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CIChem Research Group

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Abstract

The water resources as the rest of the natural environment on the earth are under pressure from ever increasing human activities in our desire for global wealth. As the analytical capabilities improve, traces of these activities are intensively emerging in the form of harmful organic pollutants recalcitrant to natural degradation. This thesis presents experimental research on the use of electrochemical oxidation (EO) for degradation of organic pollutants in water. Efficient treatment of wastewater and polluted groundwater is essential in order to prevent the discharge of these pollutants and to secure public health and our access to good quality drinking water.

EO is considered as part of the group of environmental technologies known as advanced oxidation processes (AOPs) used in treatment of soil, water, and air, and as the thesis demonstrates, it is a powerful technique for degradation of a wide range of toxic and recalcitrant organics in different types of polluted water. In this way, it is fully competitive with the other AOPs with some significant advantages when used under the right conditions. However, EO is still just on the edge of industrial and commercial breakthrough, and more knowledge on the complex chemistry in the cell and the engineering perspectives in designing and optimizing an EO treatment unit is needed before the technique can be considered a mature and ready implementable treatment solution.

This project has been carried out in cooperation with the company Watersafe DK Aps with the aim of investigating new market opportunities and increase process understanding in order to optimize the degradation reactions and minimize unwanted side reactions. From an applied experimentally based approach, complex polluted water from a site contaminated with chemical waste and polluted sea water have been subject to studies in addition to model solution studies under controlled conditions. The research was focused on using electrochemical equipment from Watersafe and studying the performance of the Ti/Pt90-Ir10 anode used in this cell in a batch recirculation setup. Another commercially available cell from Adamant Technologies with a boron-doped diamond (BDD) anode was also involved, primarily in order to investigate differences in oxidation pathways.

In the first part of the summary, the current state-of-art of EO in pollution abatement is provided through a survey of the technical principles and chemical mechanisms involved in the oxidative processes in addition to an introduction to the models developed to predict treatment performances and multiple references to and discussions of published literature.

In the second part, the experimental research is presented based on results published or submitted for publication in papers and a book chapter. EO was demonstrated to efficiently degrade a complex mixture of organo-phosphoric pesticides as parathion and malathion, mainly through indirect oxidation pathways due to electro-generated hypochlorous acid and hypochlorite. Only the Ti/Pt90-Ir10 anode experienced difficulties with the degradation product triethyl phosphate, but this substance was successively demonstrated to be degraded by the BDD anode due to a more powerful direct oxidation of this anode. EO was found to be a serious
alternative to the existing active carbon adsorption as an on-site treatment solution, suggestions are proposed on how to implement EO in future sustainable site remediation strategies.

In another study, EO was showed as capable of degradation of polycyclic aromatic hydrocarbon (PAH) micro pollutants found in sea water. The background of this investigation was issues raised, when sediment is excavated from the seabed in harbours. Next to feasibility experiments, focus in the study was detailed model solutions determining the kinetics of PAH removal and the influence of different electrolytes in solution and applied current density. The presence of chloride in the media was again showed to be important for an efficient treatment due to the oxidation caused by generated chlorine species. The study demonstrated one of the challenges in optimization of EO treatment concerning the compromise between reaction rate and efficiency, since the rate of removal decreased at decreased current density whereas the efficiency increased.

The importance of chloride for an efficient treatment can be problematic due to the risk of formation of halogenated byproducts. This issue was studied based on the PAH oxidation in pure and mixed chloride and bromide electrolytes. In pure chloride electrolytes mono- and di-chlorinated naphthalene was identified as nonpolar byproducts. Addition of small concentrations of bromide in a mixed chloride-bromide electrolyte suppressed the electrophilic chlorine substitution that was exchanged with bromination of naphthalene with identification of mono- and di-brominated species. However, the byproducts were with slower kinetics further degraded again after extended electrolysis times. The study clearly showed the importance in considering parameters as adsorbable organic halogens (AOX) or other analytical measures of quantification of organic byproducts, when evaluation of needed treatment time and reactor performance is performed and not only focusing on the parent pollutant. This challenge of byproduct formation needs to be taken seriously and researched in more detail.

The organic dye p-nitrosodimethylaniline was used as model compounds in an array of experiments investigating differences in oxidation pathways on the two involved anode materials and the influence of electrolytes and hydroxyl radical scavengers on the general oxidative performances. Despite a weaker direct oxidation power of the Ti/Pt_{90}-Ir_{10} compared to the BDD anode, it was capable of bleaching the dye solution, and the Ti/Pt_{90}-Ir_{10} was demonstrated to be more efficient, when used in indirect electro-chlorination processes in the presence of other organics that serves as hydroxyl radical scavengers, compared to BDD.

Due to the powerful oxidants generated in the process, EO possess a promising potential to be used for efficient disinfection of unwanted microorganisms in water, and the application of this feature was briefly demonstrated on *E. coli* and on the differences observed on chemical chlorination and electro-chlorination processes.

Finally, surface analysis by x-ray photoelectron spectroscopy (XPS) revealed that the chemical state of platinum at the Ti/Pt_{90}-Ir_{10} anode shifted to at least Pt(II) from Pt(0) after electrolytic evolution of oxygen and chlorine gas. The oxidized states of platinum were present in a mixed oxide layer, and are likely the ones responsible for the direct electrochemical transfer of oxygen.
from water molecules to the organics subject to oxidation. These observations support the theoretical suggested and to some extent experimentally proven formation of chemisorbed active oxygen covalently bonded to surface metals that are responsible for organic oxidation at this type of anode.

EO as a technique for degradation of organics in advanced water treatment does definitely possess a promising potential for industrial use and increasing dissemination as the preferable AOP, when facing problems with toxic, refractory, bio-incompatible organics. But, continuing efforts have to be invested in research aiming at providing a full understanding of the fate of by-products and the derived consequences.
Synopsis

Jordens vandressourcer er ligesom resten af miljøet presset af den øgede menneskelige aktivitet, som er resultatet af den stigende intensitet i jagten på global velstand. I takt med at vores evner indenfor kemisk analyse bliver bedre og bedre, dukker flere og flere spor efter disse aktiviteter op i miljøet i form af fremmede, typisk skadelige, organiske forureningsforbindelser, som kun vanskeligt nedarbes udsatt. Denne afhandling præsenterer eksperimentel forskning gennemført i et tre-årigt phd.-projekt omhandlende anvendelsen af elektrokemisk oxidation (EO) til nedbrydning og derved fjernelse af organiske forureningsforbindelser i vand. Effektiv rensning af både husholdnings- og industriospildevand samt forurenet grundvand er essentielt for at forhindre udledningen af organiske forbindelser og dermed sikre den almene sundhed og vores adgang til vandressourcer af drikkevandskvalitet.

EO er en af del af den gruppe af rensningsteknologier, der er kendt som avancerede oxidations processer (AOP’er), og som bruges til rensning af jord, vand og luft. Som afhandlingen vil demonstrere, er EO en effektiv teknik til nedbrydning af en bred række af toksiske og svært nedbrydelige organiske forbindelser i forskellige typer af vand. I den henseende er EO fuldt konkurrencedygtig med de andre AOP’er, og besidder nogle væsentlige fordele når det anvendes under de rette betingelser. Dette til trods, er EO stadig kun på grænsen af et industrielt og økonomisk gennembrud. Et øget vidensniveau om den komplekse kemi, der foregår i cellen, og de ingeniørmæssige udfordringer, der ligger i at designe og optimere en rensningsoperation baseret på EO, er nødvendig, før teknikken er modnet nok til at blive betragtet som en etableret rensningsløsning.

Projektet er blevet udført i samarbejde med firmaet Watersafe DK Aps med det formål at undersøge nye markedsmuligheder og øge forståelsen af de elektrokemiske processer for at kunne optimere nedbrydningsreaktionerne samt minimere uønskede sidereaktioner. Med udgangspunkt i anvendt eksperimentel forskning, er komplekst forurenet vand fra både en lokalitet forurenet med kemisk affald og forurenet havvand fra et havnebassin blevet undersøgt sammen med studier af modelopløsninger under kontrollerede forhold. Fokus i forskningen har været at anvende elektrokemisk udstyr fra Watersafe, og undersøge hvilke resultater der kunne opnås med den Ti/Pt90-Ir10 anode, som bliver anvendt i denne type celle. Forsøgene er udført i en batch recirkulations opstilling. I sammenligningsstudier og undersøgelser af forskelle i reaktionsveje er en anden kommerciel tilgængelig celle fra Adamant Technologies blevet anvendt. Denne celle er udstyret med en nyudviklet bor-dopet diamant (BDD) anode.

I første del af afhandlingen bliver state-of-the-art for anvendelsen af EO til forureningsbekæmpelse præsenteret. Dette sker via en gennemgang af de tekniske principper og kemiske reaktionsmekanismer, der er involveret i de oxidative processer. Derudover gives en introduktion til de modeller, der er under udvikling for at kunne forudsige virkningsgrader af EO rensning, samtidig med at der gives adskillige henvisninger til og diskussion af publiceret litteratur.
I anden del af afhandlingen bliver projektets eksperimentelle forskning præsenteret. Præsentationen er hovedsageligt baseret på resultater i artikler allerede udgivet eller under igangværende review ved internationale tidsskrifter samt et bogkapitel.

EO blev i en forsøgsrække vist at være effektiv til nedbrydning af en kompleks blandingsforurening af organiske fosforbaserede pesticider som parathion og malathion, hovedsageligt via en indirekte oxidations vej med elektrokemisk dannet hypoklorsyre og hypoklorit som primære oxidanter. Den anvendte Ti/Pl₀⁰₉₀-Ir₁₀ anode havde kun problemer med at fjerne et enkelt nedbryningsprodukt, triethyl fosfat, men dette stof blev efterfølgende vist at kunne nedbrydes succesfuldt med BDD pga. en kraftigere direkte oxidationsproces ved denne anode type. Samlet set kan EO udgøre et seriøst alternativ til den eksisterende aktiv kul adsorption som on-site rensningsteknologi, og forslag er fremsat til, hvordan man kan implementere EO i fremtidige mere bæredygtige strategier til oprensning af forurenede lokaliteter.

I et andet studie blev EO vist til at kunne nedbryde organiske mikroforureningskomponenter som polycycliske aromatiske hydrocarboner (PAH’er) i havvand. Baggrunden for denne undersøgelse er et problem, der fremkommer i forbindelse med fjernelse af sediment fra havnebassiner og sejlrender og efterfølgende krav til rensning af overskydende havvand fra spulefelterne. Udover forsøg med den rigtige matrice fokuserede studiet på detaljerede forsøg med modelopløsninger for at bestemme kinetikken for PAH fjernelsen og indflydelsen af forskellige elektrolytter og den anvendte strømtæthed. Tilstedevarsel af klorid i matricen blev igen vist til at være vigtig for at opnå en effektiv rensning pga. oxidationsbidraget fra dannet aktivt klor. Studiet viste ligeledes en af udfordringerne i optimering af EO rensning, da hastigheden hvormed PAH’erne blevet fjernet faldt ved nedsat strømtæthed, hvorimod at energieffektiviteten blev forøget. Dermed kræver en optimering at der findes et kompromis mellem disse to størrelser alt efter behov.

Det organiske farvestof p-nitrosodimethylanilin blev anvendt som modelstof i en række af eksperimenter, der blev udført med det formål at undersøge forskelle i oxidationsveje på de to anodematerialer, der blev anvendt i projektet, og indflydelsen af tilstedeværelsen af forskellige elektrolytter og en hydroxyl radikal scavenger på cellernes ydeevne mht. at affarvning. Til trods for Ti/Pt₀₀⁻Ir₁₀⁺’s svagere direkte oxidations kraft sammenlignet med BDD anoden kunne denne anode også affarve farvestofopløsningen i en inert elektrolyt. Spændende var det, at Ti/Pt₀₀⁻Ir₁₀⁺ viste sig at være mere effektiv end BDD, når den blev anvendt i en indirekte elektrokloreringsproces, hvor der var andre organiske forbindelser tilstede end farvestoffet, der fungerede som hydroxyl radikal scavenger.

På grund af de kraftige oxidanter der bliver dannet i cellen, er EO potentielt en lovende teknik at bruge til effektiv desinfektion af ønskede mikroorganismer i vand. Denne anvendelse blev i projektet kortfattet demonstreret på E. coli ved observerede forskelle på desinfektion og affarvning med kemiske klorering og elektroklorering.

Sidst, men ikke mindst – ex-situ analyser af overfladen på Watersafe’s anode ved hjælp af røntgen fotoelektron spektroskopi (XPS) viste, at platins oxidationstilstand skiftede fra Pt(0) til mere oxiderede tilstande som Pt(II/IV) efter at have været anvendt i elektrolytiske processer med udvikling af dioxygen og diklor. Platins oxiderede tilstand var bundet i et blandet platinoxid/platinhydroxid lag dannet ved oxidation af vand, og dette lag er sandsynligvis ansvarlig for den direkte overførsel af oxygen fra vandmolekyler til de organiske forbindelser. Disse eksperimentelle observationer understøtter den teori om EO, der i litteraturen teoretisk er fremsat og til et vist punkt også eksperimentelt underbygget. Teorien forudsiger, at der på en Ti/Pt₀₀⁻Ir₁₀⁺ anode vil dannes kemisk adsorberet aktiv tilt, der ved kovalente bindinger er bundet til metalatomerne på overfladen af anoden, og at det er dette aktive tilt, der er ansvarlig for oxidationen af organisk stof.

EO er som teknik til nedbrydning af organisk forurening i avanceret vandbehandling absolut lovende og besidder et vist potentiom til at blive anvendt i større skala i industrien og muligvis i fremtiden blive udbredt som den foretrukne AOP, når problemer med toksiske, modstandsdygtige, biologisk unedbrydelige organiske forureningsforbindelser skal overvindes. Dog skal yderligere kræfter og midler forsats investeres i forskning for at opnå målet med at opnå fuld forståelse for processerne, primært mht. dannelse og fjernelse af biprodukter samt de konsekvenser disse måtte afstedkomme.
Preface

This thesis is submitted in partial fulfilment of the requirement for the Ph.D. degree at Institute of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, Denmark. The Ph.D. project was carried out under supervision of Associated Professor Erik G. Søgaard from CIChem research group, Section of Chemical Engineering, Institute of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, in cooperation with the industrial partner Watersafe DK Aps, and partially funded by the Danish Ministry of Science, Technology and Innovation.

The broad area of research in this project is environmental engineering with special attention to the development of technology to be used for effective treatment of potentially toxic and non-biodegradable organic pollutants in water. This challenge is met through an electrochemical approach applying the oxidative conditions present at the anode in an electrolytic cell as the mean of degradation of the organics. Uses of electrochemical oxidation (EO) as an organic treatment solution within environmental engineering have in international research been studied increasingly intensive the last fifteen years, and currently the technology can be considered somewhere near the edge of an industrial breakthrough. However, many process questions are still not adequately clarified in addition to a lack of acquaintance to this application of the technology in e.g. Scandinavia. This project sought to contribute to enhance our understanding of the complex processes in using EO technology, explore market possibilities for EO applications, and in general focus attention to the strengths of this approach to be used to fulfill our obligations to take care of our surrounding environment.

“Theory guides. Experiment decides.”

An old saying in science, which I am very fond of and has been my guideline throughout the accomplishment of this project. Mechanisms and pathways theoretically suggested needs to the experimentally validated in order to be trustfully accepted, and the research presented in this thesis is in this spirit founded on an experimentally applied approach, where experiments and experimental evidence play the key role – of course supported by fundamental theory from electro-, inorganic as well as organic chemistry.

New technology, which potentially can add to the toolbox we as engineers have in possession to protect the environment and the natural resources on earth against our ever increasingly human activities, should be of interest to us all. My hope is that you will find the perspectives of the results presented in this thesis of interest - enjoy your reading.

“Gaudemus igitur, juvenes dum sumus”

(eng.: “Let us rejoice, while we are young”)
Acknowledgements

Many people have played a role in my thesis, and I want to express my sincere gratitude to all colleagues, friends, and other contributors, who have added value to the completion of this work. First of all, I would like to thank Aalborg University and Watersafe DK Aps for in the first place grant me the opportunity to do this Ph.D. work. It has indeed been a scientific, technical and personal challenge that in multiple ways has developed me and opened my eyes for the differences in the worlds of science and practicing engineer and that hard work is needed if the benefits of both have to be combined in a gathered mindset.

A warm thank you to my supervisor Erik G. Søgaard for your always enthusiastic and positive scientific guidance throughout not only the phd., but also several projects during my bachelor and master studies.

A warm thank you to Niels Erik Skjaerbæk, Watersafe DK Aps. We have shared many hours of transportation, meetings, and practical work, and from your rich and experienced life I have learned the value of don’t trouble trouble before trouble troubles you, look on the bright side of life and seize the opportunities life presents you.

Many thanks to my best friend, long term office/group room buddy, wingman and brother in arms, Lars, for your many contributions in all aspects of this work; discussions of all imaginable subject and problems, review of ideas and drafts of manuscripts and this thesis, suggestions for experimental trouble solving, companionship at conferences and courses and sharing of interests. I owe you a nice cold pint of the sweet nectar of gods.

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Finally, without the support, patience and encouragement from my lovely family I could never have been able to submit this work. My most special gratitude goes to my fiancée Pernille for your patience and love when I am absent-minded and stressed and for your tolerant acceptance of the, at times, long hours of work.

