatrizoate solution prepared outside of the reactor.



**Figure 6.1** The procedure for the different modes of intermittent electric current application tested with the electro-chemical oxidation of diatrizoate, where the electric current was applied intermittently every  $x$  min and stopped for  $y$  min in a cyclic pattern. Sampling points are marked with dotted arrows

Thus, only sulfate anolyte was oxidized (0.5 L; pH 2; and 100 A m<sup>-2</sup>) inside the reactor for 120 min. Meanwhile, four bottles (50 mL) of 10  $\mu$ M diatrizoate were prepared and stored outside of the reactor. Every 30 min, a 5 mL aliquot of the electro-oxidized sulfate was added to the 50 mL diatrizoate bottle and left to react over 1 h, while taking samples every 30 min. The procedure is schemed in **Figure 6.2**. These experiments were conducted with 3 different sulfate concentrations of 7.5, 25, or 40 mM.



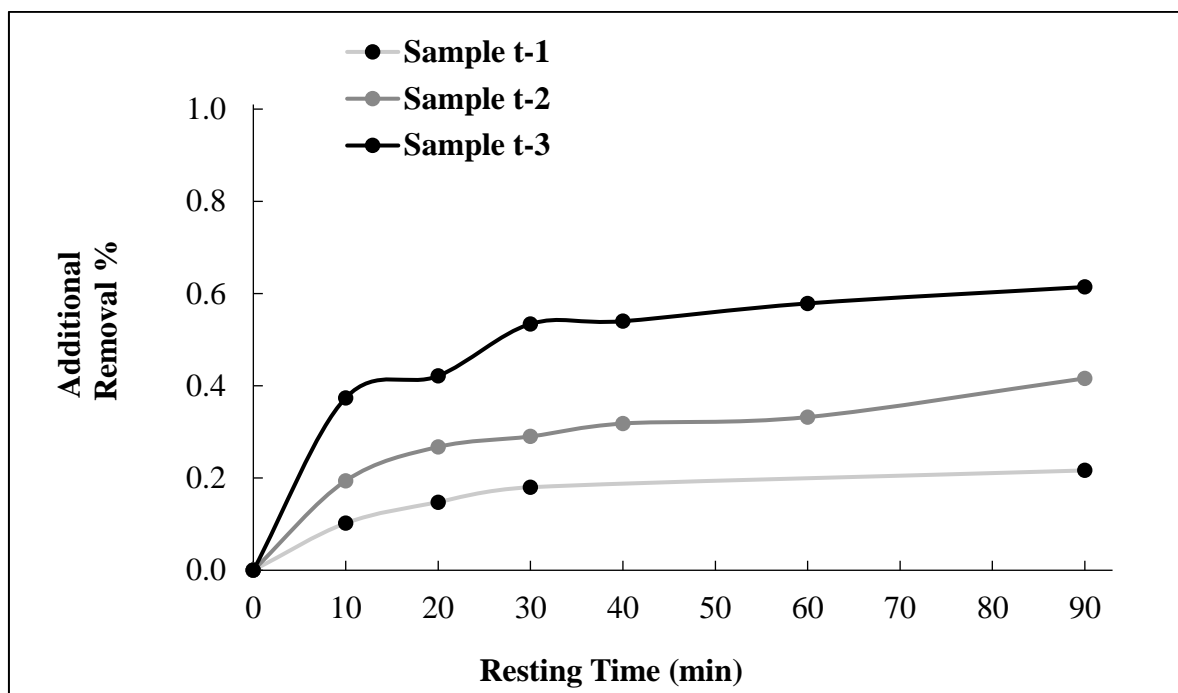


**Figure 6.2** The procedure for the off-line oxidation of diatrizoate by pre-oxidized sulfate anolyte (0.5 L; pH 2; and 4.5 mS cm<sup>-1</sup>). Sampling points are marked with dotted arrows.

After 120 min of electrooxidation of SO<sub>4</sub><sup>2-</sup>, an aliquot of 5 mL diatrizoate (10 µM) was added to the reactor solution (i.e., final DTR concentration inside the reactor is 0.1 µM after addition). The mixed solution was electro-oxidized for 1 hour so that the activated sulfate inside the reactor would degrade the diatrizoate completely. Then 5 mL aliquot of the electro-oxidized sulfate was taken and added to a 50 mL bottle of diatrizoate prepared outside of the reactor as in the previous procedure and were left to react for 60 min. This experiment was run in 3 replicates.

### 6.3 Results

The preliminary results collected in these sulfate systems (before designing the experimental plan of diatrizoate) showed that the oxidation of carbamazepine continued to a significant extent reaching 20% additional removal in a medium where the electric current was not being applied anymore. This extended oxidation was occurring over an active period of time reaching 60 – 90 min, but the largest extent of the prolonged oxidation was between 20 to 30 min, after which the removal was only slightly changing. Therefore, the resting time used in designing further experimentations on the long-life oxidants was selected to be in the range of 20 – 30 min (**Figure 6.3**).



**Figure 6.3** The additional removal (%) of the delayed quenching during the sulfate-based electrochemical oxidation of carbamazepine in three samples (t-1, t-2, and t-3), as a function of resting time (min) in order to explore the extent of prolonged oxidation (40 mM  $\text{SO}_4^{2-}$ ; pH 2; and 9.0  $\text{mS cm}^{-1}$ ; 200  $\text{A m}^{-2}$ ; and 0.5 L)

### 6.3.1 Effect of Delayed Quenching on Oxidation of Diatrizoate

**Table 6.1** shows the results of the control experiments for nitrate, persulfate and sulfate analytes employed for the electrochemical removal of diatrizoate. Within 90 min, the removal of diatrizoate was almost complete in sulfate anolyte, achieving 99% removal, whereas in the other analytes, the same time of treatment yielded partial removal at 40% and 42% in nitrate and persulfate analytes, respectively.

The electrooxidation rates of diatrizoate in nitrate and persulfate analytes were relatively similar with  $0.36 \pm 0.05 \text{ h}^{-1}$  and  $0.34 \pm 0.01 \text{ h}^{-1}$ , respectively, being 8-folds lower as compared to sulfate anolyte ( $2.90 \pm 0.1 \text{ h}^{-1}$ ). This finding further advocates that, in the absence of an activator, persulfate ions cannot be considered to be among the main sulfate-based oxidizing agents that are electrochemically generated in the BDD-based electrooxidation systems employing sulfate ions as anolyte.

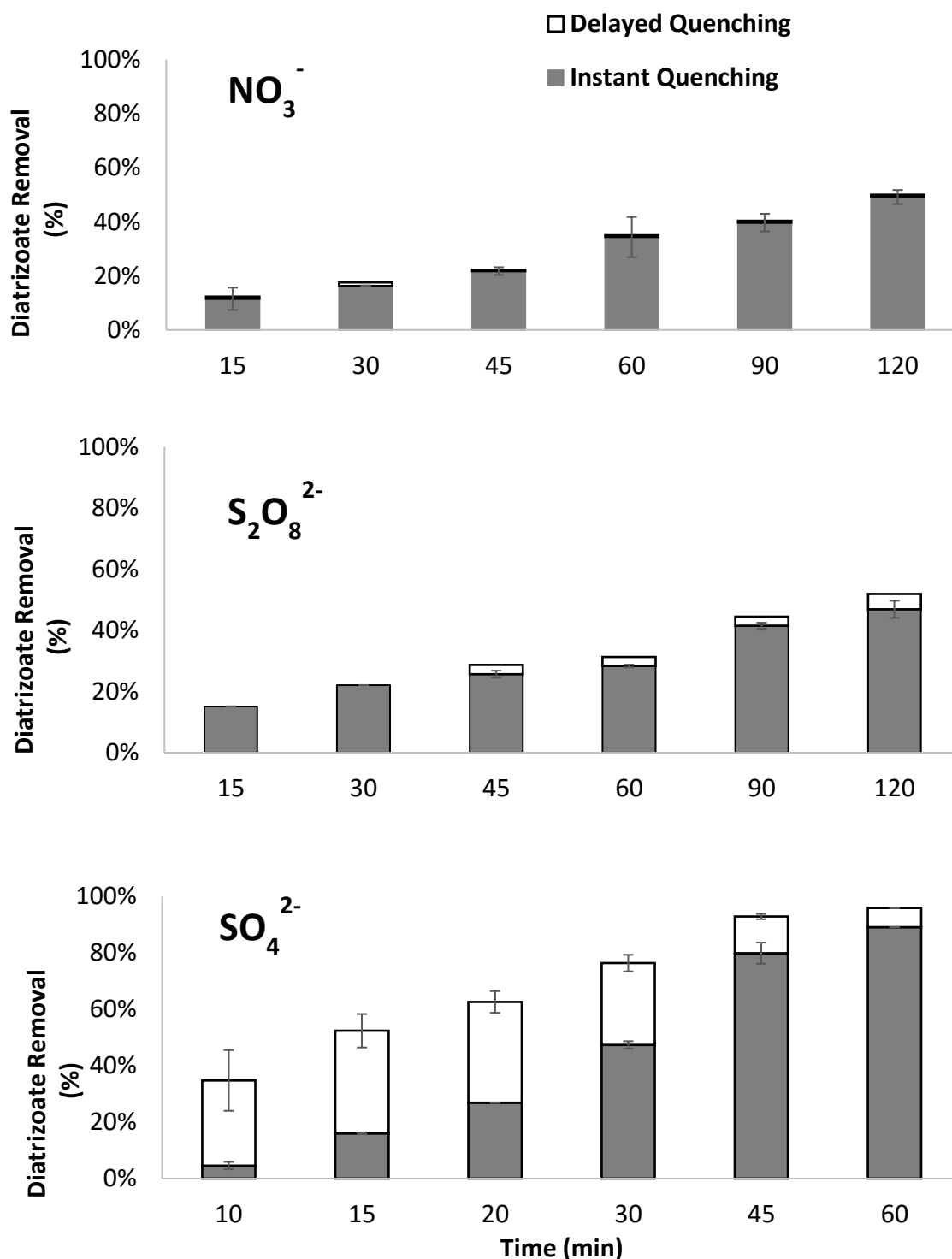
**Table 6.1 Removal percentages (%) of electrochemical oxidation of 10  $\mu\text{M}$  diatrizoate in 1.56 mM anolyte, comparing the three anolytes (nitrate, persulfate, and sulfate) prepared as 500 mL with pH 2, and  $4.75 \pm 0.3 \text{ mS cm}^{-1}$  and operated with an electric current density of  $100 \text{ A m}^{-2}$**

Time (min)	$\text{NO}_3^-$	$\text{S}_2\text{O}_8^{2-}$	$\text{SO}_4^{2-}$
0	0%	0%	0%
15	12%	15%	16%
30	16%	22%	47%
45	22%	26%	80%
60	34%	28%	89%
90	40%	42%	99%
120	49%	47%	100%

Results of the on-bench *delayed quenching* experiments showed that no significant prolonged oxidation of diatrizoate was observed when employing  $\text{NO}_3^-$  and  $\text{S}_2\text{O}_8^{2-}$  anolytes (**Figure 6.4**). All observed differences between delayed-quench samples and instantaneous-quench samples were lower than 10%, generally being within the analytical measurement error range.

However, only when  $\text{SO}_4^{2-}$  anolyte was employed, the on-bench *delayed quenching* showed a significant additional oxidation, reaching approximately 29 – 36% in the samples collected at electrolysis time,  $t = 10 - 45$  min. Whereas, this additional oxidation decreased to only 7 – 13% as the remaining diatrizoate concentration was lowered to below 20% of its initial concentration, which is not unexpected because diatrizoate is almost completely removed by this stage.

This additional oxidation indicates that energy consumption in such systems can be largely optimized, to induce massive savings. For instance, treating an influent of 10  $\mu\text{M}$  diatrizoate can be conducted for 15 minutes, thus achieving a removal of 16%, then discharged outside the reactor, where the removal is expected to exceed 50% within the next 30 minutes. The energy savings from such a procedure exceed 50%, and can achieve higher values with a proper optimization.