Esbjerg, Fall 2010

Jens Muff
List of supporting papers


III. Muff, J., Bennedsen, LR. & Søgaard, EG. Assessment of the use of p-nitrosodimethylaniline as hydroxyl radical probe compound in aqueous electrochemical oxidation studies, (Submitted 2010)


V. Muff, J. & Søgaard, EG. Identification and fate of halogenated PAHs formed during electrochemical treatment of saline aqueous solutions (Submitted 2010)

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<td>ALARA</td>
<td>As low as reasonable achievable</td>
<td>ESR</td>
<td>Electron spin resonance</td>
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<td>AOP</td>
<td>Advanced oxidation process</td>
<td>GC</td>
<td>Gas chromatography</td>
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<tr>
<td>AOT</td>
<td>Advanced oxidation technology</td>
<td>GCE</td>
<td>General current efficiency</td>
</tr>
<tr>
<td>AOX</td>
<td>Absorbable organic halogens</td>
<td>HAA</td>
<td>Halogenated acetic acid</td>
</tr>
<tr>
<td>BATNEEC</td>
<td>Best available technique not entailing excessive cost</td>
<td>HPLC</td>
<td>High pressure liquid chromatography</td>
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<td>BDD</td>
<td>Boron doped diamond</td>
<td>ICE</td>
<td>Instantaneous current efficiency</td>
</tr>
<tr>
<td>BOD</td>
<td>Biological oxygen demand</td>
<td>ISCO</td>
<td>In-situ chemical oxidation</td>
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<td>Bisphenol A</td>
<td>MEO</td>
<td>Mediated electrochemical oxidation</td>
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<td>Conductive diamond electrochemical oxidation</td>
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<td>Oxygen equivalent chemical oxidation capacity</td>
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<td>Colony forming units</td>
<td>PAH</td>
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<td>Disinfection byproducts</td>
<td>ROS</td>
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<tr>
<td>DSA</td>
<td>Dynamically stable anode</td>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>EO</td>
<td>Electrochemical oxidation</td>
<td>THM</td>
<td>Trihalomethane</td>
</tr>
<tr>
<td>EOI</td>
<td>Electrochemical oxidation index</td>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>EOTR</td>
<td>Electrochemical oxygen transfer reaction</td>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
Chapter 1
Introduction

The introduction of more stringent pollution regulations, in relation to financial and social pressures for sustainable development, has pressed toward limiting the volumes of industrial and domestic effluents discharged into our environment - as well as to increase the efforts within research and development of new or more efficient wastewater treatment technologies [1]. A basic principle in environmental culture is to reduce waste and pollution to “As Low As Reasonably Achievable” (ALARA) levels, and in order to ensure acceptable levels of environmental impact, wastewater treatment systems also have to be engineered in accordance to the principle of “Best Available Technique Not Entailing Excessive Cost” (BATNEEC). [1,2]

Industrial waste often contains a mixture of organic and inorganic compounds, in addition to solid or soluble material, and because of this diverse feature no universal strategy of remediation is feasible. As to the treatment of effluents polluted with organic compounds, biological oxidation is the cheapest process, but the presence of toxic or biorefractory molecules may hinder this approach [1]. For this reason, a diverse range of physical-chemical methods as filtration, coagulation, adsorption, flocculation, chemical oxidation with use of chlorine, ozone, hydrogen peroxide, and advanced oxidation processes (AOPs) as Fenton’s reaction, ozone/UV etc. are currently used to treat industrial effluents, depending on the specific needs. However, none of these methods are all-encompassing and all of these methods have some major drawbacks. For example, filtration and adsorption are not always sufficient to achieve the discharge limits; coagulation and flotation generates large amounts of sludge; chemical oxidation processes usually have low capacity rates and needs transportation and storage of hazardous chemicals; and advanced oxidation processes usually require high investment costs [1]. Electrochemical oxidation (EO), the water treatment principle in focus in this thesis, is by most researchers considered as a treatment method within the AOP family and has attracted a lot of attention within the last two decades. Oxidative electrochemical technologies offer an alternative solution to many environmental problems in the process industry, because electrons provide a versatile, efficient, cost-effective, easily automatizable, safe and clean reagent [2,3].

For some decades, a large number of companies have been marketing electrochemical devices for metal ion removal and metal recovery, treatment of liquors containing dissolved chromium, flue-gas desulphurization, desalination and salt splitting [1]. However, so far the role of electrochemical technologies for the treatment of organic pollutants has been relatively small. But, nowadays thanks to intensive investigations that have improved the electrocatalytic activity and stability of electrode materials and optimized reactor geometry, electrochemical technologies have reached a promising state of development and can be effectively used for
disinfection and purification of water polluted with organic compounds [2], as this thesis will demonstrate.

1.1 Advanced oxidation processes (AOPs)

Advances in chemical water and wastewater treatment have led to the development of methods termed advanced oxidation processes (AOPs) or technologies (AOTs). AOPs can broadly be defined as aqueous phase oxidation methods intermediated of highly reactive species such as (primarily but not exclusively) hydroxyl radicals in the mechanisms leading to destruction of the target pollutants [2,4,5]. With hydroxyl radicals as the main oxidative agents, a complete mineralization of pollutants to carbon dioxide, water, and inorganic compounds can be obtained, or at least a conversion of the organics into highly oxidized more innocuous products.

\[
\text{AOPs} \rightarrow OH^*_{\text{pollutant}} \rightarrow CO_2 + H_2O + \text{inorganic compounds}
\] (1.1)

AOPs can be classified either as homogenous or heterogeneous processes with the homogenous processes further subdivided into processes with or without the requirement of energy input. (Fig. 1-1) [4]. Key AOPs next to EO include heterogenous photocatalysis based on near ultraviolet (UV) or solar visible irradiation, alkaline ozonation, Fenton’s or modified Fenton’s chemistry, and combinations of UV irradiation and chemical oxidants.

![Classification of advanced oxidation processes (AOPs). Abbreviations used: O₃ ozonation; H₂O₂ hydrogen peroxide; UV ultraviolet radiation; US ultrasound energy; Fe²⁺ ferrous ion. Reprinted from Poyatos et al. (2010) Water Air Soil Pollut, 205, p. 187-204 [4], with permission from Springer.](image-url)
Another mineralization process normally considered as an AOP is wet air oxidation (WAO), where the organics are oxidized in an aqueous medium by means of oxygen from air at elevated temperature (250-300 °C) and high pressure (100-150 bar) with catalysts as Cu\(^{2+}\) present.

Water and wastewater treatment are the most common areas of research and development of AOPs, but applications within groundwater treatment, soil remediation, municipal wastewater sludge conditioning, ultrapure water production, volatile organic compound treatment and odour control are also found [2,4,5]. Within water treatment, the core themes of research covers treatment of industrial effluents of many types including distillery, agrochemical, kraft-blending, pulp and paper, textile dyehouse, oilfield and metal-plating waste. In addition, treatment of hazardous effluents including hospital and slaughterhouse wastes, removal of pathogens and persistent, endocrine disrupting pharmaceutical residues from municipal wastewater treatment (WWTP) effluents (i.e. after secondary treatment), removal of organic micro pollutants such as pesticides and to some extent heavy metals such as arsenic and chromium from water etc. [2].

The EO method for full mineralization or partly conversion of organic pollutants is a technology considered very interesting for the treatment of particularly dilute wastewater (COD < 5 g L\(^{-1}\)) [2] and is in competition with the processes of chemical oxidation with mixtures of strong oxidants, photocatalysis etc. (Fig. 1-1). However, some authors claim it to be feasible up to COD levels of 30 g L\(^{-1}\) [6] or even 100 g L\(^{-1}\) [7]. The main advantage of the EO technology is that chemicals are not used. In fact, only electrical energy is consumed for the oxidation of organic pollutants and electrochemistry is often referred to as an environmentally friendly approach, since the electron itself is considered a “clean”, safe and very effective reagent. The main pros as often stressed in the literature are [2,3]:

- **Versatility**: EO is generally not selective and can deal with many pollutants and treat from micro litres to millions of litres
- **Energy efficiency**: the electrochemical processes generally require lower temperature with respect to equivalent non-electrochemical counterparts (e.g. thermal incineration), the potential can be easily controlled and operational parameters can be designed to minimize power loss
- **Amenability to automation**: the electrical parameters used in the process are well suited for data acquisition, process automation and control

For the above reasons, electrochemistry and EO is a very interesting and promising alternative technology in environmental engineering for the prevention of pollution problems, especially within water treatment, but other fields of application as e.g. soil remediation do exist.

### 1.2 The research objectives

The research project providing the foundation for this thesis was conducted in collaboration with WATERSAFE DK Aps and WATERSAFE S.A., supplier and developer of separation technology and in particular EO reactors/cells for use in treatment of various kinds of polluted
water; swimming pools, municipal and industrial wastewater etc. Despite extensive experience in practical applications of electrolysis technology, especially on the electrode and cell manufacturing side, further knowledge on the electrochemical processes was wanted in order to better understand the fundamental principles and the theoretical background of the technique and results obtained. This information is needed in order to continue to develop and optimize the product portfolio and explore new market opportunities. In addition, study of the applicability towards other aqueous pollution problems relevant to the northern part of Europe and Scandinavia was pointed out as important, especially within the area of degradation of organics in water. As will be presented in this thesis, the fields of application of the EO technique are very wide, and the objectives of the project were initially targeted from a broad perspective and were focused around both costumer related case stories and fundamentally or operationally studies investigating role of operating parameters, oxidation pathways, efficacy towards specific organics etc, with the overall goal to mature the technique to industrial application.

The headlines providing the underlying basis for the project aims are pointed out:

- Conduct thorough literature review studies in order to clarify state of the art of international research in EO
- Experimental case study of EO as a technique for remediation of a complicated groundwater pollution through on-site treatment
- Detailed experimental studies on a selected organic pollutant family with a specific customer related target with a wide market potential
- Study the strengths and weakness’ of Watersafe’s products, in particular the anode, through comparisons of oxidation mechanisms and performance to other commercially available cells
- Explore the differences observed between chemical chlorination, electro-chlorination, and direct oxidation and the influence of electrolyte composition in general
- Study the potential issue of by-product formation, which can comprise the most serious challenge for market penetration

The aims have been met through an experimentally based applied approach, where build up of experimental experience and process knowledge using EO with equipment from Watersafe had high priority. However, the progress in the field of environmental electrochemistry these years are rapid - with the technology just on the edge of industrial break though - and continuous literature reviews and multiple conference participations have been just as important tasks throughout the project in order to keep up with international front leaders in the area.

1.3 Thesis structure and content

The thesis is structured as a summary of the research conducted in this project. The main studies comprising 6 papers are published or submitted for publication and are enclosed for
assessment in the supplements chapter, but additional yet unpublished data will be included and presented where relevant. Clear reference to the relevant papers will be given in each chapter.

After this introduction, the research area is introduced with a chapter presenting the generally accepted mechanisms of EO of organics in aqueous solution with all of the complex system of oxidative pathways involved. This is followed by a short literature review meant for demonstrating the versatility of the electrochemical technique for treatment of organic pollutants, but extensive literature references will be provided throughout the thesis in order to support propounded statements and explanations. Then, the materials and experimental approaches applied in the research are presented in Chapter 4, in addition to some selected current practical examples of full scale use of Watersafe electrolysis technology.

Chapter 5 considers the background and most important discoveries found in two case studies. The first sections consider electrochemical oxidative treatment of polluted groundwater from the most toxic contaminated site in Denmark, Høfde 42, and in addition to the results, the chapter will reflect more on the future applications of EO within on-site groundwater remediation - and as a powerful oxidation technique part of a reinjection strategy for soil remediation. The next sections consider EO as a technique for removal of a very important family of persistent organic pollutants (POPs) from water; polycyclic aromatic hydrocarbons (PAHs). The study deals with a specific problem connected to treatment of process water generated during the procedure of removal of harbour sediments, an issue of worldwide importance.

In chapter 6, the most important findings of a comprehensive series of experiments using the dye molecule p-nitrosodimethylaniline as model compound are presented. The objectives in this study were multiple; investigate the applicability of this compound as model compound for optimization of performance of EO and other AOPs, study the influence of electrolyte composition for electrochemical bleaching of dyes, and investigate the chemical oxidation mechanisms of active chlorine and the different oxidation mechanisms proposed for “active” and “non-active” anodes (explained in Chapter 2).

The principle of electro-chlorination has proved to be a very efficient technique for both disinfection of aqueous solutions and for abatement of some organics, but questions are frequently raised from customers concerning the nature of the innovatory approach in this technique compared to traditional “old-fashioned” chemical chlorination. This issue is treated in chapter 7, where reflections are made upon yet unpublished results demonstrating the differences observed on chemical vs. electro-chlorination approached from different angles.

Another very important and plausible issue, which needs to be understood and controlled before EO is matured to an environmental and healthy commercial success, is the question of by-product formation during electrolysis. This specific problem is addressed in Chapter 8 through investigations of the fate of halogenation of PAHs, when sea water is electrolysed as in the sediment remediation process considered in chapter 5.
Before the gathered conclusion is drawn, a surface analysis study is presented in Chapter 9, where the metal alloy making up the outer surface coating of the Watersafe anode is investigated by X-ray Photoelectron Spectroscopy (XPS) before and after electrolysis in different electrolytes. The aim was to study the chemical states of the atoms on the surface under different conditions, in order to support or question the EO models proposed in the literature.

The thesis will be concluded with comments on the authors view on the future possibilities of EO as a coming and possible successful treatment technique. This will include a discussion of different principles and approaches to implement this AOP - alone or in combination with other techniques - as part of a larger treatment train or strategy. A very powerful feature of the electrochemical technology is its ability to be part of a sustainable treatment strategy, if the needed electricity is supplied from (on-site) renewable sources. With the currently increasing attention on sustainability, green engineering, carbon footprint analysis etc. as being important in best practise management and choice of remediation approach, EO might have its own niche compared to some of the other AOPs.
Chapter 2
The principles and mechanisms in electrochemical oxidation (EO)

The underlying principles of the oxidation mechanisms in EO of organics have been subject to comprehensive research within the last decade. These works have resulted in a somehow generally accepted theoretical understanding on how the different anode materials, the composition of the electrolyte, and the nature and structure of the organics influence the efficiency of the organic oxidation and evolution in common parameters as chemical oxygen demand (COD) and total organic carbon (TOC) during electrolysis.

The use of electricity in order to study chemical reactions was one of the cornerstone tools in the development of modern chemistry from the mid-1700s. Despite the long history of electrochemistry originating from great notabilities as Luigi Galvani [8] and Alessandro Volta [9] in the late 18th century, and Michael Faraday [10] and John F. Daniell [11] in the early 19th century among many others, the feasibility of electrochemical conversion/destruction of organics in wastewater first attracted attention in the mid-1970’s. This interest increased steadily during the 80’s and early 90’s and much more rapidly in the late 90’s and forward.

Within the last 15 years, many research groups around the globe have been and still are involved in studying the potentials of EO due to the obvious importance in developing new technology to preserve our water resources and environment. The main contributors on the theoretical side are groups focussed around C. Comninellis [13-25], A. De Battisti [26-32], O. Scialdone [33,34], M. Panizza and G. Ceriscola [20,35], P. Cañizares [36-38], A.M. Polcaro [39-41], and E. Brillas [42], but several others could be mentioned as well. On the application side, the number of research groups is even higher, and a hunch of the number of groups involved can be obtained by going through the references in Chapter 12. However, compared to other AOPs as photocatalysis, the field is still in a growing phase and especially in Scandinavia it has so far attracted only little attention.

This chapter presents the main principles in EO of organics in aqueous solution. Electrochemistry offers different oxidation pathways, and the direct electrolysis, the electrochemical oxygen transfer reaction, and the indirect mediated oxidation processes will all be discussed. In the published literature, a large effort has been dedicated to development of theoretical models in order to predict process efficiency and optimize the performance of the electrochemical reactors and the basic principles in these models will be presented.


2.1 Short introduction to fundamental electrochemistry

The field of electrochemistry concerns either utilization of energy from spontaneous chemical reactions in the form of electricity or the other way around, to supply energy in order to get non spontaneous chemical reactions running. Electrochemistry is redox chemistry, where electrons are transferred from one species to another. A species is in this terminology said to be oxidized when it loose electrons and reduced when it gains electrons.

When chemical reactants capable of spontaneous redox reaction are physically separated and the electrons from the reaction flow through an electric circuit by means of electrodes and wires, it produces a current which can be utilized as an energy source (battery or fuel cell). The electric current is proportional to the reaction rate, and the cell voltage is proportional to the free energy change for the electrochemical reaction.

In electrolysis, non-spontaneous chemical reactions can be forced to occur at the surface of an electrode by an imposed potential difference (energy) high enough to overcome the activation energy for a reaction at the specific electrode and the resistance in the reagent media. Two electrodes, most commonly solid materials, are connected via a power supply and submerged in a solution containing the chemical reagents, termed the electrolyte. If the supplied energy is sufficient, electrons will be removed from the compounds in the electrolyte (they become oxidized) at the positive electrode (anode), while electrons will be delivered to compounds in the electrolyte (they become reduced) at the negative electrode (cathode). Electrons cannot travel freely in solutions, so the charge passed through an electrochemical cell originates from continuous simultaneous oxidation and reduction of chemical species and electrostatic and hydrodynamic transport of ions and molecules.

This system of electrodes and electrolyte, where electrochemical reactions can happen, is termed the electrochemical cell. In order to avoid reduction of the oxidized species at the cathode, the anode compartment (anolyte) and cathode compartment (catholyte) can be divided by a membrane, but just as frequently undivided cells are used due to their more simple construction and maintenance. At the electrodes both organic and inorganic molecules and ions can be involved in electron transfer in the electrolysis process. It is the EO at the anode, which have been utilized for degradation and remediation of aqueous organic pollutants in the research presented in this thesis and most of the other studies referred to.

2.2 Direct electrolysis and thermodynamics of electrochemical mineralization

In the process termed direct electrolysis, pollutants are oxidized after adsorption on the anode surface, without involvement of any substances other than the removed electron, producing an adsorbed organic radical.

\[ R_{an} \rightarrow P_{an} + ze^- \] (2.1)
Conversely, the process of electrochemical mineralization, where the organic compound is completely degraded to carbon dioxide, water and inorganic minerals, involves oxygen transferred from water molecules to the organic pollutant by help of the electrical energy imposed. This mechanism is usually in the literature termed the electrochemical oxygen transfer reaction (EOTR) [1] and is presented in detail in section 2.3. An example of EOTR is electrochemical mineralization of bisphenol A (BPA) (2.2), a known endocrine disrupting chemical that is widely used in the production of polycarbonate plastics and epoxy resins, and found frequently in surface waters contaminated with industrial effluents [43].

\[
C_{15}H_{10}O_2 + 28H_2O \rightarrow 15CO_2 + 72H^+ + 72e^- \tag{2.2}
\]

In this reaction, water is the source of oxygen atoms for complete oxidation of BPA to 15 carbon dioxide molecules at the anode of the electrolytic cell by removal of 72 electrons. The corresponding reaction feeding electrons to the solution in order to maintain charge neutrality is primarily hydrogen evolution on the cathode from the protons liberated in the oxidation reaction (2.2) or from reduction of water.

\[
72H^+ + 72e^- \rightarrow 36H_2 \tag{2.3}
\]

\[
36H_2O + 72e^- \rightarrow 36H_2 + 72OH^- \tag{2.4}
\]

From a thermodynamic view point, electrochemical mineralization is achievable also through direct electrolysis of any soluble organic compound in water at potentials comfortable below the thermodynamic potential of oxidation of water to molecular oxygen (\(E^0 = 1.23\)V). This oxygen evolution reaction given by (2.5) is in EO of organics mostly considered an energy consuming side reaction, which it is the optimal goal to avoid.

\[
2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{2.5}
\]

As an example, the thermodynamic reduction potential (\(E^0\)) of the mineralization of BPA (2.2) under standard conditions is 0.17 V, calculated using the standard Gibbs energy of reaction (\(\Delta_rG^0\)) based on the standard Gibbs free energy of formation (\(\Delta_fG^0\)) for reactants and products (-454.7 kJ mol\(^{-1}\) for BPA\(^1\), -237.13 kJ mol\(^{-1}\) for H\(_2\)O, -394.4 kJ mol\(^{-1}\) for CO\(_2\)), the number of exchanged electrons, \(n=72\), and Faradays constant, \(F\).

\[
\Delta_rG^0 = 15 \cdot (-394.4 \text{ kJ/mol}) - (-454.7 \text{ kJ/mol}) + 28 \cdot (-237.13 \text{ kJ/mol}) \tag{2.6}
\]

\[
\Delta_fG^0 = 1178 \text{ kJ/mol}
\]

\(^1\) Calculated by thermodynamic data from NIST webbook database (U.S National Institute of Standards and Technology) (\(\Delta H_f^0=-369\) KJ mol\(^{-1}\) and \(S_f=287.7\) J mol\(^{-1}\) K\(^{-1}\)) at T=298 K.
In this sense, it would theoretically be possible to treat a stream with an aqueous organic pollutant as BPA as a fuel cell with co-generation of electrical energy (fuel cell regime), if the anodic oxidation of the organic was counterbalanced by reduction of oxygen at the cathode, the reverse reaction of (2.5). The total reaction of this hypothetic fuel cell is given in (2.8).

\[
C_{15}H_{16}O_2 + 18O_2 \rightarrow 8H_2O + 15CO_3^-
\]  

(2.8)

The standard thermodynamic cell potential of such a hypothetical fuel cell would be 1.04V (1.23V - 0.17V). However, even though the thermodynamics seems favourable, the kinetics of these kinds of reactions is in practise reported to be very slow. In the actual state of the art, the fuel cell operated electrochemical mineralization is not feasible due to the lack of active electrocatalytic anode materials [44], and electrolysis, where energy is supplied, is the way forward.

### 2.2.1 Poisoning effect

The main problem of direct anodic electrolysis of organics at a fixed potential below oxygen evolution is a decrease of catalytic activity due to formation of a polymer layer on the anode surface, a process termed poisoning effect [1]. The extent of this deactivation depends on the adsorption properties of the anode surface, the concentration and nature of the organic compounds, and their oxidative intermediates. In particular it has been observed that the poisoning effect is less pronounced with anodes with weak adsorption properties (further explained in section 0), while it is more evident in the presence of high organic concentrations and presence of aromatic compounds such as phenol, chlorophenols, nitrophenols, aniline etc.

An example of poisoning is seen in the direct oxidation of 2-naphtol, which was studied by Panizza and Cerisola [45] and Panizza et al. [46] using different anode materials. Cyclic voltammetry (CV) studies showed that the anodic peak for naphthol oxidation rapidly decreased to lower potentials until a steady-state was reached after around 6 scans. This behaviour was attributed to the formation of a polymeric film as a consequence of the polymerization of naphthoxy radicals, formed by the initial step in the oxidation mechanism.

\[
\begin{align*}
\text{[2-naphtol]} & \rightarrow \text{[napthoxy radical]} \\
\text{[napthoxy radical]} & \rightarrow \text{[polymeric film]} \\
\text{Polymerization} &
\end{align*}
\]  

(2.9)

The nature of the brown organic film was confirmed by IR analysis, which showed the presence of C-H, C=C, C=C-H, and C-OH bonds on the anode surfaces [46]. The organic film was strong and resistant to washing with organic solvents and the anode fouling was observed for both
The principles and mechanisms in electrochemical oxidation (EO)

TiRuSnO\textsubscript{2}, PbO\textsubscript{2}, and BDD anodes. However, regeneration of the electrochemical activity in the same solution was possible through polarisation applying higher potentials in the region of oxygen evolution, but only using PbO\textsubscript{2} and BDD [45]. These anode materials are characterized as having a high overpotential for oxygen evolution (explained in section 0) with adsorbed hydroxyl radicals as intermediates that oxidised the polymeric film and restored the electrode activity. The PbO\textsubscript{2} and BDD electrodes belong to a class of anodes termed as so-called non-active anodes, which also will be further explained in the next section.

As this example demonstrates, the poisoning effect can be avoided by performing oxidation in the region of water discharge. Operated under these conditions simultaneous to the oxygen evolution, the organics can be oxidised electrochemically on the anode surface through EOTR or by a process termed indirect electrolysis, where redox reagent are electrochemically generated in-situ in solution as a chemical reactant to oxidize the organics.

2.3 The electrochemical oxygen transfer reaction (EOTR)

EO of organic compounds in aqueous solution can be obtained without electrode fouling by performing electrolysis at high anodic potentials in the region of water discharge due to the participation of intermediates of oxygen evolution [2]. This process results in partly conversion or full mineralization of the organics, does not need to add oxidation catalysts to the solution and does in principle not produce any by-products. However, current efficiencies are diminished by the secondary reaction of oxygen evolution during oxidation, and generally, removal efficiencies are related to operating conditions and selected electrode materials.

In 1994, Comninellis published a paper on “Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment” [24], based on earlier work by Johnson [47], which set the foundation for exploring and documenting the mechanisms involved in EO of organics in water. Prior to this paper, EO for treatment of water was recognised as a useful method for oxidation for some troublesome organics like phenols. However, the mechanisms involved were not clear, but in general believed to be rather simple in nature. The papers by Comninellis and several others published from the mid 90’ties to the early 2000 showed that the nature of the electrode material strongly influences both the selectivity and the efficiency of the process and, in particular, several anodes favored the partial and selective oxidation of pollutants (conversion), while others favored complete mineralization to carbon dioxide [1]. In order to interpret these observations, a comprehensive model was proposed for oxidation of organics at metal oxide electrodes with simultaneous oxygen evolution, which currently largely is considered as globally accepted. A recent paper from Panizza and Ceriscola reviews a lot of these results obtained by different anode materials for anodic oxidation of organics [1].
2.3.1 The reaction scheme

The first step in the electrochemical oxygen transfer reaction is the discharge of water molecules at the anode surface to form adsorbed hydroxyl radicals, where $MO_x$ denotes the metal oxide anode.

$$MO_x + H_2O \rightarrow MO_x(\cdot OH) + H^+ + e^- \quad (2.10)$$

The following steps have been shown to depend on the nature of the electrode materials and make it possible to distinguish between limiting classes of electrodes defined as “active” or “non-active” anodes. The active anodes have higher oxidation states available on the electrode surface and may interact stronger with the adsorbed hydroxyl radicals by further oxidation, forming higher oxides:

$$MO_x(\cdot OH) \rightarrow MO_{x+1} + H^+ + e^- \quad (2.11)$$

The surface redox couple $MO_{x+1}/MO_x$ is often denoted chemisorbed active oxygen and can act as mediator in the conversion or partial oxidation of organics on active anodes:

$$MO_{x+1} + R \rightarrow MO_x + RO \quad (2.12)$$

In contrast to the active anodes, the non-active electrodes are characterized by a weak electrode-hydroxyl radical interaction forming physisorbed active oxygen (hydroxyl radicals), which can assist in a complete mineralization of the organics to carbon dioxide:

$$MO_x(\cdot OH) + R \rightarrow MO_x + CO_x + H_2O + H^+ + e^- \quad (2.13)$$

Both the chemisorbed and physisorbed active oxygen undergo a competitive oxygen evolution side reaction resulting in decreased anodic process efficiency and loss of energy:

$$MO_{x+1} \rightarrow MO_x + \frac{1}{2}O_2 \quad (2.14)$$

$$MO_x(\cdot OH) \rightarrow MO_x + \frac{1}{2}O_2 + H^+ + e^- \quad (2.15)$$

The reaction scheme is usually presented as a full oxidation cycle (Fig. 2-1). According to the mechanisms, anodes with low oxygen evolution overpotential such as amorphous carbon, graphite, iridium dioxide, ruthenium dioxide, or platinum have an active behaviour, allowing mainly partial oxidation of organics. In contrast, anodes with high oxygen evolution overpotential such as antimony-doped tin oxide, lead dioxide, or boron doped diamond (BDD) have a non-active behaviour and favour complete oxidation of the organics to carbon dioxide.
The principles and mechanisms in electrochemical oxidation (EO)

Based on this approach, different anode materials are listed in Table 2-1, according to their EOTR oxidation power.

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Oxidation potential / V</th>
<th>Overpotential of O₂ evolution / V</th>
<th>Adsorption enthalpy of MOₓ(OH)</th>
<th>Oxidation power of the anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuO₂-TiO₂</td>
<td>1.4-1.7</td>
<td>0.18</td>
<td>Chemisorption of OH radical</td>
<td></td>
</tr>
<tr>
<td>IrO₂-Ta₂O₅</td>
<td>1.5-1.8</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti/Pt</td>
<td>1.7-1.9</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti/PbO₂</td>
<td>1.8-2.0</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti/SnO₂-Sb₂O₅</td>
<td>1.9-2.2</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Si/BDD</td>
<td>2.2-2.6</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


The concept of overpotential is a term referring to the potential difference needed for a specific electrolytic reaction experimentally to occur at a given anode material compared to the one thermodynamically predicted by the standard reduction potential. The difference in overpotential for oxygen evolution shown for Ti/Pt and Si/BDD in Table 2-1 is found by CV measurements in an inert electrolyte, where the 0.3V and 1.3V, respectively, are the potential differences observed from the standard reduction potential of molecular oxygen (E° = 1.23V versus SHE) to the applied potential needed for the anodic current peaks to raise (Fig. 2-2). Another term in electrochemistry useful to be aware of is the electrochemical potential window, which denotes the potential difference observed for a specific electrode material between the cathodic hydrogen evolution peak and the anodic oxygen evolution peak in CV.
In literature, the active anodes are typically denoted low oxidation power anode due to their preference to partial oxidation caused by the strong electrode-hydroxyl radical interaction. A typically example is the IrO$_2$ anode, which was used for the documentation of the formation of the higher active oxidation state IrO$_3$ [17,18,25]. The most important type of the high oxidation power non-active anodes are the reasonably newly developed BDD anodes, which since the millennium has received most attention in published research on this subject [13-16,19,20,29,35-38,48-61]. The evidence of hydroxyl radical formation on the BDD anodes during anodic polarization have been found by means of spin trapping during electrolysis of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) analysed by electron spin resonance (ESR) spectroscopy [57].

The non-active anodes are due to their capabilities of full mineralization often considered ideal for waste water treatment or other polluted water bodies, and the development of BDD anodes has definitely placed EO as a true AOP. However, despite the advantages of BDD, their high costs, mechanical resistance issues and difficulties in finding an appropriate substrate on which to deposit the thin diamond layer are major drawbacks. According to the literature, stable diamond film can currently only be deposited on silicon, tantalum, niobium, and tungsten, but these material are not considered suitable for large scale use, due to the poor conductivity and brittleness of silicon and the high costs of the latter rare earth metals [62]. Deposition on the most preferred substrate in electrode manufacturing, titanium, results so far in BDD anodes with cracks not suitable for industrial use [62].

In addition, full mineralization may not always be the preferable treatment strategy, since energy may be wasted on oxidising harmless short length oxidation products as carboxylic acids, which on the contrary in some pre-treatment application scenarios may serve as necessary carbon substrates in a subsequent biological treatment. Also, in practise the categories of electrode classification are not as sharply defined as most anodes will exhibit a mixed...
behaviour, since both reaction paths may participate in parallel in organic oxidation and oxygen evolution reactions.

The EOTR requires the transport of pollutants directly to or very near to the surface of the anode. However, another feature which influences the optimal choice of anode material is the electrochemical degradation pathway termed indirect oxidation, where reversible or irreversible oxidation of ions or other constituents in the water matrix produces oxidants capable of bulk oxidation of the organics.

2.4 Indirect oxidation pathways

The idea of indirect oxidation is to prevent electrode fouling, avoiding direct electron exchange between the organics and the anode surface and utilize the electrocatalytic potential of other anode materials. Therefore, the pollutants are oxidised through the mediation of some electrochemically generated redox reagents, which act as intermediaries for transfer of electrons between the electrode and the organics [1]. However, intended or not, the indirect oxidation processes play a role whenever a real polluted water matrix is treated through electrolysis, and if of importance for the degradation of the target pollutant, it can be emphasised and enhanced through addition of extra electrolytes.

Oxidation mediators can be metallic redox couples such as Ag(II/I), Ce(IV/III), Co(III/II), Fe(III/II), and Mn(III/II), or strong oxidising chemicals such as active chlorine species, ozone, hydrogen peroxide, persulphate, percarbonate, and perphosphate.

2.4.1 Mediated oxidation by metallic redox couples

When metallic redox couples are applied as redox reagents the process is typically termed mediated electrochemical oxidation (MEO). Metal ions in acidic solutions are anodically oxidised from their stable oxidation state ($M^{z+}$) to the higher reactive oxidation state ($M^{(z+1)+}$) in which they attack the organic feed, degrading it into carbon dioxide, inorganic salts, and water:

\[
\begin{align*}
M^{z+} &\rightarrow M^{(z+1)+} + e^- \tag{2.16} \\
M^{(z+1)+} + R &\rightarrow M^{z+} + CO_2 + H_2O \tag{2.17}
\end{align*}
\]

Reaction (2.17) returns the couple back to a stable state ($M^{z+}$) and it is then recycled through the cell in order continuously to regenerate further reaction. MEO through metallic redox reagents is mainly applied for pollution abatement in divided cells, where the anode and cathode are separated by a porous separator or an ion-exchange membrane in order to prevent reduction of the oxidative agent at the cathode [1]. The MEO process is preferably used to treat solid waste or highly concentrated solutions with an organic content higher than 20%, in order to avoid or limit the need for implementation of a solution-solution separation step to retain the key metallic ions from the discharged solution. For total organic oxidation, a redox couple with a high oxidation potential must be chosen as for instance the Ag(I/II) ($E^0=1.98V$). When this
redox pair is applied, Ag(II) ions are generated by anodic oxidation of Ag(I) ions in concentrated nitric acid in the anolyte part of the divided cell, forming a dark brown inorganic complex with nitrate ions (AgNO$_3^+$), which slows down the Ag(II) reduction by water [63]:

\[ Ag^+ + NO_3^- \rightarrow AgNO_3^+ + e^- \] (2.18)

The corresponding cathodic reaction in the other half cell is the reduction of nitric acid or NO, which can be further oxidised to nitric acid by bubbling of air through the catholyte compartment. The Ag(II) complex will mineralise the organic waste, which is fed to the anolyte compartment:

\[ AgNO_3^+ + R + H_2O \rightarrow Ag^+ + CO_2 + H^+ + NO_3^- \] (2.19)

During the oxidation, the anolyte remains clear since the steady state bulk oxidation of AgNO$_3^+$ is very low. Then, when the solution turns dark brown, it is evidence of build-up of AgNO$_3^+$ in the anolyte and full removal of the organics. Other redox couples which have been demonstrated to provide full mineralisation of various organic pollutants are Co(III/II) and Ce(IV/III) [1].

Redox couples more abundant in natural waters as Fe(III/II) and Mn(III/II) are not suited for total oxidation of organics, because of their low oxidation potential (E$_0^0$=0.77V and E$_0^0$=1.56V respectively), but they can be used for selective partial oxidation of organic compounds. However, when treating polluted water rich with iron and manganese at potentials above oxygen evolution, the oxidised ionic iron and manganese tends to precipitate as insoluble oxides after reaction with molecular oxygen produced by the anodic oxygen evolution side reaction. These reactions may induce co-precipitation of metallic pollutants, and this process known as electro-coagulation or electro-precipitation is industrial used for removal of heavy metals, where dissolution of a solid iron (or alumina) anode secures a steady feed of Fe(II) [64]. However, the electro-coagulation process can as showed also be a side process of the anodic oxidation, which also has been reported by us [65].