**Figure 6.4** Diatrizoate removal (%) during the electrochemical oxidation and the delayed quenching, in nitrate (top), persulfate (middle), and sulfate (bottom) anolyte. The grey fraction signifies the removal % in instant-quench samples and the white fraction signifies the removal % of diatrizoate in delayed-quench samples. The error bars represent the standard deviations of duplicate measurements

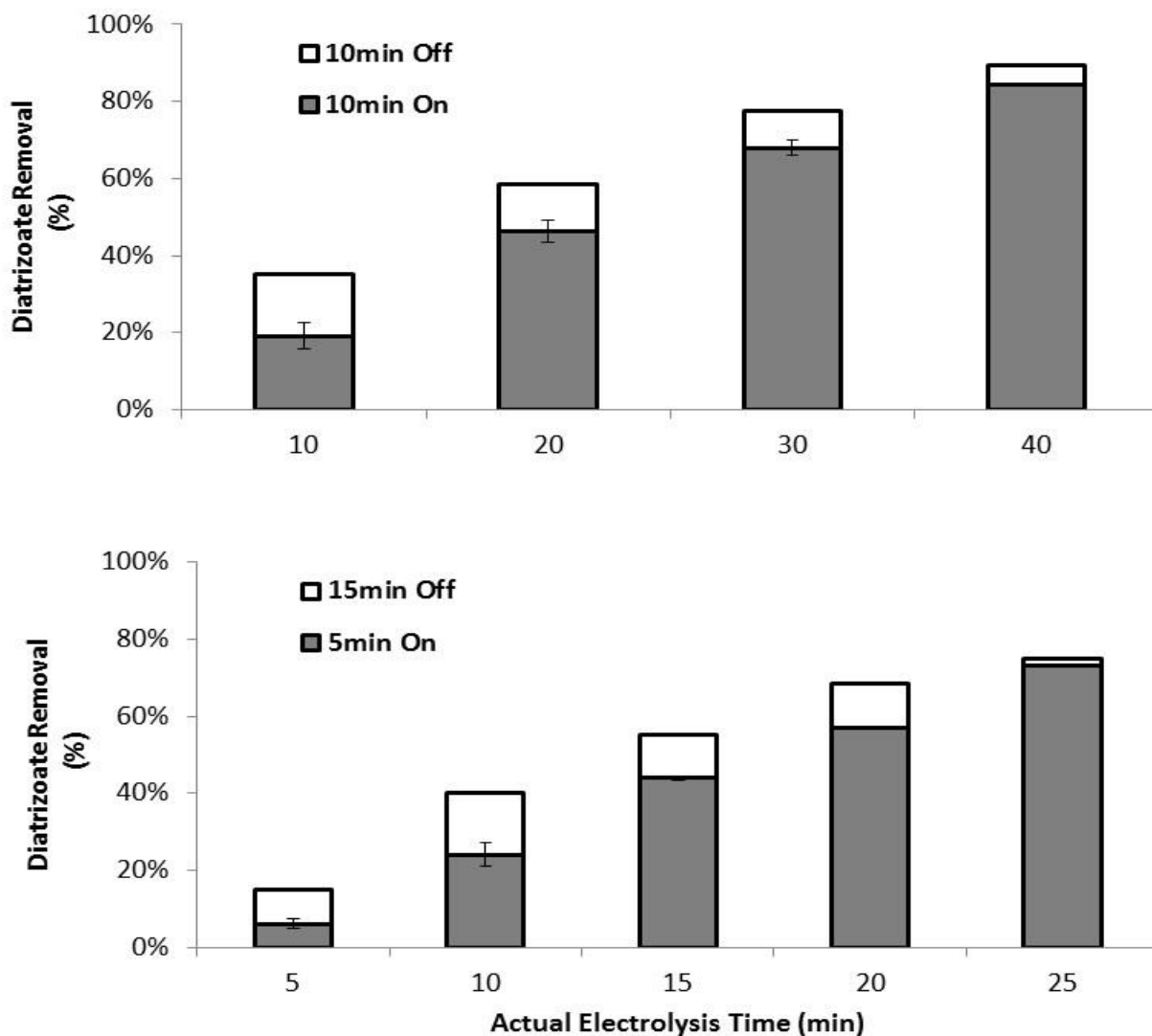
### 6.3.2 Effect of the Pulse Electric Current Modes on Diatrizoate Oxidation

These results suggest that an extended oxidation of diatrizoate is occurring after the sample was taken out of the reactor (i.e., after the electric current has been stopped), where this phenomenon is exclusively observed in the sulfate anolytes. This observed extended oxidation indicates that controlling the applied current density, such as the application of intermittent electric current or pulse electric current, can be expected to prompt substantial energy savings in these sulfate-based electrochemical systems using BDD anodes.

Results of the pulse electric current modes showed that the off-periods when current was switched off gave substantial further oxidation by an additional removal ranging from 9 – 10 % up to 16% (**Figure 6.5**). With both 10 – 10 min and 5 – 15 min scenario, diatrizoate removal exceeded ~ 75% after applying a live electric current for only 25 – 30 min, compared to 45 min of continuous electric current required to accomplish similar diatrizoate removal. When testing the removal of diatrizoate via the 1 – 19 and 1 – 9 min modes, the additional removal was smaller and in the range of 2 – 8 %, and suggest that a shorter electrolysis time can still yield further oxidation of diatrizoate. Therefore, the electrolysis time in such pulse electric current scenarios is of high importance and would require optimization.

In the case of nitrate and persulfate, no additional oxidation was observed when pulse electric current modes were tested. The final removal of diatrizoate after applying a live electric current for 40 min in nitrate was 19% which falls in accordance with the removal in the continuous current mode at  $t=30 - 45$  min (16 – 22%). Similar results were observed for persulfate with 23% removal, similar to the 22 – 26 % (at  $t=30 - 45$  min).

The total applied current required to reach 75% removal was reduced from 45 min when continuously applying the current to 30 min in the 10 – 10 min scenario and 25 min in the 5 – 15 min scenario. Such savings in the electric energy consumption from the lower electrolysis time to achieve 75% reached 33.33% in the 10 – 10 min, and up to 44.44% in the 5 – 15 min scenario.



**Figure 6.5** Diatrizoate removal (%) during the sulfate-based electrochemical oxidation using different intermittent electric current modes. The grey fraction signifies the removal % during applying the electric current, and the white fraction signifies the additional removal occurring during the resting time when the current is stopped

### 6.3.3 Effect of Off-line Diatrizoate Oxidation by pre-Oxidized Sulfate Anolyte

In order to examine the possibility of catalysis via the by-products of the organic contaminants being oxidized, electrolysing a pure sulfate solution without any organic matter inside the reactor and then adding it to a diatrizoate solution outside of the reactor was tested. The results showed that the removal % of diatrizoate was insignificant as it was obtained at less than 10% of the initial concentrations. These results suggest that the organic matter have an important role to play in the formation and activity of the long-life sulfate-based oxidizing agents.

When aliquot of 5 mL diatrizoate was added to the reactor solution after 120 min of electrooxidation of  $\text{SO}_4^{2-}$ , and left to electro-oxidize for 1 hour and then added to diatrizoate outside the reactor, the removal of diatrizoate reached up to  $18 \pm 2\%$  after injecting the system with diatrizoate. Results further indicate that the presence of organic matter is an important factor influencing the long-life time of the sulfate-based oxidizing agents, and suggest that the presence of even a very small concentration of organic matter inside the reactor would enhance the production of the sulfate-based oxidizing agents. Further optimization of the concentration of injected diatrizoate as well as the electrolysis time would further elucidate the roles of these factors in this activation method.

## 6.4 Discussion

### 6.4.1 Possible Mechanisms of the Formation of Long-life Sulfate-based Oxidants

In the absence of any chloride ions in the system, no long-life chlorine is expected to be playing any role in these experiments. Thus, the possibility of a potential contribution of other long-life oxidants such as ozone, hydrogen peroxide, or persulfate to the removal of diatrizoate can be argued since the production of these oxidants has been reported in literature (Cañizares *et al.* 2009, Panizza and Cerisola 2009, Meas *et al.* 2011). However, hydrogen peroxide and persulfate ions were both shown to be unlikely candidates (**Chapter 4, Section 4.3.2, Table 4.2**), and diatrizoate is reported to be very recalcitrant to ozone (Ternes *et al.* 2003, Huber *et al.* 2005).

The possibility of ozone and hydrogen peroxide being formed in the solution for a very short time, followed by their quick decay, where they dissociate into  $\cdot\text{OH}$  or other radical species which might activate persulfate or directly oxidize diatrizoate is also not possible. This is because the pH of the medium is highly acidic at pH 2, where ozone is not expected to report any decomposition to  $\cdot\text{OH}$  at such acidic pH (Huber *et al.* 2005), not to mention that the life-time of  $\cdot\text{OH}$  is 0.2 – 40  $\mu\text{s}$  (Burns *et al.* 2012). Moreover, Davis *et al.* (2014) previously ruled out the possibility of the electrochemical formation of ozone or  $\text{H}_2\text{O}_2$  in sulfate systems employing BDD anodes using a careful method, despite that the production of these oxidants has been earlier reported elsewhere in literature (Cañizares *et al.* 2009, Panizza and Cerisola 2009, Meas *et al.* 2011).

An anolyte sample collected from the electrochemical reactor is expected to contain only residues and by-products of diatrizoate oxidation, besides the sulfate and persulfate ions, which have been dismissed as viable long-life oxidants. The results of the off-line diatrizoate oxidation by pre-oxidized sulfate suggested that the diatrizoate residues and by-products may play a role in the extended reactive lifetime of the sulfate-based oxidants. This might be attributed to a potential activation by quinones

or other organic by-products formed during the electrooxidation of the organic contaminants (Fang *et al.* 2013). Yet, the contribution of long-life oxidants was also observed for the oxidation of other compounds such as carbamazepine by up to 20% additional removal (as shown in the preliminary results) although carbamazepine possesses completely different functional groups as compared to the iodinated diatrizoate. This adds to the ambiguity of the long-life sulfate-based oxidizing agents being produced in addition to the sulfate radicals in electrochemical treatment systems using sulfate anolytes and BDD anodes.

#### 6.4.2 Energy Savings Induced by the Sulfate-based Oxidants

The electric energy consumption per order ( $E_{EO}$ ) as well as the energy savings (%), for the four different pulse current modes, 10 – 10 min, 5 – 15 min, 1 – 9 min, and 1 – 19 min are described in **Table 6.2**. This table also compares their electric energy consumption to that for the delayed-quench experiment of sulfate (data point  $t = 30$  min) and the control experiment of continuous electric current application.

**Table 6.2 Electric energy consumption per order ( $E_{EO}$ ), expressed as electric energy, kWh m<sup>-3</sup>, to decrease the diatrizoate concentration in Na<sub>2</sub>SO<sub>4</sub> by one order of magnitude in a unit volume of treated solution for the different current application scenarios**

	Electric Energy Consumption per order (KWh m <sup>-3</sup> )	Energy Savings (%)
Control Exp.	9.2	-
Delayed quench	6.7	27%
10 – 10 min	6	35%
5 – 15 min	5.9	36%
1 – 9 min	6.1	34%
1 – 19 min	5.3	42%



Calculations show that the delayed quench experiment yielded 27% energy savings with only 6.7 kWh m<sup>-3</sup> compared to the continuous electric current requiring 9.2 kWh m<sup>-3</sup>. Whereas, the energy consumption of the electrochemical system using the different pulse current modes was reduced by 34 to 42% from 9.2 to as low as 5.3 kWh m<sup>-3</sup>.

Being able to reduce the electric energy consumption by more than one fourth in delayed quench and more than one third in pulse current application is of high significance and advocates the potential application of such sulfate-based electrochemical treatment systems.