**2.4.2 Mediated oxidation by in-situ generated chemical oxidants**

Wastewater effluents containing low concentrations of organic pollutants (organic content less than 20%) can be treated by indirect electrolysis generating in situ chemical reactants and converting them into less harmful products [1]. The oxidising chemicals can be electro-generated either by anodic oxidation such as formation of active chlorine, ozone, and persulphate, or by cathodic reduction such as formation of hydrogen peroxide. A list with oxidants sorted after their standard reduction potential is showed in Table 2-2. The most traditional and intensively studied indirect EO agent is active chlorine in a process often referred to as electro-chlorination.
The principles and mechanisms in electrochemical oxidation (EO)

Table 2-2: Thermodynamic formation potentials of several oxidants.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Standard reduction potential, E° (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl radical</td>
<td>(H₂O/OH⁺)</td>
</tr>
<tr>
<td>Ozone</td>
<td>(O₂/O₃)</td>
</tr>
<tr>
<td>Peroxodisulphate</td>
<td>(SO₄²⁻/S₂O₈²⁻)</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>(H₂O/H₂O₂)</td>
</tr>
<tr>
<td>Permanganate ion</td>
<td>(MnO₂/MnO₄⁻)</td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>(Cl⁻ /HOCl)</td>
</tr>
<tr>
<td>Chlorine</td>
<td>(Cl⁻/Cl₂)</td>
</tr>
<tr>
<td>Dichromate</td>
<td>(Cr³⁺/Cr₂O₇²⁻)</td>
</tr>
<tr>
<td>Oxygen</td>
<td>(H₂O/O₂)</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>(Cl⁻/ClO⁻)</td>
</tr>
</tbody>
</table>


2.4.2.1 Electro-chlorination of organic pollutants

Due to the natural abundance of chloride in most polluted waters, chlorine-mediated oxidation is the most widely employed in-situ generated chemical oxidant for wastewater treatment. The use of chlorine-mediated oxidation or electro-chlorination has been reported for oxidation of a wide range of model pollutants and has in particular been shown to be suitable for the treatment of wastewaters with high natural concentrations of sodium chloride. However, despite the wide use of active chlorine species as oxidation mediators, the exact natures of the electrochemical and chemical reactions that take place during EO in chloride media are complex and not entirely known [1]. It has been shown that indirect transfer of oxygen to organic molecules can be obtained both on the anode surface through adsorbed oxy-chloro species or in the bulk of the solution through chlorine, hypochlorous acid, or hypochlorite depending on pH.

\[
2Cl \rightarrow Cl₂ + 2e^- \tag{2.20}
\]

\[
Cl₂ + H₂O \xrightleftharpoons{K_{A,10^9(25\,°C)}} HOCl + H^+ + Cl^- \tag{2.21}
\]

\[
HOCl \xrightleftharpoons{pK_w=7.4(25\,°C)} OCl^- + H^+ \tag{2.22}
\]

An explanation of the mediating role of chloride ions have been proposed by the group of De Battisti [30,31]. They extended the scheme of the EOTR (Fig. 2-1) to the cases where oxygen transfer is carried out by adsorbed oxychloro species, which are considered as intermediates of the chlorine evolution reaction instead of hydroxyl radicals (Fig. 2-3) - an aspect of electro-chlorination which has been studied in this project as well and will be discussed in Chapter 7.

The presence of chloride ions was proposed to inhibit the oxygen evolution reaction causing an increase in anode potential and, therefore, a higher reactivity of adsorbed oxidised chloride species. They observed that the oxidation of organics in the presence of chloride mainly depends on chloride concentration, solution temperature, and pH, and that it was basically independent on the electrode. If the anode independence was right, Fig. 2-3 should be extended to the case of active anodes utilizing the chemisorbed active oxygen, MO\textsubscript{x}. However, despite the comprehensive work of De Battisti, some differences in the efficiency of the electrochlorination process on active and non-active anodes in the presence of organics have been noticed both by others and in this work, which will be presented in the next section and discussed in Chapter 6.

Anode materials and operative parameters of electro-chlorination

In the literature, the most used electrode materials for in-situ generation of active chlorine are based on platinum or on a mixture of metal oxides (e.g., RuO\textsubscript{2}, TiO\textsubscript{2}, IrO\textsubscript{2}) that have a good electrocatalytic properties for chlorine evolution as well as long-term mechanical and chemical stability. The ruthenium, titanium, and iridium oxide anodes belong to a class of catalytic electrodes known as dimensional stable anodes (DSA). The metal oxides are often mixed in binary or tertiary systems and coated on metal, mainly titanium, substrate. The DSAs have since the 1960’ties been used in large scale in the chlor-alkali industry, due to high stability under high current density loading and high current efficiency of the chlorine gas evolution caused by good catalytic properties for this reaction [67]. The history and success of DSAs are thoroughly reviewed by Trasatti [68]. Other electrodes can also be used such as graphite and non-active anodes as PbO\textsubscript{2} and BDD. However, in the presence of higher concentrations of organic pollutants in chloride media, the otherwise superior performance of the non-active anodes for EOTR is seriously threatened by the more efficient chlorine evolution anodes.

In electrochemical treatment of any water body at potentials above oxygen evolution, the chloride electrolysis process generating the adsorbed or bulk chlorine species amendable for
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indirect chemical oxidation coexist with the direct EOTR process giving rise to a very complex chemical reaction system, which does not easily allow predicting the role of operative parameters on the performances of the process. This prompts a difficult optimization of the process and to discrepancies between literature data. One of the most recent and ambitious papers treating this subject is Scialdone et al. [34], which theoretically and experimentally investigated the role of operative parameters of EO of aqueous organics in the absence and presence of sodium chloride. Applying oxalic acid as model compound on BDD (non-active anode) and IrO₂-Ta₂O₅ (DSA type, active anode), they found that in the presence of a “suitable amount” of chlorides, the anodic oxidation of oxalic acid was partially replaced by a homogenous indirect oxidation process. The interesting thing was that a very different influence of the nature of the anodic material, the flow rate, and the current density on the performance of the process arose in the absence and the presence of chlorides so that optimization of the two processes required very different operative conditions. In the absence of chlorides, highest current efficiency was obtained at BDD as expected, when most part of the process was under charge transfer controlled kinetics (i.e. when low current densities and high flow rates were imposed favoring the EOTR). On the other hand, in the presence of chlorides, higher current efficiencies were generally obtained at the DSA anode, when high current densities and low flow rates were imposed (i.e. when a high concentration of chemical oxidants was obtained as a result of the chloride electrolysis). As a result of the different effect of operative parameters on the processes, the addition of chlorides to the electrolytes caused an increase or decrease of the abatement of organics depending on the adopted operative conditions and applied anode materials. In particular, in the case of DSA anode the addition of chlorides gave rise to a dramatically increase of the current efficiency [34].

The electro-chlorination process can lead to either partial oxidation or full mineralization of the organics dependent on the oxidation abilities of the generated active chlorine species towards the target organics. However, the main drawback and concern of the electro-chlorination process is a likely formation of chlorinated organic compounds during electrolysis, resulting in increased wastewater toxicity, as it is known from common chlorination chemistry. Indeed, organo-chlorinated compounds are detected during electro-chlorination, which has been shown by us and others, but in most cases they are further degraded during electrolyses. However, it has been demonstrated that selecting appropriate experimental conditions, glucose as model compound can be mineralized by chlorine mediated electrolysis without formation of chlorinated organics [30]. The issues and concerns of by-product formation during the application of EO are further discussed in Chapter 8.

2.4.2.2 Anodic generation of other strong oxidants

Ozone is another strong chemical oxidant that can be electrochemically produced by anodic oxidation and employed for water disinfection and treatment. Because of its high oxidation potential (E°=2.1V) there is an increasing use of ozone in wastewater treatment, and one of the advantages of ozone oxidation is that it does not produce secondary pollutants, due to its decomposition into molecular oxygen.
However, ozone is known to be capable of formation of disinfection by-products as bromate (BrO₃⁻), when used in treatment of water containing bromide ions [69].

Other strong oxidants, which can be used as mediators in the indirect EO of organics, are persulphate (S₂O₈²⁻), percarbonate (C₂O₆²⁻), and perphosphate (P₂O₈⁴⁻) [70].

These compounds are produced by anodic oxidation of the corresponding anions in the solution, but they are only generated efficiently by non-active anodes as the BDD and PbO₂ electrodes, due to the need of high oxygen overpotentials in order to reach the formation potentials [1,71]. In addition, the formation is usually not only a direct electrochemical process, but a sequence of electrochemical and chemical stages [70].

### 2.4.2.3 Cathodic generation of hydrogen peroxide

Hydrogen peroxide can be continuously supplied to an acidic contaminated aqueous solution by a two electron reduction of oxygen gas, directly injected as pure oxygen or bubbled air, at the cathode [42].

\[
O_2 + 2H^+ + 2e^- \rightarrow H_2O_2
\]  

(2.28)

Preferable, a divided cell with a cationic membrane is applied in order to reduce the loss of hydrogen peroxide due to anodic oxidation to molecular oxygen through hydroperoxide radicals (HO₂⁺) as intermediates. Other major side reactions decreasing the current efficiency are further electrochemical reduction of hydrogen peroxide at the cathode and, to a lesser extent, disproportion in the bulk to molecular oxygen and water. The most widely applied cathode materials for the hydrogen peroxide electro-generation are based on carbon in various configurations (carbon felt, reticulated vitreous carbon (RVC), carbon sponges, carbon nanotubes (NT), or graphite) [42].

Hydrogen peroxide is despite its widespread use for odour control, bleaching purposes etc. a weak oxidant, when applied solely. In relation to inorganic and organic oxidation it is only reported effective for oxidizing reduced sulfur compounds, cyanides, aldehydes, formic acid, and some nitro-organic and sulfo-organic compounds [72]. Its oxidation power can be notably...
improved by combination with ozone, ultraviolet radiation, and transition-metal catalysts such as iron ions breaking the peroxide bond and producing hydroxyl radicals as briefly showed in Fig. 1-1. The latter technology is Fenton’s chemistry, which is the most widely spread technology adapted to indirect electrochemical hydrogen peroxide treatment and termed the electro-Fenton process.

Fenton’s chemistry has been around for more than a century with its birth being considered by most people to be the publication of a deep study on the strong promotion of the oxidation of tartaric acid by a mixture of $H_2O_2$ and $Fe^{2+}$ in 1894 by H.J.H Fenton [73]. In the 1930’s its application for oxidation of organic compounds was assumed by Haber and Weiss [74,75], who suggested a radical mechanism for the catalytic decomposition of $H_2O_2$ by iron salts. The full mechanisms of the Fenton process are extremely complex, but are very thoroughly presented in a clear manner by Pignatello et al. [5], and will not be given in full details here. However, it is generally accepted that the process is initiated by the formation of a hydroxyl radical as in accordance with the classical Fenton’s reaction.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^* + OH^-$$  \hspace{1cm} (2.29)

The hydroxyl radical then participates in a number of radical chain reactions, but are most importantly also involved in oxidation of organics. In the electro-Fenton process, the continuously in-situ produced $H_2O_2$ is mixed with an iron catalyst in the solution subjected to treatment in order to produce the hydroxyl radicals in the bulk via the Fenton’s process. In addition to the obvious advantages compared to the traditional chemical Fenton technology (no transport, storage, and handling of $H_2O_2$), the overall organic removal rates are usually higher because of the continuous regeneration of $Fe^{2+}$ at the cathode.

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$  \hspace{1cm} (2.30)

Electro-Fenton is the foundation of a range of related processes developed over the past decade. The combination with photochemistry in photo-electro-Fenton in order to promote the hydroxyl radical production and even solar-photo-electro-Fenton has been studied extensively by the group of Brillas using undivided cells combining the reductive hydrogen peroxide processes with the EOTR at the anode and the ultraviolet and visible irradiation [42].

### 2.5 Figures of merit of EO

The performance indicators, which have been used for assessing the efficiencies of the EO processes, are many, and not all have been applied in the research presented in this thesis. The indicators have been established in order to optimize operating parameters and compare electrochemical cells with different geometries and designs. The most often used and the ones evaluated in the present thesis are defined below.
2.5.1 Current efficiency

Current efficiency is generally defined as the ratio of the charge used for the oxidation of each compound to the total charge passed during electrolysis, and hence states if the electrons in the electrical circuit all come from oxidation of the target organics or if side reaction are dominant. In the literature, different expressions of current efficiency have been proposed: instantaneous current efficiency (ICE), electrochemical oxidation index (EOI) and general current efficiency (GCE) [1]. Two methods for the determination of ICE and GCE have been proposed, the oxygen flow rate (OFR) method and the chemical oxygen demand (COD) method. Determination of COD is a common parameter in wastewater treatment monitoring, measuring the amount of chemically added oxygen needed in order to oxidize all compounds in a sample amendable for oxidation. This parameter then provides the number of electrons needed to be removed from the solution in order to obtain full mineralization (4 mole e\(^-\) per mole O\(_2\)).

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O
\]  

The COD method is the one applied in the current research and ICE is calculated using the following relationship:

\[
ICE = \frac{(\text{COD}_t - \text{COD}_{t+\Delta t})}{8I\Delta t} FV
\]  

(COD)\(_t\) and (COD)\(_{t+\Delta t}\) are the chemical oxygen demand at times \(t\) and \(t + \Delta t\) (g L\(^-1\)), \(I\) is the current intensity (A), \(F\) is Faraday’s constant (96,485 C mol\(^-1\)), \(V\) is the electrolyte volume (L), and 8 is the oxygen equivalent mass (32 g O\(_2\) mol\(^-1\) / 4 e\(^-\)).

In the same way, GCE represents an average value of the current efficiency between initial time \(t = 0\) and \(t\).

\[
GCE = \frac{(\text{COD}_0 - \text{COD}_t)}{8It} FV
\]  

The electrochemical oxidation index (EOI) is the average value of the current efficiency during overall oxidation and is determined based on ICE.

\[
\text{EOI} = \frac{\int ICE \text{dt}}{\tau}
\]  

The parameter \(\tau\) represents the time at which ICE is almost zero. If considered during a period of sufficiently short time, particular in the beginning of electrolysis, the EOI can to some extend be considered specific for the compound investigated and supply information of the reactivity of the compound.
2.5.2 Specific energy consumption

An important cost optimization parameter is the determination of the amount of energy needed in order to reach removal goals. The energy consumption, $E_{sp}$, of the EO process is typically expressed as the energy consumed in kWh for removal of one kilogram of COD. It is based on the average cell voltage, $U$ (V), applied in order to reach the desired current intensity.

$$E_{sp} = \frac{tUI}{\Delta COD}$$  \hspace{1cm} (2.35)

$t$ (h) is the time of electrolysis and $\Delta$COD is the difference in initial and final COD (g L$^{-1}$).

2.6 Kinetic models

Several attempts of modeling the kinetics in EO have been published within the last decade. The approaches have been different, some using purely numerical modeling [39-41,76], some using statistical work tools as design of experiments (DOE) for optimization [53], but the so far generally most accepted kinetic models are grounded on theoretical electrochemically considerations. Polcalo et al. [39,41,76] have developed mathematical models based on the reaction between organic substrates adsorbed on inert electrode and hydroxyl radicals and on the indirect oxidation in the bulk phase by electrogenerated oxidizing agents. Canizares et al. have proposed different models, which divide the electrochemical reactors into several zones: those close to each of the electrodes and the bulk zone. In each zone, the concentration is assumed to be constant with the position [36,37]. Comninellis and co-workers developed different theoretical models based on the EOTR mechanism for non-active BDD [13,24,35] and active metal oxide anodes [21], while Scialdone [33,34] has proposed expansions to these models for the direct oxidation of oxalic acid on BDD and the indirect electro-chlorination of organics on DSA, from which the conclusions concerning the role of operating parameters in the presence of chloride was reviewed in section 2.4.2.1.

Despite the high complexity of the electrochemical process and the multiple pathways to obtain organic oxidation, the basic approaches in the models are similar. The most straightforward and widely developed is the EOTR model considering the kinetics in the mineralization reaction on BDD, but the progressing procedure applies generally. The main steps will be provided in this section in order to demonstrate the different domains under which the EO can be operated, ending with a short bullet point style guide proposed by Comninellis and co-workers on how to optimize a mineralization process of an organic pollutant based on the EOTR using BDD anodes. The full development of the model is found in Kapalka et al. [13] and Panizza et al. [35].

2.6.1 Electrochemical mineralization of organics on BDD

The starting point is to consider the current efficiency of the organic mineralization, which is assumed to take into account only two parallel reactions; the main EOTR reaction (2.36) and
the side reaction of oxygen evolution (2.37), where hydroxyl radicals in both cases act as intermediates.

\[
x_{\text{BDD}} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \·
\]

\[
BDD \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \·
\]

This initial assumption omits an additional positive indirect oxidation contribution to the mineralization from chemical oxidants generated from conceivable electroactive ions present in solution in possible much higher concentration than the pollutant. This is one of the limitations of the model.

What is additional assumed is that (i) adsorption of the organic compounds at the electrode surface is negligible; (ii) all organics have the same diffusion coefficient, \(D\); (iii) the global rate of the electrochemical mineralization of organics is a fast reaction, and it is controlled by mass transport of organics to the anode surface, which implies that the rate of the mineralization is independent of the chemical nature of the organic compound present in the electrolyte.

Under these conditions, the limiting current density, \(i_{\text{lim}}\) (A m\(^{-2}\)) for the electrochemical mineralization of an organic compound (or a mixture of organics) under given hydrodynamic conditions can be written as:

\[
i_{\text{lim}} = nFk_mC_{\text{org}}
\]

\(n\) is the number of electrons involved in the mineralization, \(F\) is Faradays constant, \(k_m\) is the mass transport coefficient (m s\(^{-1}\)), and \(C_{\text{org}}\) is the concentration of organics in solution (mol m\(^{-3}\)). When comparing the electrochemical mineralization of a generic compound with the chemical mineralization using molecular oxygen, it is possible to obtain the relation between the organics concentration, \(C_{\text{org}}\), and COD (mol O\(_2\) m\(^{-3}\)). In this way, the limiting current density of the electrochemical mineralization of organics at a given time \(t\) during electrolysis can be related with the chemical oxygen demand of the solution:

\[
i_{\text{lim}}(t) = 4Fk_m\text{COD}(t)
\]

4 is the number of exchanged electrons per mol of O\(_2\) as explained in section 2.2.

Working under galvanostatic conditions, depending on the applied current density \(i\) (A m\(^{-2}\)), different operating regimes have been identified by Kapalka et al. that are showed schematically in Fig. 2-4a and mathematically in Table 2-3.

The development of the expressions are found in [13] and are based on a defined characteristic parameter \(a\) of the electrolysis processes, which is the ratio between the applied operating current, \(i_{\text{app}}\), and the limiting current, \(i_{\text{lim}}\), calculated after (2.39):
The principles and mechanisms in electrochemical oxidation (EO)

1. \( i_{\text{appl}} < i_{\text{lim}} \): the electrolysis is under current control, organic intermediates are formed during the oxidation, the ICE is 100% and COD decreases linearly with time. This behavior persists until a critical time, \( t_{cr} \) (2.40), or to a critical conversion of organics, \( X_{cr} \) (2.41), corresponding to the time, or the conversion, at which the limiting current density is equal to the applied current density where \( \alpha = 1 \):

\[
    t_{cr} = \frac{1 - \alpha}{\alpha} \cdot \frac{V_r}{A k_m}, \quad \alpha = \frac{i}{i_{\text{lim}}^0}
\]

\[
    X_{cr} = 1 - \alpha
\]

\( A \) is the surface area of the anode (m\(^2\)) and \( V_r \) are the reservoir volume (m\(^3\)).

2. \( i_{\text{appl}} > i_{\text{lim}} \): the electrolysis is under mass transport control, organic compounds are completely mineralized to CO\(_2\) and secondary reactions (such as oxygen evolution) commence, resulting in a decreasing current efficiency. Under these conditions, ICE is below 100% and COD removal follows an exponential trend.

![Fig. 2-4: (a) Schematic current-time curves showing operating regions during constant operating current, i. (b) A similar curve showing operating regions during current step electrolysis. Reprinted from M. Panizza, A. Kapalka, C. Comninellis (2008) Electrochim. Acta, 53, p. 2289-2295 [35] with permission from Elsevier.](image)

When considering the mass balances over the electrochemical cell and the reservoir in a batch recirculation setup, models of temporal evolution in COD and ICE during electrolysis have been developed by Kapalka et al. [13] for both of the presented operating regimes (Table 2-3). From these models, equations for the prediction of needed electrolysis time, \( \tau \), and specific energy consumption, \( E_{sp} \), to reach a target COD removal has been derived as well (Table 2-3).
Table 2-3: Equations that describe ICE, COD, \( \tau \), and \( E_{sp} \) evolution during oxidation of organics at BDD anode.

<table>
<thead>
<tr>
<th></th>
<th>Under current limited control, ( i_{app} &lt; i_{lim} )</th>
<th>Under mass transport control, ( i_{app} &gt; i_{lim} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICE</td>
<td>( ICE = 1 )</td>
<td>( ICE = \exp\left(-\frac{Ak_m t}{V_r} + \frac{1-\alpha}{\alpha}\right) )</td>
</tr>
<tr>
<td>COD (mol O₂ m⁻³)</td>
<td>( COD(t) = COD_0 \left(1 - \frac{\alpha Ak_m}{V_r} t\right) )</td>
<td>( COD(t) = \alpha COD_0 \exp\left(-\frac{Ak_m t}{V_r} + \frac{1-\alpha}{\alpha}\right) )</td>
</tr>
<tr>
<td>( \tau ) (s)</td>
<td>( \tau_{cr} = \frac{XY_r}{\alpha Ak_m} )</td>
<td>( \tau_{cr} = -\frac{V_r}{Ak_m}\left[ \ln\left(\frac{1-X}{1-\alpha}\right) \frac{1-\alpha}{\alpha} \right] )</td>
</tr>
<tr>
<td>( E_{sp} ) (kWh kg COD⁻¹)</td>
<td>( E_{sp} = \frac{1}{3600} \frac{F}{8} \left( V_d + R_c A \alpha_{lim} \right) )</td>
<td>( E_{sp} = \frac{1}{3600} \frac{F}{8} \left( V_d + R_c A \alpha_{lim} \right) \frac{1-\alpha}{1+\ln\left(1-X/\alpha\right)} )</td>
</tr>
</tbody>
</table>


The latest trend in published literature is to apply multiple current step electrolysis in order to optimize the performance of the batch recirculation system for electrochemical organic mineralization on BDD, and thereby maintain a nearby 100% ICE as long as possible during electrolysis (Fig. 2-4b). The applied current density are in steps adjusted to always be near, but below, the instantaneous limiting current, and still in the potential region of water discharge to avoid fouling [13]. Panizza et al. has extended the models in Table 2-3 to apply for predictions on the evolution in COD, current efficiency, electrolysis time, and specific energy consumption by this modulated approach. They have shown that if the number of current steps is sufficiently high (corresponding to working in a semi-continuous control mode), the performance of the reactor are comparable with those achievable in an ideal diffusion controlled process without mass transfer limitations with an efficiency of 100% [35].

### 2.6.2 Approach to optimization of electrochemical mineralization on BDD

The energy consumption for the electrochemical mineralization of organics decreases strongly with increasing average current density (expressed as EOI, see (2.34)) and reaches a minimum value at EOI = 1. In order to work under these favorable conditions, electrolysis has to be carried out under programmed current, in which the applied current density during electrolysis is adjusted to the limiting value. The following steps have been proposed for optimal treatment of wastewater using EOTR on BDD based on the above model [13]:

a) Measure the initial COD of the wastewater

b) Estimate \( k_m \) of the electrolytic cell under fixed hydrodynamic conditions. This can be achieved using a given concentration of ferrocyanide, \( \text{Fe(CN)}_6^{4-} \) (50 mM), in a supporting electrolyte (1 M NaCl) and measuring the limiting current, \( I_{lims} \) (A) for the
anodic oxidation of Fe(CN)₆⁴⁻. The mass transfer coefficient can then be calculated using the relation:

$$k_m = \frac{I_{\text{lim}}}{FA[Fe(CN)_{6}^{4-}]}$$  \hspace{1cm} (2.42)

c) Estimate the initial limiting current density, \(i_{\text{lim}}\), by equation (2.39)
d) Calculate the time constant of the electrolytic cell, \(\tau_c\), using the relation:

$$\tau_c = \frac{V}{Ak_m}$$  \hspace{1cm} (2.43)

e) The temporal evolution of the limiting current during electrolysis is given by:

$$i_{\text{lim}} = i_{\text{lim}}^0 \exp\left(-\frac{t}{\tau_c}\right)$$  \hspace{1cm} (2.44)

Start electrolysis by application of a current density corresponding to the limiting value calculated in c)
f) Adjust the current density during electrolysis to the time dependent limiting value according to (2.44)
g) The electrolysis time, \(\tau\), needed in order to achieve the target final COD is found using the relation:

$$\tau = -\tau_c \log \frac{\text{COD}_{\text{final}}}{\text{COD}_i}$$  \hspace{1cm} (2.45)

The presented model and guidelines apply for the EOTR of organics, which by BDD anodes can lead to full mineralization, and has been shown to provide good agreement compared to experimental model solution results. However, the model has its limitation in the sense that it assumes that all organic oxidation proceeds at or very near by the anode surface, and that all side reaction are purely energy consuming and of no use with regards to organic oxidation, i.e. no positively contributing indirect homogenous chemical oxidation by generated oxidants. Real polluted water will in almost any case contain electroactive ions in some concentrations, i.e. chloride, sulphate etc. When considering micro pollutants as the target organics for the EO process, the concentrations of these electroactive ions may be significantly higher, not having the same mass transfer limitations as the organics.

In treating these waters, the obtained removal of COD can be faster than predicted by the model, if the target organics are amendable to chemical oxidation, since it may be possible to operate at a higher current density than predicted and still maintain a high ICE. Further modeling and discussion of the role of indirect oxidation by active chlorine species by different anode materials and optimization of treatment processes, where the indirect oxidation pathway
is of importance, has been treated by Scialdone et al. [34] and was briefly discussed in section 2.4.2.1 in this chapter.

The model presented in section 2.6 has not been applied for comparison in the research presented in this thesis, but a manuscript is under preparation, where the model has been put on experimental data from EO of polluted groundwater from another contaminated mega site in DK using both BDD and Watersafe anodes.

This introduction to the fundamental and theoretical principles in EO provides the foundations for the rest of the thesis, with the next chapter presenting the applied experimental approach and equipment used.
Chapter 3
Details on the experimental procedures and equipment

The research presented in this thesis was performed in collaboration with WATERSAFE DK Aps, Esbjerg, Denmark and WATERSE S.A., Chania, Greece, and materials supplied by these companies constituted the basis of the project. It primarily concerned a downsized laboratory/pilot scale electrochemical cell corresponding in materials and design to the primary full scale commercial products of the company. In order to fulfill the aims of the project, another electrochemical cell (Diacell) with another anode material was purchased from a competitive company for reasons of comparison, both for evaluation of efficiency issues and for studies of fundamental differences in mechanisms and oxidation pathways. The experimental setup for the project was designed to be able to deal with both real polluted wastewater matrices and model solutions, and an important criterion was that the chosen setup should be as comparable as possible to full scale use. For the analysis of the organic compounds and other chemical substances and process parameters evaluated in the project, several principles within analytical chemistry were applied.

In this chapter, the applied experimental setup will be explained in details, and the characteristics, dimensions etc. of the two cells will be presented and discussed. At last, the detailed settings of the most important applied analytical techniques will be provided.

3.1 Experimental setup

A batch recirculation setup was chosen as the preferred test principle, since the Watersafe cell up for testing was a flow through type cell. Additionally, temperature control was important, since the data obtained was used for evaluation of the kinetics involved in the degradation of organics. Continuously mixing of the solution was of importance as well as to eliminate concentration gradients in the solution and minimize sampling errors. The applied experimental setup is seen in Fig. 3-1.
It comprised a tubular doubled walled reservoir with a capacity from 3 up to 25 L of test solution with outlet in the bottom and inlet in the top. The outer wall was made of AISI 316 stainless steel, and the inner wall was made of AISI 304 coated with a chemically resistant Teflon® coating from Accoat (DK) in order to withstand the corrosive environment induced by the generated oxidants. Water for cooling was pumped through the wall gap from a standard electrically cooled water bath, and the temperature of the test solution was regulated manually through continuous temperature measurements in the reservoir and regulation of the cooling water flow. Polyethylene (PE) hoses with a 10 mm internal diameter normally used for sampling of polluted groundwater constituted the flow connections in the setup, since this material is very chemically resistant and shows a minimum of memory effect. The applied centrifugal pump was specially designed to be used for chemicals with a house made of plastic as well and with a capacity around 400 L h⁻¹ considering the pressure losses in the setup. The reservoir was mounted on a magnetic stirrer in order to ensure thoroughly mixing in the bulk of the solution and the pump was located at a slightly lower level in order to ensure automatic filling when the test solution was transferred to the reservoir and thus minimize contact with the (most often) toxic matrix. The cells were powered by a manually controlled 1.4 kW (20V/70A) analogue Mersan (TR) power supply with proper electrical connections minimizing loss of energy due to heat loss.

Sampling occurred from the reservoir according to the volumes needed for the specific analysis. When the matrix was suspected to show heterogeneous behavior (i.e. when treating real matrices), composite sampling applied where multiple small “increments” was taken and mixed to constitute the primary sample. However, sampling issues are not predominant, when working with well stirred and well defined volumes of aqueous solutions, and were in this work not considered a special problem of concern.

The setup was versatile with respect to the possibility of studying different subjects. In addition, it was easy to clean, which showed to be of high importance due to the nasty nature of most wastewaters and polluted solutions. The cleaning procedure comprised at least two times flushing of the whole setup with clean demineralised water after the tested water was discarded.
followed by thorough cleaning of the reservoir - and when needed between different experimental arrays, dismantlement of the cells and carefully cleaning with a 0.1 M HCl solution. The hoses were replaced when needed as well.

3.2 The electrochemical cells

3.2.1 The Ti/Pt90-Ir10 cell

The supplied Watersafe cell was an undivided flow through cell of tubular design and consisted of a rod-like titanium anode coated with 90% platinum alloyed with 10% iridium comprising the electrocatalytic surface in contact with the solution. The surrounding cathode was made of AISA 316 SS doped with 1% titanium in order to increase corrosion resistance. The dimensions of the Watersafe cell are found in Table 3-1 and photos are seen in Fig. 3-2a,b. This composition of the anode is the one preferred by Watersafe and the manufacturing procedure is patented [77]. However, the composition of the alloy coating of the anode might differ slightly and involve other metals in the full scale cells installed according to specific needs. The anode belongs to the category of primarily active anodes, and hence a somehow lower direct oxidation power was expected. Platinum has been used for a long time as electrode material, and the advantages of the material are very much due to a good conductivity and chemical stability even at high potentials and in very corrosive media [1], properties which provide the electrochemical cells with high durability and process continuity. Platinum anodes were among the first types used and studied for oxidation of organics, and it is widely reported to show a significant electrocatalytic activity towards some organics as methanol, ethanol, and ethylene-glycol [78]. Its behavior is reported in general to be similar to the DSA (see Chapter 2), where it induces mainly selective conversion of pollutants and produce small length aliphatic acids (as maleic, fumaric, and oxalic acid) stated to be stable towards further EO. The alloyed metal, iridium, is an element traditionally used in DSA, and is introduced due to its catalytic properties for primarily oxygen evolution and secondly chlorine evolution [68]. Despite the partial direct oxidation properties expected by the anode, it has the potential to be very efficient for mediated indirect EO, especially when chloride is present.

<table>
<thead>
<tr>
<th>Table 3-1: Physical dimensions of the two electrochemical cells.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ti/Pt90-Ir10 (Watersafe, tubular)</strong></td>
</tr>
<tr>
<td>Cell height:</td>
</tr>
<tr>
<td>Cell width:</td>
</tr>
<tr>
<td>Cell depth:</td>
</tr>
<tr>
<td>Anode diameter</td>
</tr>
<tr>
<td>Anode length</td>
</tr>
<tr>
<td>Electrode gap:</td>
</tr>
<tr>
<td>Anode surface</td>
</tr>
<tr>
<td>Inner cathode diameter</td>
</tr>
<tr>
<td>Active volume*</td>
</tr>
</tbody>
</table>

* Volume between the electrodes
3.2.2 The Si/BDD cell

In order to compare differences in oxidation mechanism and study fundamental differences in degradation of the recalcitrant organics studied during the project, an electrochemical cell with anode materials from the non-active category was purchased from Adamant Technologies, La Chaux-de-Fonds, Switzerland. The cell was of the Diacell type 100 mounted with two boron-doped diamond (BDD) electrodes. The design of the Diacell is patented as well [79]. The electrodes consist of a 1-3 μm thick layer of diamond coated on a p-silicon substrate through a hot-filament chemical vapour deposition (HF-CVD) procedure in which diamond growth takes place from a gas mixture at high temperature and under vacuum. Since both anode and cathode are made of the same material, shift in polarity are possible in order to clean the anodes. This was however not applied in this project, since no long term tests were conducted where deposited materials provided process problems. The dimensions of the BDD Diacell are seen in Table 3-1 and photos are seen in Fig. 3-2c,d. The dimensions and capacity of the cell are considered as comparable to the Watersafe cell. However, the different design of the two cells, with the electrodes in the Diacell installed in a plate like fashion results in different hydrodynamic conditions of the two cells.

![Fig. 3-2: Photos of the applied electrochemical cells. (a) the Watersafe cell with Ti/Pt_{90-Ir_{10}} anode. (b) the Watersafe cell, dismantled. (c) the Diacell with Si/BDD electrodes. (d) the Diacell dismantled.](image)

3.3 Analytical details

In order to monitor the bulk conditions of the test solutions, sensors were installed in the reservoir during the runs measuring the level of dissolved oxygen (DO), oxidation and reduction potential (ORP), pH, and conductivity in addition to the temperature. The project was focused on evaluating different potential applications of the EO technique and time or charge dependent organic degradation curves constituted the major part of the research. This required the use of several different analytical techniques for quantitative determination of the organics in question. Details on the settings and the equipment used are seen in Table 3-2.
Details on the experimental procedures and equipment

<table>
<thead>
<tr>
<th>Analytical technique</th>
<th>Applied equipment and settings</th>
<th>Used in:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Oxygen Demand (COD)</td>
<td>Merck COD Cell Test (4.0-40.0 mg L-1) 1.14560.0001 Spectrometer: Spectroquant NOVA-30 (Merck)</td>
<td>Chapter 5</td>
</tr>
<tr>
<td>Total Organic Carbon (TOC)</td>
<td>Multi N/C 2100S equipped with NDIR carbon dioxide detector (Analytik Jena)</td>
<td>Chapter 5</td>
</tr>
<tr>
<td>High Pressure Liquid Chromatography with</td>
<td>Perkin Elmer 250 LC pump with Hewlett Packard 1100 fluorescence detector Mobile phase: 56 v/v% acetonitrile/water</td>
<td>Chapter 5</td>
</tr>
<tr>
<td>Fluorescence detection (HPLC-FLU)</td>
<td>Column: Chomspher 5 (Chrompack)</td>
<td></td>
</tr>
<tr>
<td>Ultraviolet and Visible Spectroscopy (UV/VIS)</td>
<td>Cary 50 Conc. UV Visible Spectrometer (Varian)</td>
<td>Chapter 6 / Chapter 7</td>
</tr>
<tr>
<td>Gas Chromatography with Mass Spectroscopy</td>
<td>Varian 3800 Gas Chromatograph with Varian Saturn 2000 Mass Spectroscope Temperature: 120 C (constant, 2 min)</td>
<td>Chapter 8</td>
</tr>
<tr>
<td>detection (GC-MS/MS)</td>
<td>250 C (25 C/min, 13.00 min) Mobile phase: 56 v/v% acetonitrile/water Column: FactorFour Capillary Column VF-5ms</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30Mx0.25MM (Varian)</td>
<td></td>
</tr>
<tr>
<td>X-ray Photoelectron Spectroscopy (XPS)</td>
<td>X-ray syncrotron radiation beam from ASTRID electron storage ring at The Institute for Storage Ring Facilities at Aarhus University</td>
<td>Chapter 9</td>
</tr>
</tbody>
</table>

3.4 Examples of industrial use of Watersafe electrolysis technology

WATERSAFE has from the mid 1990’s produced and sold electrochemical cells for full scale applications. The primary market has been swimming pool treatment in the Mediterranean area, mainly Greece, where sodium chloride has been added to the pool water and active chlorine has been electrolytic generated in-situ in an inline process. The enhanced disinfection efficiency of the in-situ generated active chlorine compared to liquid sodium hypochlorite, which will be discussed further in Chapter 7, makes it possible to operate at low residual active chlorine concentrations, improving the pool environment for the users and minimizing the formation of disinfection by-products.