### **6.5 Concluding Remarks**

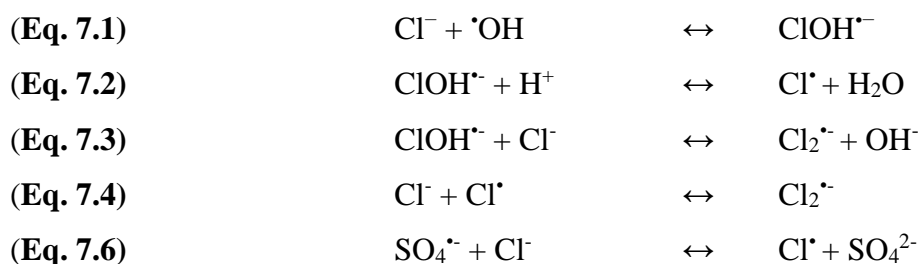
This chapter explored the formation of long-life sulfate-based oxidizing agents and reported their ability to oxidize chemicals even after the applied current is stopped. This finding suggested large savings in electrical energy consumption in the novel current applications of these sulfate-based electrochemical systems in the removal of persistent organic contaminants. The on-bench delayed quenching as well as the application of intermittent electric current using several different pulse modes provided solid evidence of the formation of these long-life sulfate-based oxidizing agents. The ‘organics-free’ electrochemical oxidation of sulfate ions followed by its addition to the diatrizoate prepared outside the reactor with and without spiking with a small concentration of diatrizoate suggested that the presence of the organic matter at the time of the electrolysis of sulfate ions is an important factor governing the formation of these long-life sulfate-based oxidizing agents. The possibility of a potential contribution of ozone, hydrogen peroxide, or persulfate was ruled out, and the similar results obtained for other organic compounds added to the ambiguity of the nature of these long-life sulfate-based oxidizing agents being produced in addition to the sulfate radicals in electrochemical treatment systems using sulfate anolytes and BDD anodes. Regardless of the nature of the oxidizing agents being produced, this work further confirmed the formation of long-life sulfate-based oxidizing agents, capable of significantly oxidizing persistent organic contaminants such as diatrizoate and carbamazepine, while inducing large energy savings due to their extended reactive lifetime.

## **Chapter 7: Impact of Chloride on Resorcinol Oxidation by Electro-Activated Sulfate**

This chapter presents the results of investigating the influence of the presence of chloride ions on the performance of BDD electrooxidation of resorcinol as a surrogate for natural organic matter (NOM), in Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub> anolyte. Resorcinol was chosen instead of diatrizoate because it acts as a surrogate for natural matter and also because of the impracticality of using large initial concentrations of diatrizoate (~ 100 mg L<sup>-1</sup>), several order of magnitude higher than what is being detected in water bodies. The electrochemical removal of resorcinol (Section 7.3.1), and its mineralization (Section 7.3.2), were compared in sulfate and nitrate solutions at various chloride concentrations in this Chapter. It also investigated the formation of chlorinated organic by-products measured as adsorbable organic chlorine (Section 7.3.3), as well as of the toxic inorganic by-products such as chlorate and perchlorate (Section 7.3.4). The effect of sulfate addition on chloride-based electrooxidation of resorcinol was also presented in this chapter (Section 7.3.5), as well as the performance of these systems at acidic pH and neutral pH (Section 7.3.6).

## 7.1 Introduction

One of the main limitations of electrooxidation processes is the formation of toxic chlorinated organic and inorganic by-products in the presence of chloride (Bergmann and Rollin 2007). Anodic oxidation of  $\text{Cl}^-$  generates reactive chlorine species such as chlorine ( $\text{Cl}_2$ ) and hypochlorous acid ( $\text{HOCl}$ ), which react rapidly with unsaturated bonds and electron-rich moieties to form chlorinated organic by-products (Deborde and Von Gunten 2008). In addition, chloride ions are also electrochemically oxidized to chlorine radicals ( $\text{Cl}^\bullet$  and  $\text{Cl}_2^{\bullet-}$ ) (Park *et al.* 2009, Cho and Hoffmann 2014). Although the exact mechanisms of the reaction of chloride ions with  $^\bullet\text{OH}$  and  $\text{SO}_4^{\bullet-}$  electrogenerated at the BDD anode have not been explained yet, they can be assumed as analogous to their reaction with the homogeneously formed radical species. While  $^\bullet\text{OH}$  reacts with  $\text{Cl}^-$  via  $\text{ClOH}^{\bullet-}$  intermediate to form  $\text{Cl}^\bullet$  and  $\text{Cl}_2^{\bullet-}$  radicals (Eqs. 7.1–7.4),  $\text{SO}_4^{\bullet-}$  directly forms  $\text{Cl}^\bullet$  radicals (Eq. 7.6),  $k = 3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (Das 2001).



Compared to  $^\bullet\text{OH}$  ( $E^0 = 2.38 \text{ V}$ ) and  $\text{SO}_4^{\bullet-}$  ( $E^0 = 2.43 \text{ V}$ ), the chloride radical ( $\text{Cl}^\bullet$ ,  $E^0(\text{Cl}^\bullet/\text{Cl}^-) = 2.41 \text{ V}$ ) (Schwarz and Dodson 1984, Wardman 1989) reacts with aromatics at similar second-order rate constants ranging from  $10^8$ - $10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Neta *et al.* 1988).  $\text{Cl}^\bullet$  is converted into a weaker oxidant, namely dichloride radical ion ( $\text{Cl}_2^{\bullet-}$ ,  $E^0(\text{Cl}_2^{\bullet-}/2\text{Cl}^-) = 2.09 \text{ V}$ ) (Schwarz and Dodson 1984, Wardman 1989), in the presence of higher chloride concentrations. Both radical species react via hydrogen abstraction and electron transfer, as well as addition to double bonds, with the latter resulting in the formation of toxic organochlorines (Costa *et al.* 2009, Grebel *et al.* 2010). It is noteworthy to mention that redox potential values often cited in literature are in fact of limited information mainly because reactions are principally driven by kinetics rather than by thermodynamics.

In addition, the presence of chloride may yield toxic chlorate, and also perchlorate, at higher current densities typically applied in electrooxidation at BDD anode (Bergmann *et al.* 2009). While chlorate can be formed chemically and electrochemically, perchlorate generation is strictly electrochemical and limited to further oxidation of chlorate at the anode surface (Bergmann and Rollin 2007). In Chapter 4, we have observed electrochemical activation of sulfate, which yielded 10 – 15 folds-higher

removal rates of several persistent organic contaminants as compared to  $\cdot\text{OH}$ -based anodic oxidation, i.e., oxidation at the BDD anode in the absence of  $\text{SO}_4^{2-}$ . The presence of  $\text{SO}_4^{2-}$  and its presumed activation to  $\text{SO}_4\cdot^-$  at the BDD anode may have a significant impact on the electrooxidation of organic matter as well as on the electrogeneration of both organic and inorganic chlorinated compounds.

Therefore, the objective of this study was to investigate the performance of BDD electrooxidation of resorcinol as a surrogate for natural organic matter (NOM), in  $\text{Na}_2\text{SO}_4$  anolyte and in the presence of chloride, and compare it to inert  $\text{NaNO}_3$  anolyte. The potential scavenging effect of  $\text{Cl}^-$  on the removal of resorcinol was investigated primarily at acidic pH 2, which yields the same redox potentials for  $\text{SO}_4\cdot^-$  (i.e., 2.5 – 3.1 V) and  $\cdot\text{OH}$  (i.e., 2.38 – 2.7 V) and minimises the hydrolysis of  $\text{SO}_4\cdot^-$  into  $\cdot\text{OH}$ , which is expected to occur at high pH (Buxton *et al.* 1988, Neta *et al.* 1988, Wardman 1989, Zhang *et al.* 2014). Given that pH has a different effect on the respective scavenging of  $\text{Cl}^-$  by  $\cdot\text{OH}$  and  $\text{Cl}^-$  by  $\text{SO}_4\cdot^-$ , a set of experiments was also performed at neutral pH. This work investigated the removal of resorcinol and total organic carbon (TOC), as well as the formation of chlorinated organic by-products measured as adsorbable organic chlorine (AOCl), and the inorganic by-products chlorate and perchlorate.

## 7.2 Materials and Methods

### 7.2.1 Experimental Setup

The same CEM-divided electrochemical reactor as described in the **Cell Design and Reactor Specifications (Section 3.1)** was used for all pH 2 experiments. The reactor was modified for the experiments at neutral pH to an undivided one-chamber cell, having the same volume as the anodic chamber of the divided cell and thus maintaining the same active vs. total volume ratio in all experiments. The solution pH in the undivided cell was controlled at  $\text{pH } 6.96 \pm 0.3$  using a *Liquisys M* pH controller from Endress+Hauser (Switzerland). All experiments were conducted with 2 L solutions of  $100 \text{ mg L}^{-1}$  resorcinol, pumped at  $200 \text{ mL min}^{-1}$  at room temperature ( $23 \pm 2 \text{ }^\circ\text{C}$ ). Chronopotentiometric experiments were performed during 6 h at the applied current density of  $200 \text{ A m}^{-2}$  (resulting anode potential was  $3.1 \pm 0.1 \text{ V vs SHE}$ ). In periodic sampling, 26 mL samples collected every hour were immediately quenched with 260  $\mu\text{L}$  of 1.0 M sodium bisulfite ( $\text{NaHSO}_3$ ).

To investigate the effect of chloride on sulfate-based electro-oxidation at BDD anode, the removal of resorcinol was studied with 0, 5, 10, 20, and 40 mM of  $\text{NaCl}$  in  $\text{Na}_2\text{SO}_4$  or  $\text{NaNO}_3$  anolytes ( $\text{pH } 2 \pm 0.1$  and  $8.7 \pm 1.0 \text{ mS cm}^{-1}$ ). In order to prepare all anolyte solutions at similar initial pH and

conductivity while containing different chloride concentrations (0 – 40 mM), sulfate or nitrate solutions were adjusted to pH 2 by adding concentrated H<sub>2</sub>SO<sub>4</sub> or HNO<sub>3</sub>, respectively. The final SO<sub>4</sub><sup>2-</sup> concentration in all cases was fixed at 20 mM, whereas the NO<sub>3</sub><sup>-</sup> concentrations needed to prepare the anolyte solutions with pH 2 and ~ 9.0 mS cm<sup>-1</sup> was 40.9 ± 8.3 mM, except in the absence of chloride where NO<sub>3</sub><sup>-</sup> concentrations needed was 60 mM. A set of experiments was designed at fixed 10 mM Cl<sup>-</sup>, while varying the sulfate concentration (0, 5, 10, and 20 mM). In the neutral pH experiments, the employed electrolytes were Na<sub>2</sub>SO<sub>4</sub> (20 mM) and NaNO<sub>3</sub> (80 mM) in the presence of 10 mM NaCl (pH 6.96 ± 0.3 and 9.1 ± 0.2 mS cm<sup>-1</sup>), where the pH was adjusted by adding concentrated NaOH.

### 7.2.2 Chemical Analysis

Total organic carbon (TOC) was measured using a Shimadzu TOC-L CSH Analyser (Japan). High-performance liquid chromatography (HPLC) equipped with a diode array UV detector (SPD-M10AVP) from Shimadzu, Japan was employed to measure resorcinol. The concentrations of Cl<sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, and ClO<sub>4</sub><sup>-</sup> were determined using Dionex ICS-2100 ion chromatography (IC) (Sunnyvale, CA), equipped with a DS6 heated conductivity detector. The measurement of free chlorine was not possible during electrolysis in Na<sub>2</sub>SO<sub>4</sub> anolyte, due to the interference of the formed persulfate in the N,N'-diethyl-p-phenylenediamine (DPD) method. For this reason, we could not compare the residual chlorine in NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> anolyte. Adsorbable organic chloride (AOCl) was determined using AQF-2100H Shimadzu system (Japan) for a limited number of samples only, due to cost limitations. Details of the analytical methods are summarized in Chapter 3 (**Section 3.3**).