A challenging step just on the edge to move forward has been entering the market for wastewater treatment and COD abatement. Some full scale facilities have been installed treating both municipal and industrial wastewater with Watersafe EO as the primary oxidation technique responsible for primarily COD removal (Fig. 3-3).
Fig. 3-3: Examples of full scale installations with Watersafe electrochemical cells for COD removal. (a) two parallel cells for in-line hotel swimming pool treatment, Chania, Greece. (b) 8 parallel cells for treatment of 800 m$^3$ d$^{-1}$ of municipal wastewater by both indirect and direct oxidation, Kalives, Greece. (c) a single cell for pretreatment of hotel wastewater, Kos, Greece. (d) 6 parallel cells installed for COD abatement of olive oil wastewater (OMW), 500 m$^3$ d$^{-1}$, Spain.

The experiences with large scale installations are still in a development phase and process optimization is complicated, but the funding for construction of further treatment plants based on the electrochemical technology are currently in the pipeline. The applications are many, and three major advantages compared to biological treatment are limited space requirements, control of unpleasant odor, and ease and stability of operation. However, the conditions needs to be right and special requirements may need to be present for electrolysis to be chosen as treatment method. In a country as Denmark, biological treatment of municipal and most wastewaters is widespread used and the paramount dogma, when treatment strategy is decided - and as prices are, the cheapest way to treat large volumes of water if the organics are compatible to biological conversion. Here, industrial wastewater or other types of polluted water with more specialized organic treatment issues (toxic, bio-refractory etc.) will be a better market to explore, a discussion in line with the use of the other AOPs as discussed in the introduction. Other possibilities are as either pre-treatment or tertiary polishing before or after a biological treatment step. This discussion of possible applications of EO in a market as the Danish will be continued in the following chapters.
Chapter 4
Literature study: The versatility of EO degradation

Especially since the millennium, a vast amount of papers have dealt with EO and its potential efficiency and applicability for the treatment of many types of primarily industrial effluents of different kinds and as a technique for the abatement of many different aqueous organic pollutants considered of concern for the environment and human beings. Comprehensive reviews on EO treatment of wastewater are published by Martinez-Huitle and Ferro [80] and on decontamination of dye containing wastewater by Martinez-Huitle and Brillas [81]. The intention of this chapter is not to extend beyond these reviews, but to present some selected studies of treatment of both real wastewater and specific compounds in order to demonstrate the versatility of the EO process and its many applications.

4.1 Examples of EO for wastewater treatment

4.1.1 Olive oil mill wastewater

Olive mill wastewater (OMW) constitute a serious environmental problem in the Mediterranean region, due to features as seasonal and localized production, low flow rates and high organic load up to 220 g L⁻¹ of COD mainly consisting of phenols, lipids, sugars, and tannins [82]. Its treatment by electrolysis has been the topic of several papers applying EO in different configurations concerning cell designs and active (DSA, Ti/Pt) versus non-active anodes (BDD) [53,82-88]. The most recent paper by Papastefanakis et al. [83] studied the removal of COD, colour etc. using a DSA type Ti/RuO₂ anode, and achieved acceptable removals of phenols (84%), colour (86%), COD (52%), and TOC (38%) after oxidation at 28 Ah L⁻¹ (50 mA cm⁻²) and addition of NaCl. Both partial and full mineralization occurred, but important to mention is that ecotoxicity was eliminated as well despite the residual COD. The treatment using DSAs was very much dependent on indirect oxidation routes, and the overall performance could be dramatically affected by the presence of various salts. Using almost one third of the current density (15 mA cm⁻²), the passing of the same amount of charge (28 Ah L⁻¹) through the OMW resulted in an increase of COD removal from less than 7% in a salt-free test volume to 54 % after addition of 20 mM NaCl. Watersafe S.A. has cooperated with the Technical University of Crete, Greece, for development of the Watersafe electrolysis technique as a solution for OMW treatment.

4.1.2 Landfill leachate

Landfill leachate is another type of polluted water, which treatment by EO has been studied in several papers [49,89-93]. Leachate is produced when rain water percolate through dumps of municipal waste disposed at landfills, and is characterized by a very complex composition containing a large number of compounds, many of them recalcitrant to biological conversion [49]. In leachate, in particular the ratio between biological and chemical oxygen demand
(BOD/COD) and the concentration of ammonium, and heavy metals are parameters of interest. Heavy metals may be reduced at the cathode in an undivided cell or removed by electrocoagulation, but COD and ammonium are the parameters mainly targeted by EO. One of the first series of papers on this subject was published by Chiang et al. [92,93] where complete removal of 2.6 g L$^{-1}$ NH$_4^+$ and 92% reduction of COD was obtained after 4 h by addition of 0.75% NaCl and using tertiary Sn-Pd-Ru DSA. Recently, a pilot scale study using 1.05 m$^2$ BDD showed that efficient treatment by this anode material was possible too, and NH$_4^+$ removal was due to indirect chlorine oxidation and COD removal was mainly due to surface or near-surface EOTR [49]. The general assessment was that EO is a very suitable technique for treatment of the bio refractory part of leachate compared to other AOPs [49], especially in combinations with pre-treatment methods as membrane filtration in order to decrease volumes and concentrate pollutants.

4.1.3 Dyehouse effluents

Treatment of dyehouse effluents or other wastewaters containing synthetic organic dyes is another area, which has received lots of attention using EO [54,81,94-99]. Discharge of these coloured compounds in the environment causes considerable non-aesthetic pollution and serious health risk factors [81]. Both the EOTR by BDD, indirect active chlorine oxidation and the electro-Fenton processes have proved to be efficient routes for bleaching and degradation of dyes. Chatzisymeon et al. [95] has published a study on treatment of dyehouse effluent by use of a Watersafe type anode and a slightly different cell design, with the only difference that small amount of tantalum was added to the Pt-Ir coating in order to increase the durability. They found that EO with the applied anode was capable of oxidizing the chromophore groups of dyes achieving decolorization of synthetic wastewater already after 10-15 min with low energy consumption. However, energy consumption increased significantly treating the real dyehouse effluent. The extent of COD removal varied between 30-90 % after 180 min, depending on the operating conditions, but the treatment performance was generally found to be improved by increased salinity, current intensity and decreased pH. An alarming observation was that ecotoxicity of the dye effluent increased in the final samples from a low initial level, despite the color and COD removal. A proposed and feasible explanation was the formation of persistent toxic by-products [95].

The importance of indirect chlorine oxidation for bleaching of dyes has also been a topic in this project, and the results obtained are found in paper III. The subject is treated from another angle, since the dye in focus, p-nitrosodimethylaniline (RNO), is used as spin trap for detection of radicals and thus studied from this perspective, but the discussion of EO of dyes and the efficiency of color removal using different types of anodes are continued more thoroughly in Chapter 6.
4.2 Examples of EO for degradation of persistent organic pollutants (POPs)

Despite the POPs treated in the papers attached to this thesis, organophosphoric pesticides as parathion, methylparathion, and malathion (Paper I) and polycyclic aromatic hydrocarbons (PAHs) (Paper II and V), numerous other organics has been the subject of study by EO. Some selected studies are presented here.

4.2.1 Chloromethylphenoxy herbicides

The presence of herbicides in natural waters comes from their widespread use for agricultural and non-agricultural purposes generating continuously rinsate, waste product, and contaminated soil. The degradation of 4-chloro-2-methylphenoxyacetic acid and two other related herbicides was studied by Boye et al. [50] in an inert 1 M HClO4 electrolyte using BDD. In short terms of this comprehensive study, they showed that all herbicides were degraded and totally mineralized following first order kinetics in the batch recirculation system under mass transfer control - as predicted by the theoretical model (section 2.3). The intermediate aromatic products and generated carboxylic acids were identified and a general pathway for the electrochemical mineralization of herbicides was proposed.

4.2.2 Acetaminophen (Paracetamol)

Pharmaceutical compounds are increasingly often found as contaminants in sewage effluents, surface water, and groundwater [100]. An example is acetaminophen (N-(p-hydroxyphenyl)-acetamid), which has been found in sewage at concentrations up to 6 μg L⁻¹ and is in this context considered as a micro-pollutant. The risk of discharge of pharmaceuticals into nature mainly concerns development of resistant strains of microorganisms, but other unknown implications may develop in the future. EO of acetaminophen was studied by Waterston et al. [100] using different anode materials, and non-active types of anodes (BDD and Ti/SnO₂) led to full mineralization, whereas Ti/IrO₂ generated benzoquinone as the exclusive product except at very long electrolysis times (again according to the theory suggesting different classes of anodes). Current efficiencies for mineralization up to 26% were achieved without optimization of the cell design.

4.2.3 2,4,6-Trinitrotoluene (TNT)

A problematic pollutant mostly related to army depots and artillery sites in northern America, is the family of nitro-aromatic compounds such as trinitrotoluene (2,4,6-TNT) and dinitrotoluene (2,4-DNT, 2,6-DNT), due to its large manufacture and use as explosives [101]. The electrochemical aqueous removal of this pollutant has been studied by Rodgers and Bunce [102], not through oxidation, but by direct reduction at a Ni plate cathode in a divided cell. The reactions are a four electron reduction to phenylhydroxylamine at pH > 4, and a six electron reduction to aniline at lower pH, involving both electrochemical and chemical steps. The experiments gave high chemical yield of the products, and the treatment process was further extended by re-oxidation of the reduced products at the Ti/IrO₂ anode to induce oligomerization of the organic products and ease the removal of the products. Electro-Fenton has also with
success been showed to remove TNT from solution through mineralization in the cathodic chamber in a combined direct reduction and indirect Fenton oxidation process [103].

4.2.4 Perchloroethylene (PCE)

A very common family of pollutants is chlorinated compounds as perchloroethylene, trichloroethylene etc. that is highly relevant with regards to the Danish environment too. Chlorinated solvents constitute the main source for contaminated sites and groundwater pollution in Denmark [104]. The EO of chlorinated solvents in aqueous solution has so far been little explored with a few papers focusing mainly on the cathodic reduction reaction, where the conversion of the organics occur in the potential region near hydrogen evolution reaction decreasing current efficiency [105]. However, a recent paper by Sáez et al. [106] has compared cathodic, anodic, and combined degradation of PCE in water and studied the influence of several operating parameters. They found that an undivided configuration provided the best results under the experimental conditions investigated. The main degradation of PCE still occurred at the cathode, but the contributing anodic oxidation made the final level of intermediate products much lower than in the case of the pure cathodic reduction. These results have just currently been supported by Scialdone et al. [107] using BDD as anode and silver as cathode for abatement of PCE and DCE, and confirmed the superior performance of the undivided cell.

The number of published studies on applied use of EO for degradation of troublesome organic pollutants is as briefly demonstrated comprehensive and still growing. Most of the papers demonstrate that the possibilities are promising and larger scale use in the industry should be achievable, when the technology has matured. The coming chapters in this thesis will present the most important results and implications found in our research of using EO in the area of environmental engineering, introduced with case story studies on real polluted water matrices followed by detailed model solution studies investigating fundamental coherences and influences of some of the many parameters involved.
Chapter 5
EO for process water treatment and possible soil/sediment remediation

This chapter presents the background and most important results of two experimental arrays, which have dealt with treatment of two different kind of process water; pesticide polluted groundwater and PAH polluted sea water. Both studies are related to specific societal interesting environmental problems; remediation of contaminated sites and removal and remediation of contaminated sediment. The first study is a case study with focus on COD and the specific contaminant removal performance, whereas the second study after initial trials with the real matrix digs deeper into understanding the influence of different electrolytes and operating parameters. The intention of this chapter is to demonstrate the performance of EO on two prevailing environmental issues and reflect on the implications of the most important discoveries of these studies.

5.1 Pesticide polluted groundwater case story

The main study is published and enclosed as Paper I [65], but unpublished data will be presented as well. The background for this study will be outlined in addition to the most important results, and the application of EO in this area of environmental engineering will be discussed.

5.1.1 Background

In the 1950’ties, large amount of chemical waste, sludge, and wastewater was legally dumped in the sand dunes near Groyne 42 (Høfde 42) on the western Danish shore to the North Sea (Fig. 5-1a). The waste came primarily from a large manufacture of chemical pesticides as methyl-parathion and parathion, but even governmental agencies used the pit for disposal of pest controlling chemicals during this period. The disposal ended in 1962, and due to increasing public awareness and impact, remedial actions was finally taken in 1981. Around 1200 tons of chemical waste was removed by excavation, but ca. 120 tons still remained buried in the pit under the ground water table. Seepage from the remaining waste and further contamination of the surrounding areas were detected and measured during the 80’ties, and in 1989 drains were installed as a temporary solution for minimization of the damages. Finally, in 2006 the hot spot area was immobilized by construction of 14-15 m height sheet piles surrounding the waste pit (Fig. 5-1b), while technological development projects were initiated for screening in-situ remediation possibilities.
In case of leakage, the water table was lowered by drains within the piled area in order to ensure an inwards flow gradient. The drainage water is currently treated by adsorption on granulated active carbon (GAC), but the efficiency towards naturally occurring degradation products is poor. Active carbon adsorption is due to its easy implementation, versatility, and other advantages often the preferred choice of remediation companies, when facing on-site treatment prior to discharge into recipient, but as it is often stated it is merely transfer of contaminants from one media to another, and degradation is preferred. The soil is in the hot spot area mainly sand, and thus the content of natural organic matter (NOM) is low. Due to the age of the pollution, a range of naturally occurring degradation products has been produced by biological conversion from the parent pesticides in the more slightly contaminated periphery of the hot spot. The objective with this study was to investigate the possibilities to treat this very complex, toxic and recalcitrant polluted groundwater for substituting the GAC adsorption with an EO unit operation.

5.1.2 Results and implications

COD was used as overall parameter for evaluation of the oxidation performance. The Watersafe cell with the Ti/Pt<sub>90</sub>-Ir<sub>10</sub> anode was used in the batch recirculation experiments, which showed that COD was readily removed by EO following first order kinetics. Due to the location of the pit next to the sea, the natural salinity of the drainage water was quite high, 0.7 w/w%, and it was expected that indirect active chlorine oxidation was an important pathway for the COD removal. Galvanostatically, addition of sodium chloride up to 2.0 w/w% did slightly enhance the removal rate, while a further increase up to 4.0 w/w% showed a reverse effect and a significant deviation from the first order kinetics. A proposed explanation was that the increased electrolyte concentration and “cloud” of negatively charged ions in the diffusive part of the double layer inhibit the transport of oxidation products from the chloride electrolysis out in the bulk phase amendable for oxidation of organics. Operated potentiostatically, the increased sodium chloride concentrations resulted in increased current densities and hence increased COD removal rates, and a linear correlation was demonstrated between the first order rate constant and the resulting current density (Fig. 5-2a).
The adverse effect of COD removal induced by chloride disappeared, since the overall rate of reactions (current density) was allowed to increase resulting in a higher active chlorine concentration and hence higher COD removal. This showed the importance of the indirect oxidation pathway. When the evolution of COD was evaluated against the specific amount of charge passed through the solution at the different current densities (Fig. 5-2b), the data were almost convergent, typically seen for indirectly oxidation controlled COD removal processes. However, the efficiency at 4.0 w/w% was slightly decreased, probably due to buildup of active chlorine faster than removal by organic oxidation.

Analysis of the specific organophosphoric pesticides showed that both the parent compounds, parathion, methyl-parathion, and malathion, and all of the degradation products were degraded during the EO process. Only a single tri ester, O,O,O-triethylphosphoric acid (or triethyl phosphate (TEP)) showed a recalcitrant behavior and was found in residual concentrations. This compound was resistant towards oxidation both by the chemically bonded oxygen, MOx+1, at the surface of the active classified Watersafe anode and the active chlorine species. Model solution experiments were performed with this single component in order to use this hardly degradable compound as reference for a comparison between the performance of the Ti/Pt90-Ir10 and the Si/BDD anodes.
In 0.050 M NaCl and TEP in elevated concentration, the superior oxidation power of the non-active BDD anode was evident due to the actions of the physisorbed hydroxyl radicals (Fig. 5-3). This was confirmed through TOC analysis, which showed that full mineralization occurred through BDD electrolysis of TEP and that TOC remained constant at Ti/Pt$_{90}$-Ir$_{10}$ (Fig. 5-4).

Related to the specific case, TEP does not compose a significant risk to the environment in the residual concentration level found in the natural drainage water after electrolysis. Substitution of the GAC adsorption unit is definitely a possibility, when the process is optimized in a continuous operation mode including a neutralization/quenching step of residual oxidant. Further studies of the risk of by-products formation should be performed prior to that implementation, but the GC spectra recorded during analysis revealed no unidentified peaks from the samples, indicating that at least the production of non-polar by-products may be limited.
EO for process water treatment and possible soil/sediment remediation

The main bulk part of the contamination is located in-situ in the pit, and different remediation techniques are considered and evaluated for its remediation. In-situ chemical oxidation (ISCO) using Fenton’s chemistry or activated persulphate is in play as a strong bet for an efficient technique. However, EO may be an efficient innovative approach to address the polluted soil by electrochemical generation of a strong oxidant from the ions present in the hot spot water concurrent with organic oxidation by EOTR and reinfiltration back in-situ of the oxidized solution utilizing the chemical oxidation potential for remediation of the polluted soil matrix. Due to the high salinity of the groundwater in the pit, active chlorine species will be the main oxidants in such a solution. Initial steps was taken to investigate this innovative approach, and it was found that half and half mixing of the polluted drainage water and electrochemically generated oxidant removed all of the organophosphoric compounds present except TEP. Similar results were obtained using chemical chlorination in comparable active chlorine concentration, but with a higher level of residual TEP.