## 7.3 Results and Discussion

### 7.3.1 Effect of chloride addition on the electrooxidation of resorcinol

The apparent electrooxidation rate constants of resorcinol in NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> anolyte and with the addition of different chloride concentrations are summarized in **Table 7.1**. In the absence of chloride, electrooxidation of resorcinol was approximately 8-fold faster in Na<sub>2</sub>SO<sub>4</sub> anolyte due to electrochemical activation of sulfate, which is in agreement with the results obtained in previous chapters. Addition of incremental amounts of chloride to NaNO<sub>3</sub> background anolyte increased the apparent rate constants for resorcinol oxidation from 0.26 ± 0.03 h<sup>-1</sup> (0 mM Cl<sup>-</sup>) to 1.2 ± 0.13 h<sup>-1</sup> (40 mM Cl<sup>-</sup>). Chloride has an inhibiting effect on the degradation of organic contaminants by the homogeneously formed <sup>•</sup>OH, particularly at low pH, due to the formation of radical chlorine species (Cl<sup>•</sup>, Cl<sub>2</sub><sup>•-</sup>) which are weaker oxidants than <sup>•</sup>OH (Pignatello 1992, Kiwi *et al.* 2000, Seiss *et al.* 2001,

Maciel *et al.* 2004, Moraes *et al.* 2004, Afzal *et al.* 2012). The enhancing effect of chloride observed in NaNO<sub>3</sub> anolyte can be ascribed to an increased generation of free available chlorine (Cl<sub>2</sub>/HOCl) by the electrolysis of chloride at BDD anode (Bergmann and Rollin 2007). Resorcinol (pK<sub>a1</sub>= 9.43, pK<sub>a2</sub>= 11.21) is an electron-rich compound susceptible to electrophilic aromatic substitution by chlorine, particularly at pH 2 where its reactivity with chlorine is exponentially increased ( $k = 8.6 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$ ) (Rebenne *et al.* 1996). Thus, electrooxidation of resorcinol in NaNO<sub>3</sub> anolyte and in the presence of chloride concentrations seems to be dominated by electrochlorination.

The addition of chloride gradually decreased the apparent rate constant of resorcinol removal in Na<sub>2</sub>SO<sub>4</sub> from  $2.4 \pm 0.18 \text{ h}^{-1}$  (0 mM Cl<sup>-</sup>) to  $0.61 \pm 0.06 \text{ h}^{-1}$  (20 mM Cl<sup>-</sup>). This inhibiting effect of chloride could be a consequence of more pronounced scavenging of Cl<sup>-</sup> and conversion of SO<sub>4</sub><sup>•-</sup> to less reactive halogen radicals (**Eq. 7.6**). Yang *et al.* observed a greater impact of Cl<sup>-</sup> on the SO<sub>4</sub><sup>•-</sup>-based oxidation than in the case of <sup>•</sup>OH-based oxidation at neutral pH (Yang *et al.* 2014). They explained this by the direct formation of Cl<sup>•</sup>, compared to reactions involving ClOH<sup>•-</sup> intermediate in the latter case (**Eqs. 7.1–7.2**). Although acidic pH causes the balance of the **Eq. (7.2)** to move to the right, the formation of Cl<sup>•</sup> from <sup>•</sup>OH remains a two-step process.

Addition of chloride in excess to sulfate slightly increased the apparent rate constant of resorcinol from  $0.61 \pm 0.06 \text{ h}^{-1}$  to  $0.81 \pm 0.11 \text{ h}^{-1}$  at 40 mM Cl<sup>-</sup>, probably due to chlorine being generated in more significant amounts at the anode and thus enhanced contribution of electrochlorination to the removal of resorcinol. It is important to note that the impact of halides on SO<sub>4</sub><sup>•-</sup>-based oxidation seems to depend on the target contaminant removed, and it can either inhibit or promote their degradation (Liang *et al.* 2006, Fang *et al.* 2012, Yang *et al.* 2014). Thus, while it may be possible to extrapolate the results obtained here to electron-rich compounds of similar structure to resorcinol, the effect of chloride on electrooxidation in the presence of sulfate may differ for other contaminants, and particularly for electron-deficient molecules.

**Table 7.1 Apparent first-order rate constants ( $\pm$ error at 95% confidence level) for electrooxidation of resorcinol ( $k_{\text{RES}}$ , h<sup>-1</sup>) in Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub> anolytes at pH 2 and 9 mS cm<sup>-1</sup> in the presence of 0 – 40 mM NaCl.**

$k_{\text{RES}}$ (h <sup>-1</sup> )	0 mM Cl <sup>-</sup>	5 mM Cl <sup>-</sup>	10 mM Cl <sup>-</sup>	20 mM Cl <sup>-</sup>	40 mM Cl <sup>-</sup>
NaNO <sub>3</sub>	$0.26 \pm 0.03$	$0.27 \pm 0.04$	$0.44 \pm 0.03$	$0.77 \pm 0.19$	$1.2 \pm 0.13$
Na <sub>2</sub> SO <sub>4</sub>	$2.4 \pm 0.18$	$1.1 \pm 0.18$	$0.60 \pm 0.09$	$0.61 \pm 0.06$	$0.81 \pm 0.11$

### 7.3.2 Effect of chloride addition on TOC removal

In terms of TOC removal, Na<sub>2</sub>SO<sub>4</sub> anolyte yielded 2.7-fold higher degradation rate compared to NaNO<sub>3</sub> anolyte in the absence of chloride (**Table 7.2**). Addition of chloride to NaNO<sub>3</sub> anolyte did not have a significant effect on the mineralization of resorcinol, and the apparent rate constant for TOC removal remained relatively constant at around 0.062 – 0.076 h<sup>-1</sup>. This is in accordance with the abovementioned assumption of electrochlorination being the dominant mechanism of resorcinol oxidation in the absence of sulfate. Electrophilic substitution of resorcinol with chlorine and/or addition of chloride radicals to a benzene ring are likely to lead to its transformation to chlorinated aromatic by-products, rather than mineralization. Thus, a higher concentration of anodically formed chlorine present in excess is not expected to have a substantial effect on the TOC removal efficiency of the process. Previously, removal of TOC in sulfamethoxazole electrooxidation at BDD anode was found to be current-controlled (i.e., proportional to the supplied charge) and independent of chloride concentration (Boudreau *et al.* 2010).

In addition, in the presence of high chloride concentration, most of the electrogenerated <sup>•</sup>OH can be expected to be scavenged by the Cl<sup>-</sup> and converted to chlorine radicals (Cl<sup>•</sup>, Cl<sub>2</sub><sup>•-</sup>) (Park *et al.* 2009), which are also capable of bond breakage, albeit that chlorine radicals are weaker oxidants than <sup>•</sup>OH (Cho *et al.* 2014). The Cl<sup>-</sup> scavenging of <sup>•</sup>OH leads to the formation primarily of Cl<sub>2</sub><sup>•-</sup> (E<sup>0</sup>(Cl<sub>2</sub><sup>•-</sup>/2Cl<sup>-</sup>) = 2.09 V) (Schwarz and Dodson 1984, Wardman 1989), in the presence of excess chloride (Kiwi *et al.* 2000, Yang *et al.* 2014). Formation of a stronger oxidant of Cl<sup>•</sup>, (E<sup>0</sup> Cl<sup>•</sup>/Cl<sup>-</sup>) = 2.41 V) (Schwarz and Dodson 1984, Wardman 1989), can be expected only for chloride-to-substrate ratios lower than 1 (Gilbert *et al.* 1988, Buxton *et al.* 2000), which was not the case in the present study because the initial concentration of resorcinol was only 0.91 mM (100 mg L<sup>-1</sup>). Similar to <sup>•</sup>OH, Cl<sub>2</sub><sup>•-</sup> reacts with aromatics via hydrogen abstraction, electrophilic addition, and direct electron transfer mechanisms, and was likely responsible for bond breakage and organic matter degradation in the presence of Cl<sup>-</sup> (Park *et al.* 2009).

Yet, Cl<sup>-</sup> exhibited an inhibiting effect on the resorcinol mineralization in Na<sub>2</sub>SO<sub>4</sub> anolyte. For example, the apparent TOC removal rate constant was halved from 0.19 ± 0.02 h<sup>-1</sup> to 0.09 ± 0.01 h<sup>-1</sup> after addition of 40 mM Cl<sup>-</sup> (**Table 7.2**). Similar to what was observed for the apparent rate constants of resorcinol removal in the presence of Cl<sup>-</sup>, this result is likely a consequence of a more efficient scavenging of SO<sub>4</sub><sup>•-</sup> by Cl<sup>-</sup>, compared to an <sup>•</sup>OH-initiated oxidation. Nevertheless, TOC removal was still higher in Na<sub>2</sub>SO<sub>4</sub> than in NaNO<sub>3</sub> anolyte for all investigated chloride concentrations, demonstrating again a stronger oxidizing capacity of BDD electrolysis in the presence of SO<sub>4</sub><sup>2-</sup>.

**Table 7.2 Apparent rate constants ( $\pm$ error at 95% confidence level) for the TOC removal ( $k_{TOC}$ ,  $h^{-1}$ ) in the electrooxidation of resorcinol in  $Na_2SO_4$  and  $NaNO_3$  anolytes at pH 2 and 9  $mS\ cm^{-1}$  in the presence of 0 – 40 mM NaCl.**

Chloride concentration (mM)	$k_{TOC}$ ( $h^{-1}$ )	
	$NaNO_3$	$Na_2SO_4$
0	$0.068 \pm 0.007$	$0.19 \pm 0.02$
5	$0.066 \pm 0.003$	$0.14 \pm 0.02$
10	$0.062 \pm 0.003$	$0.11 \pm 0.01$
20	$0.072 \pm 0.006$	$0.081 \pm 0.004$
40	$0.076 \pm 0.006$	$0.090 \pm 0.006$

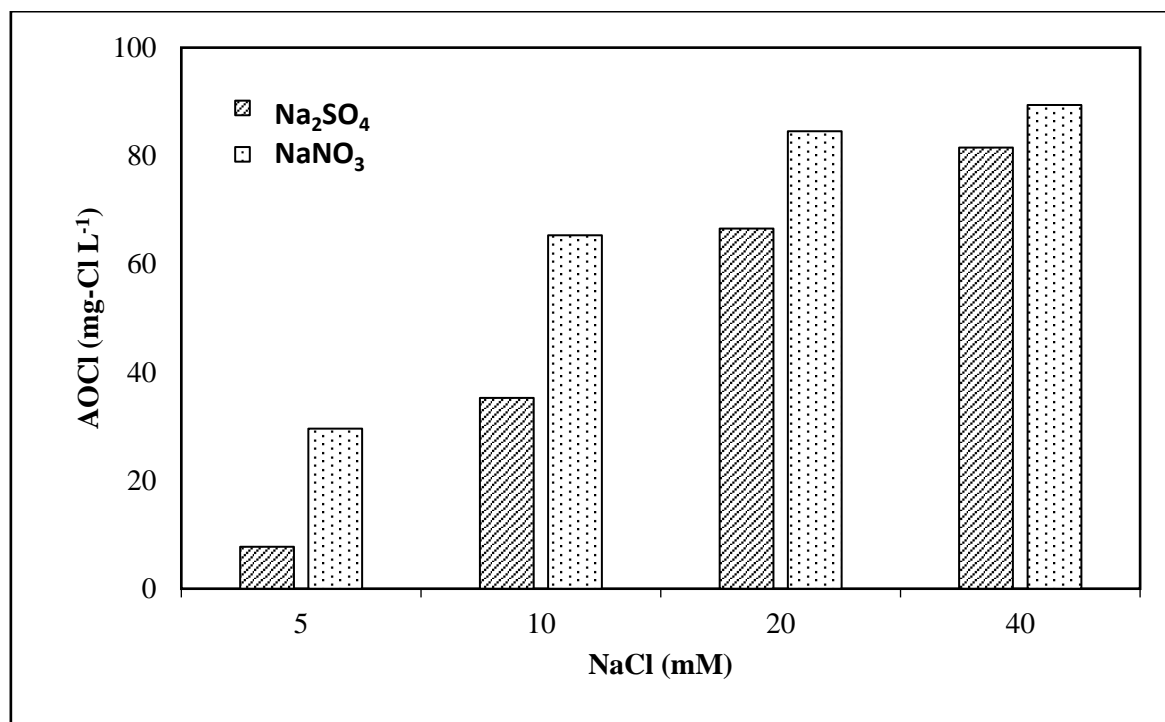
### 7.3.3 Effect of chloride addition on the formation of chlorinated organics

The formation of chlorinated organic by-products, measured as AOCl for the final samples at  $t = 6$  h from the electrolysis experiments is presented in **Figure 7.1**. These results suggested, as expected, that higher concentration of  $Cl^-$  yielded more chlorine-based oxidants formed at the anode, and thus increased the formation of AOCl in both anolytes. AOCl generation was enhanced in  $NaNO_3$  anolyte due to the prevailing role of anodically formed chlorine in electrochlorination, which is a long-lived oxidant able to diffuse away from the anode surface into the bulk liquid. The enhanced electrochlorination of resorcinol in  $NaNO_3$  anolyte is also evident from the observed faster disappearance of resorcinol with increasing  $Cl^-$  concentrations (**Table 7.1**). Yet, AOCl was formed in lower amounts in  $Na_2SO_4$  anolyte compared to  $NaNO_3$  anolyte, particularly for  $[SO_4^{2-}]:[Cl^-] > 1$ . Given the more efficient conversion of  $Cl^-$  to  $Cl_2^{\bullet-}$  in sulfate anolyte, electrochlorination of resorcinol may have been more dominated by the short-lived radical chlorine species rather than chlorine, compared with nitrate anolyte. Thus, in  $Na_2SO_4$  anolyte the formation of chlorinated organics would be confined to the vicinity of the anode surface, thus subjecting the process to mass transfer limitations.

In addition, based on the previously discussed data for TOC removal, electrolysis in the presence of sulfate at low chloride concentrations seems to have higher oxidizing capacity than the equivalent system with  $NaNO_3$  as background anolyte. In experiments using less than 20 mM NaCl (i.e.,  $[SO_4^{2-}]:[Cl^-] > 1$ ), AOCl appeared to form at much lower concentrations in  $Na_2SO_4$  compared to  $NaNO_3$  (**Figure 7.1**). This could be expected from a more efficient degradation of resorcinol and its chlorinated organic by-products by the electrogenerated  $SO_4^{\bullet-}$ . This is in accordance with results of



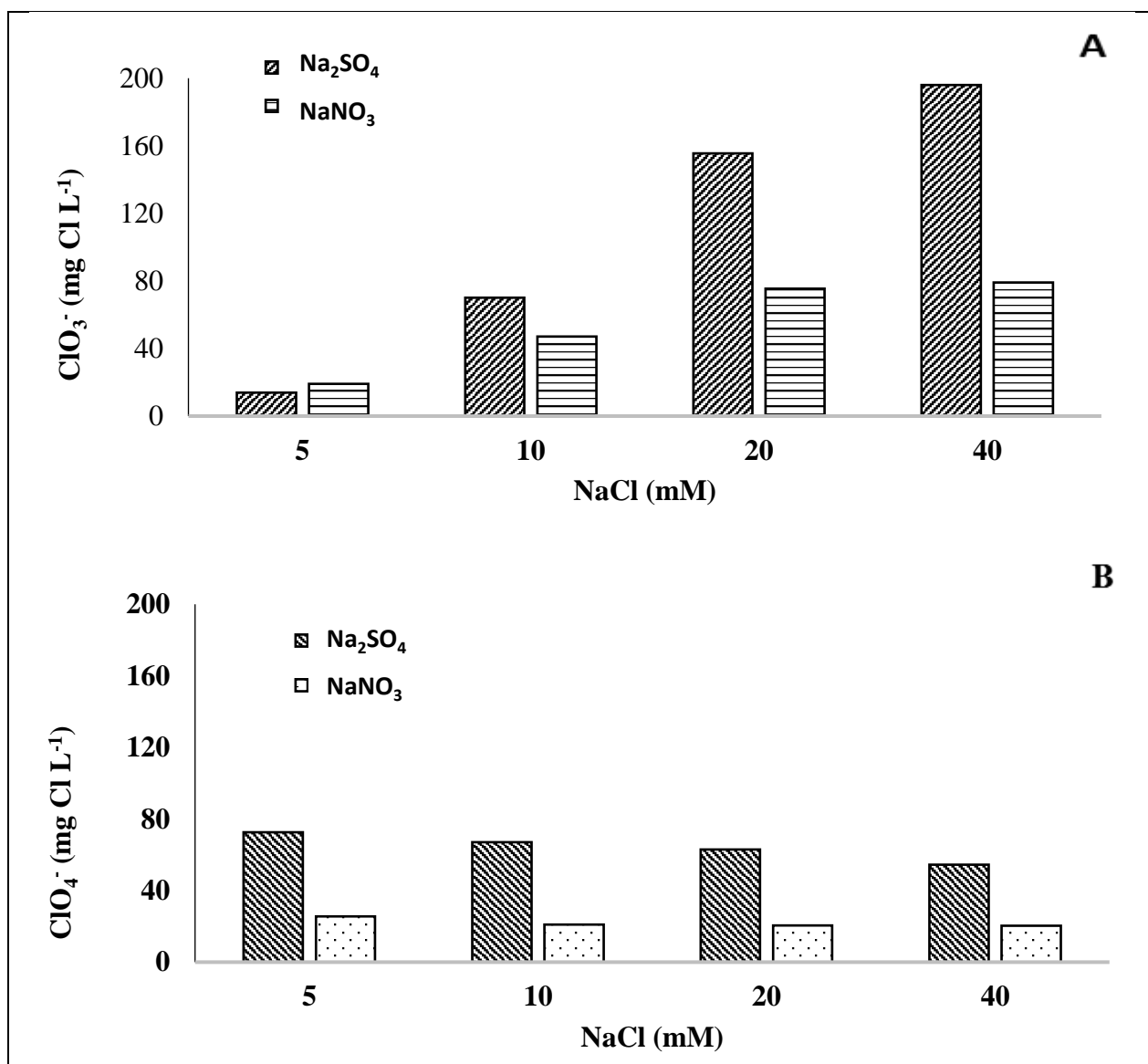
Chapter 4, where electrolysis rates of several poly-halogenated compounds (e.g., triclopyr, triclosan, tribromophenol, and X-ray contrast media) at BDD anode were 10 – 15 fold higher in  $\text{SO}_4^{2-}$  than in  $\text{NO}_3^-$ . The difference between the formed AOCl in  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  appeared to become less pronounced for  $[\text{SO}_4^{2-}]:[\text{Cl}^-] \leq 1$ , probably due to a greater scavenging of  $\text{SO}_4^{\bullet-}$ , and thus less efficient degradation of organic matter.



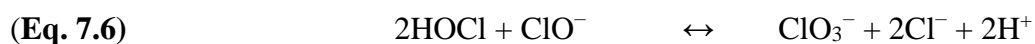
**Figure 7.1** Formation of adsorbable organic chlorine (AOCl, in  $\text{mgCl}^- \text{L}^{-1}$ ), after  $2.4 \text{ Ah L}^{-1}$  of specific electrical charge supplied in the electrooxidation of resorcinol in  $\text{Na}_2\text{SO}_4$  and  $\text{NaNO}_3$  analytes ( $\text{pH } 2$  and  $9 \text{ mS cm}^{-1}$ ) in the presence of  $5 - 40 \text{ mM NaCl}$

### 7.3.4 Effect of chloride addition on the formation of chlorate and perchlorate

Chlorate and perchlorate concentrations measured in each of the relevant experiments showed that the differences and trends discussed in this chapter were significant (**Figure 7.2**). The formation of chlorate was directly proportional to the concentration of  $\text{Cl}^-$ , where chloride addition enhanced the anodic generation of chlorate in both analytes. Similar results have been previously reported by other authors (Jung *et al.* 2010, Li and Ni 2012). In anodic oxidation, chlorate is formed either electrochemically, by the subsequent electrolysis of  $\text{Cl}^-$ ,  $\text{OCl}^-$ , and  $\text{ClO}_2^-$  ions (Bergmann and Rollin 2007), or by a purely chemical reaction of  $\text{HOCl}$  with  $\text{ClO}^-$  in the bulk solution (**Eqs. 7.6 – 7.7**) (Garcia-Segura *et al.* 2015):

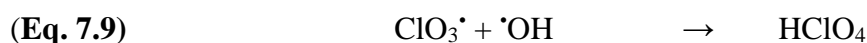


**Figure 7.2** Concentrations of chlorate (A) and perchlorate (B) (in  $\text{mg Cl}^{-1} \text{ L}^{-1}$ ), after  $2.4 \text{ Ah L}^{-1}$  of specific electrical charge supplied in the electrooxidation of resorcinol in  $\text{Na}_2\text{SO}_4$  and  $\text{NaNO}_3$  anolytes (pH 2 and  $9 \text{ mS cm}^{-1}$ ) in the presence of 5 – 40 mM NaCl



Given that chemical formation of  $\text{ClO}_3^{-}$  is favored in the pH range 6 – 9, it was unlikely to contribute to the chlorate formation in the experiments conducted at pH 2 (Gordon and Tachiyashiki 1991). Thus, increasing the initial concentration of chloride ions enhanced their direct electrolysis and yielded higher concentrations of  $\text{ClO}_3^{-}$ . However, an increasing amount of chloride did not increase the formation of perchlorate in both  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  anolyte. Similar results were reported by Bergmann *et al.* (2009) who observed less  $\text{ClO}_4^{-}$  formed for higher initial  $\text{Cl}^{-}$  content. This was

explained by the adsorption of  $\text{Cl}^-$  at the anode surface, which limits the available active sites for further  $\text{ClO}_3^-$  oxidation. The formation of perchlorate at BDD anode is considered to be purely electrochemical (Bergmann and Rollin 2007). Direct electrolysis of  $\text{ClO}_3^-$  is the rate-determining step in the multistep pathway of oxidation of  $\text{Cl}^-$  to  $\text{ClO}_4^-$  at the BDD anode (Bergmann and Rollin 2007). The mechanism was postulated to proceed as a two-step process involving direct electrolysis of  $\text{ClO}_3^-$  at the BDD surface to form  $\text{ClO}_3^\bullet$  radicals (**Eq. 7.8**), and their subsequent solution-phase reaction with the electrogenerated  $\bullet\text{OH}$  to yield  $\text{ClO}_4^-$  (**Eq. 7.9**) (Azizi *et al.* 2011). Thus, given that the first step is a surface-based reaction, the presence of high concentrations of competitive ions such as  $\text{Cl}^-$  may decrease the formation of  $\text{ClO}_4^-$ .



In terms of the anolyte effect, both chlorate and perchlorate were formed in higher amounts in  $\text{Na}_2\text{SO}_4$  anolyte compared to the  $\text{NaNO}_3$ , for the same initial chloride concentration (**Figure 7.2**). This could be a consequence of a greater effect of  $\text{NO}_3^-$  adsorption at the anode surface. The ionic mobility ( $u_i$ ) of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ions was estimated using the Nernst–Einstein relationship (**Eq. 7.10**) to be  $7.67 \times 10^{-13}$  and  $4.30 \times 10^{-13} \text{ m}^2 \text{ mol J}^{-1} \text{ s}^{-1}$ , respectively (Moon *et al.* 2004).