This electrochemical reinfiltration twist to traditional ISCO is considered a very interesting approach to use EO within soil and groundwater remediation. In the Høfde 42 case, the high chloride concentration made the Ti/Pt-Ir anode suitable due to the good properties for chlorine evolution by this material. At different sites where other ions as sulphate, phosphate, or (hydrogen)carbonate are present in high concentrations, BDD is a very interesting possibility for the on-site generation of strong oxidants. In addition, chlorine is infamous for the risk of by-product formation (is discussed further in Chapter 8) and this behavior needs to be studied in more detail before this oxidant solution can be recommended.

5.2 Runoff water from a sediment removal process

The details of this study is published and enclosed in the supplements to this thesis as paper II [109]. The reason to enter this issue is presented in a background section followed by the most important results and a discussion of the implications they provide.

5.2.1 Background

Sediments act as a sink for hydrophobic, recalcitrant and hazardous compounds, and organic pollution of sediment is a worldwide problem. The pollution may be complex, but the most important organic compounds as stated in literature are polycyclic aromatic hydrocarbons (PAHs) and organo-tin compounds as tributyl tin (TBT), di-, and mono-buthyl tin [110]. As long as resting on the seabed, contact with humans and aquatic organisms (except organisms living in the sediment) are not an alarming problem due to the often low solubility of these compounds. However, when harbours are dredged in order to maintain sail channels, the contaminants hidden in the dark are mixed and suspended with the sea water.
In Denmark, the most frequently used method to remove slightly contaminated sediment is to pump it ashore to artificial inland lakes or upland sites just next to the shore, in a water consuming process using five parts water per one part sediment in order to make the media pumpable (Fig. 5-5). The water is then discharged back into the sea, but has now changed status to process water and is subjected to strict discharge limits (PAH: 0.010 μg L⁻¹). Traditionally, sand filtration has been the preferred solution, since removal of the suspended part of the pollutants adsorbed to sediment particles has been sufficient. But now, increasingly strict demands to the removal have made it necessary to come up with new approaches to attach the pollutants in the water phase. The task then was to remove already low concentrations of organic PAHs to even lower concentrations at an acceptable expense, a task often faced when working with treatment of micro-pollutants, where mass transfer limitations are hard to avoid due to the small concentrations.

5.2.2 Results and implications

Due to the high salinity and hence high conductivity typically found in the sea water media, it was straightforward to investigate the possible application of EO as a solution. The initial test runs using the Watersafe cell showed that the compounds in the main family of pollutants present, the PAHs, were all degraded after electrolysis using 13.2 kWh m⁻³ of energy (Fig. 5-6).

In another treatment approach, intermixing of electrochemically generated oxidant and the harbour water was again used to investigate the possibility of passing only a minor part of the discharge stream through the electrochemical cell and utilizing the remaining residual oxidant to degrade the pollutants in the rest of the stream through indirect oxidation in an electro-chlorination like process. An intermixing ratio of 1 to 3 (oxidant to sea water) removed all PAHs in the final sample using ca. 19 kWh m⁻³ treated sea water (Fig. 5-6), but both processes are subject to further optimization. The organo-tin compounds were not found in the sea water sample obtained from Odense Harbour and was thus not evaluated.
EO for process water treatment and possible soil/sediment remediation

Fig. 5-6: Initial and final concentrations of PAHs compounds from tests with runoff process water from Odense Harbour. Two different treatment approaches applied; direct passing through the cell and an indirect electrochlorination approach. Published in paper II [109], reprinted with permission from IWA publishing.

These results induced a much more detailed investigation of the electrochemical degradation of PAHs in aqueous solution. PAHs are an important family of pollutants considered generally as mutagenic, teratogenic, and carcinogenic due to their benzene analogue structures having two or more fused rings in diverse alignments [111]. Three PAHs were selected for model studies; naphthalene - the most soluble (two rings) and anticipated most reactive specie; fluoranthene and pyrene – since they were among the ones present in the harbour sample, both structured of 4 rings, but in different alignment. The solubility of the PAHs in the model solutions was artificially increased using small volumes of acetonitril as cosolvent to the demineralized water.

The experiments showed that all three PAHs could be oxidized through a direct oxygen transfer reaction when treated in a 0.10 M Na₂SO₄ electrolyte using the Watersafe anode. A notably difference was observed on the reaction kinetics, where naphthalene removal followed second order kinetics whereas fluoranthene and pyrene showed the common first order behavior. The reason is proposed to be involvement of a dimerization process in the initial steps of naphthalene degradation – a mechanisms known to be part of the PAH formation process in combustion reactions, but the explanation is still not evident. Due to the use of fluorescence as detector, it was the initial oxidation step of the PAH and the subsequent loss of the specific emission wavelength, which was measured during the electrolysis. In order to be certain that the loss of fluorescence was due to actual degradation, GC analysis was used for confirmation in one of the runs.

The presence of electroactive chloride ions in the electrolyte significantly enhanced the PAH oxidation rates due to indirect oxidation pathways. Naphthalene was influenced the most, probably due to its higher solubility compared to the other PAHs and thus higher affinity to participate in the indirect homogenous chemical oxidation reaction. An important discovery was that shifts of applied current density showed a mixed behavior, not as straightforward as with the pesticides discussed in section 5.1. It was studied in a 0.14 M NaCl electrolytes and when the current density was decreased step-wise from 200 mA cm⁻², a local minimum value of the
rate constant was found at 50 mA cm\textsuperscript{-2}, with a slightly higher reaction rate observed at the lower 25 mA cm\textsuperscript{-2}. The trend was proposed to be caused by a shift in main oxidation routes, where the indirect chlorine oxidation at the low applied cell potentials becomes less important as the chloride electrolysis is challenged more by the EOTR by MO\textsubscript{x+1}.

This observation indeed demonstrated the optimization challenges in EO. A fast kinetics is definitely important, since the rate of oxidation determines the needed retention times in reaction vessels (reservoir in a semi-batch recirculation process) and hence the dimensions of these vessels according to fit the needed capacity. Faster kinetics means smaller dimensions and cheaper vessels. However, the efficiency is another just as important parameter as energy waste equals higher costs. As presented in section 2.5, COD measurements are the traditional parameter in play when calculating the efficiency of the electrochemical performance. However, when considering micro pollutants with (in relation to wastewater) very low organic concentrations of below 0.5-2 mg L\textsuperscript{-1} in total, these procedures are not convenient (COD analysis typically has a detection limit of 4 mg L\textsuperscript{-1}). We have proposed a quite simple relative measure, the current efficiency constant, $k_q$, as a measure in the evaluation of which settings provided the best efficiency with respect to the individual organic. The constant is defined analogous to the rate constant, but based on concentrations evaluated against the specific charge passed through the solution.

$$\frac{d[\text{PAH}]}{dQ} = -k_q \cdot [\text{PAH}]$$  \hspace{1cm} (5.1)

When the current efficiency constants of the naphthalene oxidation curves were determined, the reverse trend compared to the kinetics was evident, with much faster oxidation per ampere spent in the process at the lower applied current densities (Fig. 5-7). At the higher currents, much more energy is wasted on side reactions as primarily oxygen evolution and probably accumulation of residual chlorine. From a plant design perspective, this is of course very important, but the actual removal rate at 25 mA cm\textsuperscript{-2} was still less than half of the one obtained at 200 mA cm\textsuperscript{-2}. This low rate reduces the capacity of a given plant, which might be more expensive than cost of the lower energy efficiency.
5.3 Summary of main points and perspectives

EO using the Watersafe cell with Ti/Pt$_{90}$-Ir$_{10}$ anode has in two cases of treatment of real saline polluted water matrices showed to be capable of degradation of recalcitrant and toxic organics primarily organo-phosphoric pesticides and PAHs. The first study demonstrated a potential application of EO in on-site treatment of polluted groundwater from the most toxic contaminated site in Denmark as a substitution to a present GAC adsorption. The indirect oxidation pathway through active chlorine species was important for the abatement of the present organic content, and utilizing this chemical oxidation by the residual oxidants was suggested as a possible pathway for soil remediation in an ISCO like on-site reinfiltration approach.

The second study showed that EO is an applicable technique for removal of PAHs from slightly polluted sea water, also with the mediated chlorine oxidation being an important pathway for organic removal. However, both studies revealed that increased knowledge is needed in order to elucidate the extent of by-product formation in these saline waters before final recommendations can be given.
In both cases, the majority of the pollution is adsorbed to the solid matrix. At a contaminated site, the source area is easier to define than in the case of polluted marine sediments, but in both cases the soil matrices are the ones actual in focus from a remedial perspective. The key point in ISCO in order to optimize the possibilities of a successful outcome is the delivery of the oxidant and to provide good contact between the pollutant and the oxidant. On-site soil mixing combined with chemical oxidation is a developed method used currently in the field. A proposal for an on-site soil remediation procedure is to suspend the soil on-site in a vessel containing an electroactive electrolyte and use EO for continuous production and regeneration of oxidant and oxidation of the water phase organics. Systems for soil washing are already on the market for removal of metals or using surfactants for extraction of pollutants. Such a system could be combined with electrochemical regeneration of oxidants from a suitable electrolyte solution (formation water with added salts) in a sort of Dig’n’Wash process. This approach is considered interesting in order to decrease the expenses and transport of chemical oxidants.

The next chapter will deal with experimental studies on an organic dye model compound used for evaluating both operating performance and fundamental oxidation pathways.
Chapter 6
Electrochemical bleaching of RNO: Mechanisms in color removal

The formation of hydroxyl radicals, chemisorbed active oxygen, chlorine, ozone, hydrogen peroxide or other more or less strong oxidants on different anode materials have been an important subject in the development of EO for wastewater treatment. The search for hydroxyl radicals and demonstration of their significance for obtaining full mineralization has been treated in many electrochemical papers [14,16,24,57,112], aiming at optimizing the operative parameters of the EO process. However, due to their very reactive and aggressive nature, the lifetime of hydroxyl radicals are in most waters measured in nano seconds with second order rate constants \( k > 10^9 \text{ M}^{-1} \text{s}^{-1} \) for reactions with many organics [5,113] and direct detection are extremely challenging. For this reason, indirect techniques usually applies, where an organic compound is used as “spin trap”, trapping the hydroxyl radical in an addition reaction forming a more stable organic radical, the “spin adduct”.

\[
\text{spin trap} + \text{OH}^* \rightarrow \text{spin adduct}
\]  

(6.1)

In its reactions with organic molecules, hydroxyl radicals behave as an electrophile and readily add to unsaturated bonds [113]. A common spin trap compound is 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), which hydroxyl radical spin adduct is detected by electron spin resonans (ESR) spectroscopy [57]. Another spin trap compound for hydroxyl radical detection is the dye p-nitrosodimethylaniline (RNO). The molecular structure with multiple conjugated double bonds gives a strong adsorption band at 440 nm in the visible range of the electromagnetic spectrum, which is lost when it reacts with hydroxyl radicals producing the spin adduct. However, discrepancies were found in the literature, where some claimed RNO to be very selective to hydroxyl radical oxidation [114-116], whereas other observed bleaching by other chemical oxidants and using active anodes not producing hydroxyl radicals [112,117,118].

In this research, RNO bleaching was put through a comprehensive experimental investigation in order to clarify these questions, and demonstrate differences in EOTR and indirect chlorine oxidation pathways on the Watersafe and BDD anode. In addition, due to the ease of analysis using UV/VIS spectroscopy, the compound was studied for its ability as a model compound used in optimization of the EO performance and in comparison with other AOPs. Finally, RNO was used to gain experience in using EO for bleaching of dyes, a treatment process relevant for many industrial effluents as demonstrated in Chapter 4. The full study of EO of RNO has been submitted for publication and is enclosed as paper III. The comparison of the performance to others AOPs is included in a published co-authored paper studying photocatalytic bleaching of RNO and is enclosed as paper IV.
6.1 Bleaching of an organic compound in different electrolytes

The Watersafe anode was once again the primary one used. Bleaching due to surface oxidation was studied in 0.050 M Na$_2$SO$_4$ electrolyte, where 70% colour removal was obtained after 4 h of electrolysis at 32 mA cm$^{-2}$ (Fig. 6-1a). Since the Ti/Pt$_{90}$-Ir$_{10}$ anode is considered as an active anode, it is not believed to produce hydroxyl radicals in significant amounts, which indicated that oxidation of RNO was possible through oxidation by chemically bonded active oxygen, MO$_x$+1. A possible hydroxyl radical production at the Watersafe anode was further investigated (as will be presented in the next section), but was not found in significant amounts, thus confirming that bleaching of RNO could occur through other means than hydroxyl radicals. In the sulphate electrolyte, the disappearance of the absorption peak occurred steadily with no emergence of intermediate peaks (Fig. 6-1b).

![Fig. 6-1: (a) Bleaching of RNO in different electrolytes. (b) UV/VIS spectra recorded during bleaching in 0.050 M Na$_2$SO$_4$, and (c) similar spectra obtained during bleaching in 0.050 M NaCl. Submitted for publication in paper III [119].](image)

The bleaching was dramatically increased in 0.050 M NaCl electrolyte at the same applied current (equal overall rate of reaction), where 70% reduction was obtained in less than 6 min of electrolysis. This had to be ascribed to indirect oxidation by the generated active chlorine species, which through the homogenous chemical bulk oxidation not were limited by the transfer of RNO to the anode surface. In addition, the possibility exist that adsorbed oxychloro species on the surface (as proposed by Bonfatti et al. [31] and explained in section 2.4) were more effective for RNO oxidation than the chemisorbed active oxygen. The bleaching kinetics were in both cases first order (explained in detail in Paper III), with the electro-chlorination process being a pseudo first order process. This was due to an excessive build up of active chlorine as showed by the emergence of the peak at 290 nm, identified as hypochlorous acid/hypochlorite absorption (Fig. 6-1c). However, the very rapid initial bleaching of 38% observed within the first minute is not that easy explained, since electrolysis time has not yet been sufficient to establish a stable concentration of aqueous active chlorine that either has to go the way through EO of chloride and hydrolysis of molecular chlorine, or the chlorine radical...
may react directly with the chemisorbed oxygen forming adsorbed hypochlorite. A possible explanation of the rapid initial bleaching can involve oxidation through more or less stable hydrated chlorine radicals, electrochemically generated as intermediaries in the molecular chlorine formation, which might be capable of travelling into the bulk and hence escape the limitations of the surface mass transfer. The mechanisms in electro-chlorination of RNO are further discussed in the next section, where the Watersafe anode was compared to the performance of BDD.

Generally considering RNO as a dye, efficient bleaching by the Watersafe anode required the presence of suitable amounts of chloride in the electrolyte, where the treatment can be operated as an electro-chlorination process. However, in this practical application as well, any by-product formation should be clarified prior to industrial implementation, and the extent of total mineralization was not considered due to too low organic load in the treated solutions. Significant by-product formation during electro-chlorination of dyes has been showed in literature [95].

6.2 Oxidation mechanisms at Ti/Pt\textsubscript{90-Ir\textsubscript{10}} versus BDD

Tertiary buthanol (t-BuOH) is due to rapid reaction with hydroxyl radicals a widely applied scavenging agent used for removal of this oxidizing specie. In this study it was added in excess to the RNO solution in experiments aimed at confirming that no significant production of hydroxyl radicals occurred on the Watersafe anode, and that the bleaching observed was due to chemically bonded active oxygen. Similar experiments was conducted with the Diacell in order to observe if the expected pattern would appear using the BDD anode, with the hydroxyl radical induced bleaching being inhibited in the presence of the scavenger.

Clear differences were discovered using the two cells. The experiments showed that in 0.050 M Na\textsubscript{2}SO\textsubscript{4} using the Watersafe anode, the bleaching was unaffected by the presence of the scavenger, which did not compete with RNO for the available oxidation sites (Fig. 6-2a). At the BDD anode, the bleaching rates without scavenger were in general faster than using the Watersafe anode, but the presence of t-BuOH did not completely hinder the bleaching and some background bleaching was observed (Fig. 6-2b). At least two explanations to this behavior can be proposed; either does some direct electron transfer from RNO to BDD occur even in the applied potential range above water discharge, or some of the oxidation sites on the BDD can be comprised of more strongly bonded active oxygen not scavenged by the presence of t-BuOH, but still capable of bleaching as on the Ti/Pt\textsubscript{90-Ir\textsubscript{10}}. The active versus non-active classification of anodes are limiting cases of anode behavior, and in practice the oxidation pathways has by other authors [1] been stated to be of more mixed behavior. However, BDD is by most authors considered as the currently limiting case of a non-active anode [1], which favours the first suggestion and indicate that direct electrolysis of RNO might be the explanation.
Fig. 6-2: Bleaching of RNO by (a) the Watersafe cell with Ti/Pt90-Ir10 anode and (b) the Diacell with Si/BDD anode. Experiments are conducted with and without the presence of hydroxyl radical scavenger (t-BuOH). Submitted for publication in paper III [119].

The same experimental comparison was conducted using an electro-chlorination process, which revealed some very interesting results. Using the Watersafe anode, the bleaching was completely unaffected by the presence of t-BuOH (Fig. 6-2a), whereas on the BDD the bleaching due to electro-chlorination was completely blocked and downgraded to the former observed background level (Fig. 6-2b). These results clearly demonstrated that chloride electrolysis on the Ti/Pt90-Ir10 anode is genuine direct electrochemical electron transfer between the chloride ion and the anode surface, whereas on BDD the oxidation of chloride is of chemical nature through reaction between hydroxyl radicals and chloride.