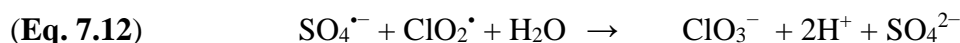
$$\text{(Eq. 7.10)} \quad u_i = \frac{D_i}{R \times T},$$

where  $D_i$  is the diffusion coefficient of species  $i$  in the solution ( $\text{m}^2 \text{ s}^{-1}$ ),  $R$  is the gas constant number ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ), and  $T$  is temperature (298 K). The estimated ionic mobility ( $u_i$ ) of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HSO}_4^-$  ions in dilute solution (**Table 7.3**), allow for the elimination of the ionic mobility of species  $i$  (i.e.,  $u_i$ ,  $\text{m}^2 \text{ mol J}^{-1} \text{ s}^{-1}$ ), as an independent parameter. Higher mobility of  $\text{NO}_3^-$  ions compared to  $\text{SO}_4^{2-}$  ions leads to their greater adsorption at the active sites at the anode surface and thus higher inhibition of the multi-step reactions of electrochemical formation of  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$ . Nevertheless, this phenomenon was not contributing significantly to the observed enhanced resorcinol oxidation in  $\text{Na}_2\text{SO}_4$ , where the differences in its removal rates were not reflected by the difference between the ionic mobilities of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ions. Resorcinol oxidation rate was 8-fold higher in  $\text{Na}_2\text{SO}_4$  compared to  $\text{NaNO}_3$  in the absence of chloride, whereas the ionic mobility of  $\text{NO}_3^-$  is only 1.8-fold higher than that of  $\text{SO}_4^{2-}$  ion. In addition, electrooxidation rate constants of the seven persistent organic contaminants in  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  anolytes were one order of magnitude higher in sulfate despite that the higher or lower nitrate concentration used.

**Table 7.3 Estimated ionic mobility ( $u_i$ ) of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HSO}_4^-$  ions in dilute solution using the Nernst–Einstein relationship.**

Ion species (i)	Diffusion coefficient ( $D_i$ ), $10^{-9} \text{ m}^2 \text{ s}^{-1}$	Ionic mobility ( $u_i$ ) at 298 K, $10^{-13} \text{ m}^2 \text{ mol J}^{-1} \text{ s}^{-1}$
$\text{Cl}^-$	2.03	8.19
$\text{NO}_3^-$	1.90	7.67
$\text{SO}_4^{2-}$	1.066	4.30
$\text{HSO}_4^-$	1.39	6.60

The enhanced oxidation rate of chloride ions by  $\text{SO}_4^{\bullet-}$  formed at the anode surface may also contribute to the higher concentrations of  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  observed in  $\text{Na}_2\text{SO}_4$  anolyte because of the competition reactions with  $\cdot\text{OH}$ . For example, in the presence of 40 mM NaCl, chloride was oxidized at rate of  $0.066 \pm 0.004 \text{ h}^{-1}$ , in  $\text{Na}_2\text{SO}_4$  anolyte, and  $0.038 \pm 0.007 \text{ h}^{-1}$  in  $\text{NaNO}_3$  anolyte, as shown in **Table 7.4**, where the rates of chloride oxidation were calculated based on chloride loss as measured by IC. Electrolysis of chloride at BDD anode in  $\text{Na}_2\text{SO}_4$  anolyte seems to favor the multi-step oxidation of  $\text{Cl}^-$  to  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  over its oxidation to  $\text{Cl}_2$ . Electrogenerated  $\cdot\text{OH}$  and  $\text{SO}_4^{\bullet-}$  can possibly react with  $\text{HOCl}$  to form  $\text{ClO}_2\cdot$  and other oxychlorine radicals. Both radical species can react further with  $\text{ClO}_2\cdot$  with bimolecular rate constants in the order of  $10^9 \text{ M}^{-1} \text{ s}^{-1}$  to form  $\text{ClO}_3^-$  (**Eqs. 7.11 – 7.12**) (Lutze *et al.* 2015, Qian *et al.* 2016):

**Table 7.4 Apparent rate constants ( $\text{h}^{-1}$ ) of chloride oxidation in  $\text{Na}_2\text{SO}_4$  versus  $\text{NaNO}_3$  anolyte, and in the presence of 5, 10, 20, and 40 mM NaCl at pH 2, except where mentioned pH 7 (10 mM NaCl).**

$\text{Cl}^-$ ( $\text{h}^{-1}$ )	$\text{Na}_2\text{SO}_4$	$\text{NaNO}_3$
5 mM	$0.130 \pm 0.009$	$0.094 \pm 0.007$
10 mM	$0.096 \pm 0.014$	$0.066 \pm 0.009$
20 mM	$0.077 \pm 0.016$	$0.039 \pm 0.001$
40 mM	$0.066 \pm 0.004$	$0.038 \pm 0.007$
10 mM (pH=7)	$0.086 \pm 0.004$	$0.072 \pm 0.014$

Previous studies reported stoichiometric conversion of  $\text{Cl}^-$  to  $\text{ClO}_3^-$  in  $\text{SO}_4^{\cdot-}$ -based oxidation processes at acidic pH (Lutze *et al.* 2015, Qian *et al.* 2016). Although the reactions above were investigated for the homogeneously formed radical species,  $\text{ClO}_2^{\cdot}$  can also be formed at the BDD anode and was postulated to be an intermediate in the anodic generation of chlorate (Hubler *et al.* 2014). Thus, higher amounts of oxidizing species (i.e.,  $\text{SO}_4^{\cdot-}$ ) formed at the BDD anode in sulfate anolyte yielded higher amounts of formed chlorate than in the case of nitrate anolyte.

### 7.3.5 Effect of sulfate addition on chloride-based electrooxidation of resorcinol

The strong reactivity of sulfate radicals with active chlorine species was further evidenced with elevated sulfate concentrations (0, 5, 10, and 20mM) at a fixed 10 mM chloride concentration (**Table 7.5**). Results further confirmed that higher sulfate concentration yielded faster removal of resorcinol and TOC. While the effect of higher  $\text{Cl}^-$  concentrations has been shown to increase the formation of AOC1,  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$ , the effect of higher  $\text{SO}_4^{2-}$  concentrations at fixed  $\text{Cl}^-$  concentration led to lower AOC1 formation, yet yielded higher generation of  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$ . This indicated the strong oxidation of sulfate radicals, where higher concentrations of sulfate would generate more  $\text{SO}_4^{\cdot-}$  which would oxidize resorcinol and AOC1 at a higher rate, leading to lower accumulation of AOC1 compounds. More  $\text{SO}_4^{\cdot-}$  would also react with chloride ions to produce more chloride radicals that will be further oxidized to produce more chlorate and subsequently perchlorate.

**Table 7.5 Reaction rate constants ( $\text{h}^{-1}$ ) for the removal of TOC and resorcinol, along with the formation of AOC1 ( $\text{mgCl}^- \text{L}^{-1}$ ), at different sulfate concentrations (0, 5, 10, and 20 mM) (pH 2; 200 A  $\text{m}^{-2}$ ; and 10 mM  $\text{Cl}^-$ )**

$\text{SO}_4^{2-}$ (mM)	Reaction Rate Constants ( $\text{h}^{-1}$ )		Formed chlorinated compounds ( $\text{mg-Cl L}^{-1}$ )		
	TOC	Resorcinol	AOC1	$\text{ClO}_3^-$	$\text{ClO}_4^-$
0	0.063±0.002	0.44±0.02	65±3.8	47±0.4	21±0.5
5	0.077±0.002	0.58±0.04	61±1.9	61±4.2	27±0.7
10	0.082±0.003	0.60±0.02	56±3.1	68±2.1	31±0.7
20	0.108±0.005	0.76±0.04	35±3.5	70±4.2	69±1.2

### 7.3.6 Impact of chloride on the electrooxidation of resorcinol at neutral pH

Electrooxidation of resorcinol was investigated at neutral pH in the presence of 10 mM Cl<sup>-</sup>, and compared for NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> electrolyte. Increase in pH to pH 7 did not affect significantly the rates of resorcinol and TOC removal in NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> anolytes, and very similar rate constants were obtained to electrolysis at acidic pH (**Table 7.6**). For example, the apparent removal rate constant of resorcinol in Na<sub>2</sub>SO<sub>4</sub> anolyte at neutral pH was  $0.66 \pm 0.03 \text{ h}^{-1}$ , similar to that observed at pH 2 ( $0.60 \pm 0.09 \text{ h}^{-1}$ ). At pH 7, hydrolysis of SO<sub>4</sub><sup>•-</sup> radicals to <sup>•</sup>OH is expected to be slow ( $10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) (Moad and Solomon 2005), and electrogenerated SO<sub>4</sub><sup>•-</sup> are still expected to participate in the electrooxidation of resorcinol. Higher pH is expected to favour the oxidation of water over chloride, thus enhancing the formation of <sup>•</sup>OH, and consequently SO<sub>4</sub><sup>•-</sup> radicals (Martínez-Huitle *et al.* 2015). Yet, enhancement in the formation of <sup>•</sup>OH and possibly SO<sub>4</sub><sup>•-</sup> at neutral pH may be counteracted by the less intense electrochlorination of resorcinol, as explained further in the text.

**Table 7.6 Apparent rate constants ( $\text{h}^{-1}$ ) for TOC and resorcinol removal ( $\pm$ error at 95% confidence level), in Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub> anolytes at pH 7 and 9 mS cm<sup>-1</sup> in the presence of 10 mM NaCl as well as the formed concentrations of AOCl, ClO<sub>3</sub><sup>-</sup>, and ClO<sub>4</sub><sup>-</sup> (in mgCl<sup>-</sup> L<sup>-1</sup>), measured after 2.4 Ah L<sup>-1</sup> of supplied specific electrical charge in the resorcinol electrooxidation**

	Apparent Removal Rate ( $\text{h}^{-1}$ )		Chlorinated by-products ( $\text{mgCl}^{-} \text{L}^{-1}$ )		
	Resorcinol	TOC	AOCl	ClO <sub>3</sub> <sup>-</sup>	ClO <sub>4</sub> <sup>-</sup>
NaNO <sub>3</sub>	$0.39 \pm 0.02$	$0.061 \pm 0.002$	$28 \pm 4.6$	$58 \pm 4.9$	$24 \pm 3.5$
Na <sub>2</sub> SO <sub>4</sub>	$0.66 \pm 0.03$	$0.096 \pm 0.004$	$17 \pm 4.0$	$79 \pm 0.7$	$34 \pm 2.8$

Increasing the pH to pH 7 seemed to reduce AOCl formation in NaNO<sub>3</sub> (from 66 to 28 mgCl<sup>-</sup> L<sup>-1</sup>), and also in Na<sub>2</sub>SO<sub>4</sub> (from 36 to 17 mgCl<sup>-</sup> L<sup>-1</sup>). A lower amount of AOCl formed at neutral pH would likely be the consequence of the lower oxidizing power of active chlorine (HOCl and OCl<sup>-</sup>). While chlorine is present in the form of Cl<sub>2</sub> and HOCl at acidic pH, the dominant species at pH 7 are HOCl and OCl<sup>-</sup>. Thus, electrochlorination at neutral pH is expected to proceed at a lower rate than the acid-catalysed electrochlorination due to the lower redox potential of OCl<sup>-</sup> ( $E^0 = 0.89 \text{ V}$ ) compared to Cl<sub>2</sub> ( $E^0 = 1.36 \text{ V}$ ) (Martínez-Huitle and Brillas 2009). Similar results on the higher concentration of

chlorinated organic by-products at lower pH, have been previously reported for electrooxidation of acid black 210 at BDD anode (Costa *et al.* 2009).

In terms of chlorate and perchlorate formation, neutral pH yielded somewhat higher concentrations of  $\text{ClO}_3^-$  compared to acidic pH, which is similar to previous studies (Jung *et al.* 2010, Li and Ni 2012). The most affected was the formation of  $\text{ClO}_4^-$  during electrolysis in  $\text{Na}_2\text{SO}_4$  electrolyte, as increasing the pH from pH 2 to pH 7 lowered the final concentration of  $\text{ClO}_4^-$  from 67 to 34  $\text{mgCl}^- \text{L}^{-1}$  (Table 7.3, Figure 7.2). Nevertheless, the effect of pH on the formation of chlorate and perchlorate in the presence of sulfate should be further investigated by accounting for the impact of current density and flow rate. Previously, lower current densities and higher flow rates were reported to reduce the perchlorate formation at BDD anodes (Bergmann *et al.* 2009). Also, pH was found to affect differently the formation of chlorate at BDD anode depending on the current density applied (Garcia-Segura *et al.* 2015). The formation of chlorate and perchlorate is also dependant on the presence of organics and their reactivity with the formed  $\cdot\text{OH}$ . For example, organic compounds reacting faster with  $\cdot\text{OH}$  at the anode surface were found to minimize the amount of  $\text{ClO}_4^-$  formed at the BDD anode (Donaghue and Chaplin 2013). Applied current/potential and mixing regime are also likely to have a pronounced effect on the participation of chlorine radicals in the formation of halogenated organic by-products in the presence of sulfate, and may be optimized to minimize the toxicity of a treated effluent.

#### 7.4 Concluding Remarks

This study investigated the implications of chloride ions to the electrooxidation of a natural organic matter surrogate resorcinol, in the presence of sulfate. The electrooxidation in sulfate yielded up to eight-fold enhancement in the removal of resorcinol and TOC at both acidic and neutral pH. Chloride addition to  $\text{Na}_2\text{SO}_4$  inhibited the resorcinol oxidation and mineralization, whereas it enhanced resorcinol oxidation in  $\text{NaNO}_3$ . Furthermore, sulfate inhibited the electrogeneration of chlorinated organics by  $\sim 2 - 4$  folds compared to nitrate at low  $\text{Cl}^-$  concentrations (i.e.,  $[\text{SO}_4^{2-}]:[\text{Cl}^-]>1$ ). Although increasing pH from pH 2 to pH 7 yielded two folds lower amounts of chlorinated organics, the electrooxidation in  $\text{Na}_2\text{SO}_4$  enhanced the generation of undesired chlorate and perchlorate at both acidic and neutral pH.

## Chapter 8: Conclusions and Implications

The sulfate-based solutions such as  $\text{Na}_2\text{SO}_4$  have been widely used as ‘inert’ supporting electrolytes for electro-degradation of contaminants at BDD anodes, where the electrooxidation pathways have been widely explained by the role of  $\cdot\text{OH}$  and other reactive oxygen species. At the same time, the electrochemical production of persulfate from sulfate ions has also been reported and typically explained via the formation of sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) from  $\text{SO}_4^{2-}$  either directly or through the reaction with  $\cdot\text{OH}$  radicals. Similar to  $\cdot\text{OH}$ ,  $\text{SO}_4^{\cdot-}$  are known to be strong oxidants in chemical oxidation processes, reporting high degradation rates when employed for the removal of organic contaminants.

Therefore, in this work, the role of sulfate ions in the electrooxidation of organic contaminants at BDD anodes was re-examined. The electrochemical removal of several persistent organic pollutants was performed in sulfate anolytes and compared to other electrolytic solutions such as nitrate (Chapter 4). The effect of different operating conditions was explored including the anolyte concentration and volume as well as the applied current density (Chapter 5). To further characterize the reactivity properties of the oxidizing agents and the potential energy savings, intermittent modes of electric current application were tested (Chapter 6). Investigating the effect of matrix components such as chloride ions on the performance of sulfate systems was also conducted (Chapter 7).



***Role of sulfate ions in the electrooxidation of recalcitrant organics at BDD anodes***

Results of this study showed that electrooxidation kinetics of seven persistent organic contaminants at BDD anode were quantified to be significantly enhanced by 10 – 15 folds in the presence of sulfate ions compared to sulfate-free electrolytes. This finding, reported in Chapter 4, was particularly noteworthy because it indicated that a sulfate solution cannot be considered as an inert electrolyte in such systems, especially not at high current densities and potentials, typical of electrochemical treatment using BDD electrodes.

The superiority of sulfate-based electrochemical systems using BDD anodes was apparent over a wide range of various operating conditions where higher removal rates of organic contaminants compared to nitrate was observed in all the examined cases (Chapter 5). At the lowest concentration of sulfate (5 mM), diatrizoate removal rate was faster compared to the rate measured with a 12-fold higher concentration of nitrate (60 mM). A significantly higher electrochemical oxidation of diatrizoate was still reported in sulfate anolyte even at half the applied current density ( $100 \text{ A m}^{-2}$ ) compared to nitrate ( $200 \text{ A m}^{-2}$ ). Moreover, the treatment of 2.0 L of diatrizoate in sulfate was faster than electrooxidizing only 0.25 L diatrizoate in nitrate. Even the lowest investigated sulfate concentration of 1.56 mM (i.e.,  $\sim 150 \text{ mg L}^{-1}$ ) operated with the lowest current density ( $100 \text{ A m}^{-2}$ ), yielded higher degradation rate for diatrizoate than nitrate electrolyte with higher concentration and current density (i.e. 60 mM and  $200 \text{ A m}^{-2}$ ).

Since the inert systems employing nitrate anolytes are expected to oxidize these persistent organic contaminants primarily via their electrogenerated  $\cdot\text{OH}$  radicals, this superiority of sulfate anolyte, by one order of magnitude, advocates the possible formation and participation of electrochemically generated sulfate-based oxidizing species in the electrooxidation of these persistent organic contaminants. These oxidizing species are possibly characterized by a strong oxidation capacity, similar or higher than  $\cdot\text{OH}$  radicals.

***Possible mechanisms for the electrochemical activation of sulfate***

The mechanism of the electrochemical formation of persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) from sulfate ions has been widely investigated. Such studies can potentially provide some evidence on the nature of the main sulfate-based oxidizing species contributing to the higher electrooxidation rate. Persulfate ion was suggested by many authors to be the main sulfate-based oxidizing specie in the electrooxidation process because  $\text{S}_2\text{O}_8^{2-}$  is recognized as a strong oxidant in the presence of known activators such as

metal ions as well as high pH and temperature. Moreover, sulfate radical species ( $\text{SO}_4^{\cdot-}$ ) are also strong oxidants that can potentially be contributing to the higher electrooxidation rate and they are formed as an intermediate in the electrochemical production of  $\text{S}_2\text{O}_8^{2-}$ . Therefore, the most likely sulfate-based species present in such electrochemical oxidation systems are to be in the form of persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) and/or sulfate radical species ( $\text{SO}_4^{\cdot-}$ ).

#### ***Role of persulfate ions and hydrogen peroxide in the sulfate-based electrooxidation process***

The role of persulfate ions in sulfate-based electrochemical oxidation systems was elucidated in Chapter 4 by conducting chemical oxidation reactions of persulfate with the seven persistent organic contaminants in the absence of electric current, and in the absence of an activator such as metal ions, heat or high pH. Results revealed that persulfate have slow oxidation kinetics when reacting with these persistent organic contaminants in the absence of any known activator.

The potential role of hydrogen peroxide was also explored because  $\text{H}_2\text{O}_2$  has been reported to be formed in electrooxidation systems, and has also been considered to be a potential activator of persulfate ions by several works (Chapter 4). Results in this work showed that  $\text{H}_2\text{O}_2$  was not detected ( $< \text{LOD} = 1 \text{ mg L}^{-1}$ ) in either sulfate or nitrate electrochemical systems. Furthermore, its chemical oxidation kinetics with the seven persistent organic contaminants were very slow in the absence or presence of persulfate. Therefore, the possibility of electrogeneration of hydrogen peroxide and its potential oxidation capabilities in directly degrading these persistent organic contaminants or its potential catalysis of persulfate activation were ruled out.

Thus, the possible additional oxidation of these organic contaminants in the bulk of the solution via persulfate ions or hydrogen peroxide could be largely discounted. Furthermore, electrolysis of diatrizoate investigated in the presence of persulfate as anolyte showed much slower removal rates than with sulfate present, suggesting a similar removal mechanism as in nitrate being via  $\cdot\text{OH}$  since no known activators were present in the system (Chapter 6).

#### ***Role of sulfate radicals in the sulfate-based electrooxidation process***

Without any direct spectroscopic evidence of electrochemical formation of  $\cdot\text{OH}$  or  $\text{SO}_4^{\cdot-}$  at BDD anodes to date, it can only be speculated that  $\text{SO}_4^{\cdot-}$  are likely to be these active, sulfate-based oxidizing species in such processes. The radical scavengers, such as *tert*-butanol and methanol, have been employed previously to attempt to segregate the effects of  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  in chemical oxidation

systems. Thus, in order to determine the major participating oxidants at a BDD anode, this study also compared the electrooxidation of diatrizoate with sulfate in the presence of *tert*-butanol and methanol, in sulfate and nitrate (Chapter 4). Similar removal rates of diatrizoate were observed in *tert*-butanol and methanol, although it was expected to have slightly higher removal in *tert*-butanol because it is expected to react approximately 1000 times faster with  $\cdot\text{OH}$  compared to  $\text{SO}_4^{\cdot-}$ . This suggested that a significant role in the generation of  $\text{SO}_4^{\cdot-}$  at the BDD anode was played by the  $\cdot\text{OH}$ , where scavenging of  $\cdot\text{OH}$  affected the yield of  $\text{SO}_4^{\cdot-}$  in the sulfate-based electrooxidation systems.

Similarly, nitrobenzene has previously been tested as a typical  $\cdot\text{OH}$  probe compound due to its slower oxidation kinetics with  $\text{SO}_4^{\cdot-}$  ( $< 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) compared to  $\cdot\text{OH}$  ( $> 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). Thus, the electrooxidation of nitrobenzene was compared in sulfate and nitrate. Nitrobenzene was also expected to react 1000 times slower with  $\text{SO}_4^{\cdot-}$  compared to  $\cdot\text{OH}$ .

However, the electrochemical removal of nitrobenzene was unexpectedly slightly faster in sulfate not nitrate. These results further advocate that the distribution percentage of radicals in the sulfate-based electrochemical oxidation systems using BDD anodes is largely dominated by sulfate radicals rather than  $\cdot\text{OH}$ . Thus, the higher nitrobenzene removal in sulfate is attributed to the formation of much higher concentrations of the electro-generated  $\text{SO}_4^{\cdot-}$  compared to  $\cdot\text{OH}$  in these sulfate-based electrochemical oxidation systems using BDD anodes.

However, as  $\text{SO}_4^{\cdot-}$  are radicals, they are characterised by their very short life-time, typically not exceeding milliseconds. But the long-life experiments showed that other sulfate-based oxidizing agents are able to oxidize the organic contaminants even after stopping the electric current. These results suggested that these sulfate-based oxidants are able to have a long reactive life-time reaching up to an hour, which is contrary to what is conventionally known about radicals. The ‘organics-free’ electrochemical oxidation of sulfate ions followed by its addition to the diatrizoate suggested that the presence of the organic matter in the electrolysis cell is an important factor governing the formation of these long-life sulfate-based oxidizing agents.

These findings added to the ambiguity of the nature of these sulfate-based oxidizing agents but revealed more of their remarkable characteristics being strong oxidants and possessing an extended reactive life-time. Both of these characteristics can induce significant savings in the electrical energy consumption needed in the application of these sulfate-based electrochemical systems for the removal of organic contaminants from polluted waters.

***Impact of chloride ions on the sulfate-based electrooxidation of organic matter at BDD anode***

Electrochemical oxidation systems involving chloride ions generate reactive chlorine species such as  $\text{Cl}_2/\text{HOCl}$ , which react rapidly with organic matter, leading to the formation of chlorinated organic and inorganic by-products. Thus, the presence of chloride in sulfate-based electrochemical oxidation is expected to interact with sulfate radicals and impact the electrooxidation performance as well as the formation of the hazardous by-products (Chapter 7).

Electrochemical oxidation of resorcinol revealed that the presence of chloride ions along with sulfate ions in the anolyte solution inhibited the resorcinol oxidation and TOC removal. This was attributed to the possible competition between the formed sulfate radicals and the chlorine radicals for oxidizing the organic matter. In contrast, the addition of increasing concentrations of chloride ions to nitrate anolyte slightly enhanced the oxidation and mineralization of resorcinol.

The electrogeneration of chlorinated organic compounds was inhibited in the presence of  $\text{SO}_4^{2-}$  by several folds compared to nitrate, due to the lower formation and accumulation of these compounds in the presence of sulfate. However, the electrolysis in  $\text{Na}_2\text{SO}_4$  enhanced the generation of undesired chlorate and perchlorate primarily because sulfate systems possess a stronger oxidation capacity.

***Potential applications, impacts and perspectives of the findings from this study***

The electrooxidation of all the organic contaminants being substantially faster in sulfate than in nitrate anolytes by 10 – 15 folds resulted in a drastic decrease in the electrolysis time and significantly large savings in the electric energy consumption required for the anodic oxidation process. For example, removal of diatrizoate in sulfate anolyte, required 8.5 minutes and an energy consumption of  $2.44 \text{ kWh m}^{-3}$ , compared to 180 minutes and  $45.6 \text{ kWh m}^{-3}$  in nitrate anolyte, thus inducing almost 20-folds lower energy consumption.

In addition, the on-bench delayed quenching provided evidence that the sulfate-induced oxidation process possesses an extended reactive life-time and is capable of continuing the oxidation of the persistent organic contaminants even after stopping the electric current. Furthermore, the application of intermittent electric current using several different pulse modes showed that these electro-formed long-life sulfate-based oxidizing agents can induce further significant energy savings that can reach approximately 50%.

Therefore, the electrochemical removal of a persistent organic contaminant such as diatrizoate, regardless of the electrolysis time required to achieve complete removal, can be achieved using ~ 40-folds lower electric energy consumption with a sulfate anolyte compared to a sulfate-free anolyte, while using an intermittent electric current. Further optimization of the trade-off between electrolysis time and electric energy consumption can be accomplished via testing further modes of intermittent power supply at different current densities.

The effect of anolyte concentration showed high efficiency in the removal of persistent organic contaminants even at very lower sulfate concentrations such as  $150 \text{ mg L}^{-1}$ , already detected in natural water systems or even below regulations and guidelines (i.e.,  $< 250 \text{ mg L}^{-1}$ ). Since sulfate concentrations have been also detected in many surface and ground waters at concentrations up to  $630 \text{ mg L}^{-1}$ , this activation of sulfate at BDD electrodes polarized at a sufficiently high anode potential may have significant implications on the treatment of sulfate-containing waters. Such sulfate activation may also act as a feasible alternative to persulfate injection for *in-situ* chemical oxidation (ISCO) of groundwater. By placing an electrochemical reactive barrier, it would seem to be possible to activate the sulfate present in the contaminated groundwater plume to degrade persistent organic contaminants, without any additional chemical supply. The continuous innovations and advances in the production of electricity from renewable energy sources such as hydro, solar and wind energy further endorses such implementation because of the availability and accessibility of electric power generated from such resources without the need for transportation of chemicals, which reduces the operating burden, and promotes its application in isolated locations where transportation of chemicals is a limitation of the treatment application..

Further experimental optimization of the operating conditions can be potentially conducted in order to identify the lowest anodic current/potential required for the formation of these sulfate-derived oxidizing species. Though our tests show that lower applied current yielded slower removal kinetics, but in cases where the electrolysis time is considered a less important factor than the electric energy consumption, such threshold value or range would play a significant role in designing the electrochemical oxidation systems.

Moreover, future studies could attempt to better understand the mechanisms involved with the electrochemical activation of sulfate and identify the nature of these sulfate-based oxidizing agents that are characterized not only by their strong oxidation capacity but also with an extended reactive life-time. While the formation of sulfate radicals has been postulated to be formed either via direct oxidation of sulfate ions on the anode surface, or via the contribution of  $\cdot\text{OH}$  radicals in the oxidation

of sulfate ions, the actual mechanism has not been proven yet. On the other side, the mechanism of the formation of long-life sulfate-based oxidants is still difficult to even postulate. This extended reactive life-time can possibly be attributed to the formation of long-life oxidants such as persulfate, which is a weak oxidant by itself, but can be activated to sulfate radicals over an extended life-time of 30 to 60 min.

Investigating the nature of this activation and the potential activator(s) would constitute a key element in producing a comprehensive mechanistic model of the system. The potential activation of persulfate via quinones or other organic by-products formed during the electrooxidation of the organic contaminants can be argued (Fang *et al.* 2013). Further investigation of extended sulfate-based oxidation employing aliphatic organic compounds instead of aromatic compounds can potentially give an insight on the reaction mechanism of the extended oxidation and the potential role of quinones in this process. The perfluorocarboxylic acids which are described to be bio-accumulative, recalcitrant, and potentially toxic can be tested as an example of aliphatic compounds.

Sulfate radicals have been reported to be effective in the destruction of a wide range of aliphatic organic compounds, such as chlorinated volatile organic compounds (VOCs) (Block *et al.* 2004), and non-VOCs (Liang *et al.* 2003). Moreover, one of the 8 aromatic compounds, electrochemically oxidized in this study using sulfate electrolytes, was resorcinol. It is very likely that the oxidation of resorcinol would involve sulfate radicals attacking the aromatic ring of resorcinol, thus leaving behind various aliphatic intermediate compounds such as the widely reported disinfection byproducts (DBPs): trichloromethane and chloral hydrate. The removal of total organic carbon (TOC) was measured for oxidation of resorcinol in sulfate, reporting up to 90% removal after 6 hours. This signifies that these aliphatic intermediate compounds were most likely also oxidized by sulfate radicals.

It can also be argued that  $\cdot\text{OH}$  radicals might be activating persulfate (Lau *et al.* 2007, Salari *et al.* 2009, Khataee and Mirzajani 2010, Velo-Gala *et al.* 2014), inducing some kind of a chain reaction involving sulfate radicals that may extend over 30 to 60 min. However, that might not be largely expected considering the ambiguity of such possible chain reaction. Such scenario can be difficult to test for because if the concentration of  $\cdot\text{OH}$  radicals was increased in the reaction medium (for example, by adding activated  $\text{H}_2\text{O}_2$ ) without changing the concentration of sulfate ions in the solution,  $\cdot\text{OH}$  radicals are still capable of influencing the production of sulfate radicals from sulfate ions, besides activating persulfate.

Another possibility is the electrochemical formation of ozone which can be acting as an activator for persulfate (Amr *et al.* 2013), where the potential synergistic effect of ozone and persulfate on the oxidation of organic compounds is worth studying. It is crucial to note that investigating the potential effect of a formed ozone scenario requires additional care with the detection method for ozone due to the large interference of most analytical methods when both ozone and persulfate are being co-formed in the same medium.

Nevertheless, studying the intermediate compounds that are being produced from the main organic compounds, being investigated in this sulfate-based extended oxidation process, would certainly be of most significant importance as this would shed light on the potential mechanisms of the activation process. The sulfate-based degradation pathways, which include the formation and oxidation of the intermediate compounds from several aromatic and aliphatic compounds, can also be further explained with such investigations as these would provide more information on the nature and role of the activators in the extended oxidation phenomenon observed with sulfate. The nature of the intermediate compounds being formed is expected to give information about the sites of attack of the radicals and oxidants, and the type of reaction being electron transfer, hydrogen abstraction or addition, as well as the functional groups being involved in these reactions.

A broader investigation of the effect of the matrix on sulfate systems is also of high importance, especially the presence of ionic compounds such as carbonate, which is omnipresent in most wastewaters. The effect of other ions such as phosphate and bromide are also crucial to further expand the knowledge on the performance of these sulfate-based systems in the electrochemical treatment of real wastewaters.

The generation of organic DBPs as well as chlorate and perchlorate from chloride in these electrochemical systems employing sulfate anolytes can be further optimized. Some of the DBPs expected to form in these electrochemical treatment processes in the presence of chloride could possibly be trichloromethane ( $\text{CHCl}_3$ ) and chloral hydrate ( $\text{CCl}_3\text{CH}(\text{OH})_2$ ), as well as 1,1-dichloropropanone ( $\text{CH}_3\text{COCHCl}_2$ ), and 1,1,1-trichloropropanone ( $\text{CH}_3\text{COCCl}_3$ ). All of these DBPs, besides chlorate and perchlorate, are regulated for their detrimental effects, and their production is a key limitation for the implementation of this technology to drinking water treatment.

The effect of pH on the formation of chlorate and perchlorate in the presence of sulfate should be further investigated for oxidation at neutral pH since the current study shows lower formation of these

products at neutral pH. Furthermore, such optimization of the pH would increase the applicability of such technology on real-world applications.

Applied current/potential and mixing regime are also likely to have a pronounced effect on the participation of chlorine radicals in the formation of halogenated organic by-products in the presence of sulfate, and may be optimized to minimize the toxicity of a treated effluent. Lower current densities and higher flow rates have been previously reported to reduce the perchlorate formation at BDD anodes. Therefore, further optimization of the applied current/potential and pumping/mixing flow rates can enhance the performance of these sulfate systems in the presence of chloride ions, in order to lower the formation of chlorinated compounds such as chlorate and perchlorate and reduce the concentrations of the toxic electrogenerated organic by-products. Nonetheless, the production of these inorganic and organic halogenated by-products is not the only limitation of the implementation of this technology, as the cost limitation is still significant, especially with the large capital cost of the BDD anode materials.

The characteristics of the BDD anode surface such as the  $sp^3/sp^2$  ratio also play an important role in the production of oxidizing agents such as persulfate and chlorine radicals. The information of  $sp^3(\text{diamond})/sp^2(\text{graphite})$  ratio reports the level of  $sp^2$ -impurities on the diamond film surface, where higher impurities were reported to improve the production of specific oxidants such as persulfate (de Paiva Barreto *et al.* 2015). Therefore, investigating the level of impurities of a BDD anode as in its  $sp^3/sp^2$  ratio is one potential factor that can affect the production of sulfate-based long-life oxidizing agents as well as the chlorine radicals and oxyanions.

Moreover, since BDD anode materials are considered as high cost elements that might burden the industrial applicability of such process, the capability of cheaper non-active anode materials that has relatively high oxygen over-potential such as  $\text{IrO}_2$ ,  $\text{PbO}_2$ ,  $\text{SnO}_2$ , or  $\text{TiO}_2$  to produce such sulfate-based oxidizing species is worth investigating. These non-active anode materials are characterized by an oxidation potential reaching up to 2.2 V versus SHE, which is slightly lower than that of BDD (2.2 – 2.7 V vs SHE). Even anode materials such as platinum (1.3 – 1.6 V versus SHE) have been reported to be capable of generating persulfate electrochemically, and therefore might be worth examining for the formation of sulfate-based oxidants. The ability of such cheaper anodes to produce high concentrations of sulfate-based oxidizing agents would further enhance the chance for such sulfate-based electrochemical oxidation systems to be economically competitive with chemical oxidation processes.



Although the high cost of the BDD anodes might not be the only economic barrier for a large-scale implementation, depending on the characteristics of the contaminated stream to be treated, the need for these electrochemical systems for degrading persistent organic compounds, which are not known to efficiently degrade via other methods, will encourage the large-scale industrial application of this technique. Moreover, such systems can be ideal for applications in remote areas using renewable energy sources, which would reduce the need for manpower as well as the addition and transportation of chemicals. Besides, further optimization of the operating parameters and advancements in the efficiency of these anodes materials as well as the reduction in prices over time would further boost its applicability.

The extended reactive life-time of these sulfate-based oxidants can also be assessed on these anode materials as this unique characteristic will achieve additional energy savings and could increase the feasibility to apply such methods for the treatment of “*flowing*” contaminated water systems such as groundwater bodies or river streams.

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