These deductions are in line with the theory presented in section 2.3 on oxidation pathways and mechanisms in EO and electro-chlorination. The implications of the results are that care needs to taken in the choice of which anode material to select to a specific application. The unilateral oxidation pathway of the BDD might not always be preferable, since the presence of more or less harmless organics may serve as scavengers in i.e. a process with disinfection as the main objective or where an electro-chlorination process is wanted. In such a case, the selective chloride electrolysis of an active type anode as the Watersafe or dedicated DSAs will be a better choice.

6.3 RNO as model compound for optimization of AOP performance

Heterogeneous photocatalytic oxidation is another AOP that has been widely investigated for use in water treatment for degradation of toxic and recalcitrant organics [120,121]. A semiconducting material, most frequently titanium dioxide, is used as catalyst for the production of an electron/hole pair in the bulk of the material by irradiation of high frequency UV light. The general accepted theory is that the electron/hole pair diffuse to the surface of the catalyst particle, where the hole at the solid-water interface directly oxidize adsorbed organics or react with surface hydroxyl groups or water molecules to produce hydroxyl radicals.
amendable to further organic oxidation. In the study published in paper IV, the performances of different photo reactors were evaluated using RNO as model compound. RNO has not proved to be the perfect selective hydroxyl radical probe compound, but as a model compound used in evaluation of the overall oxidation performance it is very applicable taking account of several oxidizing species, due to properties such as low volatility, low toxicity, acceptable water solubility, and especially the ease of analysis using UV/VIS spectrometry with a linear calibration curve at least in the 0-20 mg L⁻¹ range.

An important challenge to overcome in photocatalytic water treatment is to reach high degradation rates in a process where the catalyst is immobilized in some kind of photo reactor thus avoiding the need of a separation step. Typically such reactors suffers from non-uniform irradiation and hence activation of the surface [122,123].

![Fig. 6-3: Evolution in the removal of RNO by three advanced oxidation processes (AOPs); Conductive-diamond electrochemical oxidation (CDEO), UV activated persulphate, and heterogeneous photocatalysis. Each AOP is represented by two sets of operating parameters. Published in paper IV [124], reprinted with permission from Elsevier.](image)

The results obtained in the photocatalytic bleaching were compared to bleaching results using the BDD cell (in this study termed conductive-diamond electrochemical oxidation (CDEO)). In addition, results obtained in another study using UV activated persulphate oxidation were included. The rates of the bleaching using the different AOPs were dependent on several operating parameters selective to each process, but in general the EO process was the most efficient technique with the lowest energy consumption for achieving a 90% colour removal (Fig. 6-3 and Table 6-1) using the electro-chlorination process.
Table 6-1: Figures of merit for the AOPs regarding reaction rates of first order bleaching and energy consumption.

<table>
<thead>
<tr>
<th>Energy source</th>
<th>Energy consumption (90% bleaching) / kWh m⁻³</th>
<th>k / s⁻¹</th>
<th>t₁/₂ / min</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDEO (0.05 M Na₂SO₄) Power supply (10.6W)</td>
<td>7.2</td>
<td>3.1·10⁻⁴</td>
<td>36.9</td>
</tr>
<tr>
<td>CDEO (0.05 M NaCl) Power supply (12.0W)</td>
<td>0.7</td>
<td>3.6·10⁻³</td>
<td>3.2</td>
</tr>
<tr>
<td>UV/S₂O₈²⁻ (RNO:S₂O₈²⁻ = 1:2) UV lamp (400W)</td>
<td>19.8</td>
<td>6.5·10⁻⁴</td>
<td>17.9</td>
</tr>
<tr>
<td>UV/S₂O₈²⁻ (RNO:S₂O₈²⁻ = 1:4) UV lamp (400W)</td>
<td>8.6</td>
<td>1.5·10⁻³</td>
<td>7.8</td>
</tr>
<tr>
<td>UV/TiO₂ (coated liner) UV lamp (14W)</td>
<td>18.9</td>
<td>1.6·10⁻⁴</td>
<td>73.0</td>
</tr>
<tr>
<td>UV/TiO₂ (suspension) UV lamp (14W)</td>
<td>2.1</td>
<td>1.4·10⁻³</td>
<td>8.0</td>
</tr>
</tbody>
</table>


Comparison studies between the different AOPs are very important in order to increase knowledge in which process is best in terms of efficiency and economics as a solution to a given problem. In the literature, some papers are published on comparison of AOPs for different treatment processes and in abatement of different organics [51,52,125-129], and EO is very often declared the preferable choice. Cañizares et al. [51] has recently proposed the Oxygen-Equivalent Chemical-Oxidation Capacity (OCC) as a single parameter for comparisons of AOPs. It is defined as the kilogram of O₂ that are equivalent to the quantity of oxidant reagents used in each AOP to treat 1 m³ of wastewater [51]. It is analogous to the common COD with the main difference that COD is used to determine the organic load of the waste and OCC is proposed to quantify the amount of oxidant supplied in the oxidation process. OCC is related to common oxidants as ozone and hydrogen peroxide (Fenton’s chemistry) according to the expressions (6.2)-(6.4), obtained from stoichiometrical calculations taken account of the number of electrons exchanged in the reduction of the oxidant.

\[
\text{OCC}(\text{kg} \ O_2 \text{m}^{-3}) = 0.298 \cdot Q(\text{kAhm}^{-3}) \tag{6.2}
\]

\[
\text{OCC}(\text{kg} \ O_2 \text{m}^{-3}) = 1.000 \cdot O_1 \text{ kgO}_2 \text{m}^{-3} \tag{6.3}
\]

\[
\text{OCC}(\text{kg} \ O_2 \text{m}^{-3}) = 0.471 \cdot H_2O_2 \text{ kgH}_2O_2 \text{m}^{-3} \tag{6.4}
\]

The OCC parameter only provides information about the chemical efficiency of the oxidants involved in the treatment with these AOPs, but does not give any additional information about the real cost of the treatment as the price of the oxidants used can vary. However, the OCC is a very useful comparative parameter to use and will be used in coming research focusing on these issues. In addition, OCC will be a valuable parameter, when different combinations of treatment
37 processes is evaluated in order to optimize the treatment efficiency, as will be briefly discussed in Chapter 11.

### 6.4 Summary of main conclusions and implications

EO used for color removal in wastewater treatment is definitely an applicable solution. In many cases, and what is the case with the studied dye p-nitrosodimethylaniline, only an initial one or two electron oxidation is sufficient to destroy the system of conjugated double bonds in the dye removing the characteristic absorbance in the visible wavelength range providing the colour of the solution. This initial oxidation may be rapid as in the case of electro-chlorination, but in order to obtain either full mineralization or a significant COD reduction longer reaction times are needed. Using a hydroxyl radical scavenger, the pathways of EOTR and electro-chlorination was demonstrated to be different on the Watersafe Ti/Pt_{90}-Ir_{10} and the Diacell Si/BDD anodes as in accordance to the literature and proposed theoretical models. Efficient applications of AOPs mean doing comprehensive experimental studies in order to optimize performances and decrease costs. P-nitrosodimethylaniline was found to be a very applicable compound for these studies of evaluation of the overall oxidation performance in a potential AOP, taking care of several oxidizing species generated in the process. Many AOPs requires some kind of energy source for the process to run, and in a comparison based on energy consumption, EO was demonstrated to be the most efficient process.

The next chapter will present and explore the differences observed, when electro-chlorination is compared to chemical chlorination using sodium hypochlorite in order to dig deeper into the explanations of the very increased efficiency almost always seen when EO is used in a chloride containing electrolyte.
Chapter 7
Electro-chlorination versus chlorination

Electrolysis of aqueous sodium chloride (brine) is a huge industrial process used in what is known as the chlor-alkali industry for the production of chlorine gas (processed further into sodium hypochlorite in a later production step) in the anode compartment along with sodium hydroxide and hydrogen in the cathode compartment. The two half cells are divided by an ion exchange membrane or previously a diaphragm. The process has been well known for more than 100 years. The use of chlorine for disinfection dates all the way back to 1823, where it was used in hospitals even before the discovery that bacteria were responsible for the transmission of certain diseases. However, it was not until 1910, where it began to be used for disinfection of drinking water through chlorination that the basis for a major increase in chlorine production and consumption was established [130]. Today, chlorination of water is a technique widespread used throughout the world for disinfection of surface water and wastewater.

When introducing the EO technique as a new approach to water treatment and environmental engineering societies, the importance of the presence of chloride for a successful treatment, which is seen in many cases, is often considered “just to be due to ordinary chlorination” and thus is considered rather old fashioned. However, electro-chlorination with the in-situ formation of oxidative chlorine species has in many comparison studies proved to be much more efficient than ordinary chlorination [131-134]. Particular within the area of water disinfection, this observation has been frequently reported. Typically, the reason has been attributed to the many other possible oxidative species generated in the electrochemical process, but the generated chlorine species itself may also be much more efficient when “freshly” produced as indicated shortly in section 6.1.

7.1 Comparison of organic dye bleaching

RNO was again used as model compound in this comparison. In Fig. 6-1, the distinct difference in bleaching rate of the direct surface oxidation by the chemisorbed active oxygen (Na₂SO₄ electrolyte) and the indirect chlorine-mediated oxidation (NaCl electrolyte) was reported. If this difference in rate can be explained just by means of chemical oxidation by common active chlorine species as hypochlorite and hypochlorous acid (7.1), then the bleaching would be expected to continue with a significant rate even if the power was turned off during the electrolysis, since \( r_{\text{Bleach}, \text{Na}_2\text{SO}_4} \) showed to be rather slow.

\[
r_{\text{Bleach}, \text{NaCl}} = r_{\text{Bleach, Na}_2\text{SO}_4} + r_{\text{Bleach, ClO}^-}
\]  

(7.1)

This argument was initially tested in an electrolysis start/stop experiment, where the power supply was turned on and off in specific intervals during the bleaching of RNO. This
experiment was performed in a 0.154 M NaCl electrolyte, since it was part of an experimental array studying the use of Watersafe in salt water swimming pools, where this salinity (0.9%) is used. A low current density of 16.6 mA cm\(^{-2}\) (1A) and a large volume of electrolyte (10 L) was used in order to slow the bleaching rate and to obtain more samples prior to full bleaching.

![Fig. 7-1: Bleaching of RNO during on and off electrolysis at 16.6 mA cm\(^{-2}\) in 0.154 M NaCl. Unpublished data.](image)

As is seen in Fig. 7-1, 40% color removal was obtained within the first 6 min. of electrolysis, which almost completely stopped, when the voltage was cut off. The concentration of active chlorine generated to this time step (6 min) was apparently not sufficient to continue a further chemical bleaching in the solution. According to measurements of the active chlorine production capacity of the cell in a similar electrolyte (but without the presence of RNO), the concentration of active chlorine would be around 5.3 mg L\(^{-1}\) after the six minutes (the data for this calculation is presented in the next paragraph). If active chlorine was consumed in a 1:1 ratio with RNO, still 4 mg L\(^{-1}\) would be present at the start of the first power off period. When the voltage supply was reestablished, the bleaching continued unaffected. At the next power off period (18 min), the concentration of active chlorine was sufficient to continue the bleaching.

The results from the start/stop experiment did not indicate that the chemical bleaching by active chlorine solely could provide an explanation of the difference in bleaching in Na\(_2\)SO\(_4\) and NaCl. In order to simulate the in-situ formation of active chlorine, another experiment was conducted where liquid sodium hypochlorite was added to the RNO solution in the same amount and in the same rate as the chloride electrolysis would generate active chlorine species. The active chlorine production capacity of the cell in the 0.154 M NaCl electrolyte was found by analyzing the evolution of active chlorine with time at different applied current densities (Fig. 7-2a). Linear correlations were found up to the upper limit investigated of 690 mA cm\(^{-2}\), and the rate of formation was found to be linearly correlated with the applied current (Fig. 7-2b), as expected. The electrochemical chlorine production capacity under the given conditions was found to be 9.4 mg L\(^{-1}\) A\(^{-1}\), thus giving a current efficiency of 55% in the 0.154 M NaCl electrolyte. When the bleaching of RNO at 32 mA cm\(^{-2}\) (1.9 A) was compared to the chemical bleaching by hypochlorite fed at the same rate (1.18 mL min\(^{-1}\) of 14 g L\(^{-1}\) NaOCl) to the reservoir by a HPLC pump, the superiority of the electro-chlorination was evident (Fig. 7-3).
The chemical bleaching was despite a fast initial removal of 30% of the color not capable of any significant further reduction of the solution absorbance within the 40 min it took for the electro-chlorination process almost completely to bleach the solution. These experiments clearly demonstrate that other reactive species than the ordinary active chlorine are generated in the electro-chlorination process, increasing the efficiency under conditions comparable with chemical chlorination.

7.2 Electrochemical disinfection of E. coli

Disinfection of water is maybe the most important process within drinking water treatment and generally constitutes the final step in the treatment. Since it represents the last barrier against pathogenic microorganisms, its effectiveness is a crucial point in ensuring public health. Obviously, production of drinking water from surface water requires very high standards of disinfection, and electrochemical techniques has emerged as one of the most feasible alternatives to the common traditional chlorination, which has drawbacks as formation of several potentially toxic by-products.

Numerous electrochemical systems and electrode materials have been tested against a variety of microorganisms, and their effectiveness to the abatement of bacteria, viruses, and protozoa is largely dependent on the electrochemical reactor, anode material, electrolyte composition, and electrolysis conditions. Some of the studies within electrochemical drinking water disinfection have recently been reviewed by Martinez-Huitle and Brillas (2008) [135] and Kraft (2008) [136]. Table 7-1 show some other selected examples of logarithmic reductions of relevant microorganisms by different anode materials.
Table 7-1: Results of selected electrochemical disinfection studies. The presented results are only intended to serve as examples, and do not provide a full overview of the research done in this area. * High-voltage electrical field study. ** Indirect treatment.

<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Anode</th>
<th>Current density</th>
<th>NaCl</th>
<th>Reduction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>E. coli</td>
<td>Pt/Nb</td>
<td>4 mA/cm²</td>
<td>0.058%</td>
<td>log-7</td>
<td>[137]</td>
</tr>
<tr>
<td>E. coli</td>
<td>Ti/RuO₂</td>
<td>5 mA/cm²</td>
<td>0.058%</td>
<td>log-3</td>
<td>[138]</td>
</tr>
<tr>
<td>E. coli</td>
<td>Ti/TiO₂</td>
<td>8 mA/cm²</td>
<td>0.008%</td>
<td>log-3</td>
<td>[131]</td>
</tr>
<tr>
<td>E. coli</td>
<td>Graphite</td>
<td>7.5 mA/cm²</td>
<td>0.85%</td>
<td>log-3</td>
<td>[139]</td>
</tr>
<tr>
<td>Legionella*</td>
<td>Ti/RuO₂</td>
<td>-</td>
<td>0.1%</td>
<td>log-3</td>
<td>[140]</td>
</tr>
<tr>
<td>Legionella</td>
<td>B-doped diamond</td>
<td>150 mA/cm²</td>
<td>0.7%</td>
<td>log-1</td>
<td>[141]</td>
</tr>
<tr>
<td>Pseudomonas au.</td>
<td>Ti/RuO₂</td>
<td>20 mA/cm²</td>
<td>-</td>
<td>log-6</td>
<td>[142]</td>
</tr>
<tr>
<td>MS2</td>
<td>Pt/Nb</td>
<td>24 mA/cm²</td>
<td>-</td>
<td>log-6</td>
<td>[137]</td>
</tr>
<tr>
<td>Cryptosporidium p.**</td>
<td>-</td>
<td>-</td>
<td>0.001%</td>
<td>log-3</td>
<td>[143]</td>
</tr>
</tbody>
</table>

The most popular electrochemical method is not surprisingly electro-chlorination, either through on-site production of disinfectants from brine or direct production of oxidants from the water to be treated by the electrolysis unit. Both processes have been shown to provide significantly better disinfection efficiencies compared to traditional chlorination, which generally are attributed to production of other strong oxidants than active chlorine species in the disinfectant. Especially, the role of reactive oxygen species (ROS), to which category the hydroxyl radicals, atomic oxygen, hydrogen peroxide, and ozone belongs, has been studied. However, the short lifetime of particular the radical ROS makes it only possible to underline their role in disinfection using the direct treatment strategy by passing the subject water through the cells. In a chloride free electrolyte using BDD, hydroxyl radicals were found by Jeong et al. (2006) [144] to be the most important reactive species for inactivation of E. coli. The same authors examined the role of electrode material on the generation of oxidants to be used for disinfection, and found that, in accordance with the theory, hydroxyl radicals was mainly produced by BDD, where they play a key role in generation of ozone [145] in addition to active chlorine as showed previously in Chapter 6. The production of active chlorine was most efficient at the DSA Ti/IrO₂, but an important observation was also that in the presence of a hydroxyl radical scavenger (t-BuOH) in inert electrolyte (KH₂PO₄) platinum showed the best disinfection efficiency, since the chemisorbed active oxygen was not scavenged in the same way as the hydroxyl radicals at BDD (as confirmed by us in Chapter 6).

In the array of swimming pool treatment experiments, electrochemical disinfection of E. coli in saline water was investigated by the Watersafe cell and compared with common chemical chlorination using the Selleck-Collins model for disinfection efficiency of coliform bacteria in domestic wastewater effluent by chlorination [146].
\[
\frac{N}{N_0} = 1 + 0.23 \cdot C \cdot t^{-3}
\]  

(7.2)

\(N_0\) is the initial \(E. coli\) concentration, \(N\) is the concentration after chlorination, \(C\) (mg L\(^{-1}\)) is the initial active chlorine concentration, and \(t\) (min) is the contact time.

The 0.154 M NaCl and \(E. coli\) electrolyte solution was passed a single time through the cell at different applied current densities. When electrolyzed, the sample was quenched with sodium thiosulphate (Na\(_2\)S\(_2\)O\(_3\)) to remove residual oxidants. The contact time from the point of entrance to the electrochemical cell to quenching in the sample beaker was 2.3 s calculated from the total volume in cell and hoses (260 mL) and the flow rate (400 L h\(^{-1}\) = 0.111 L s\(^{-1}\)). The number of surviving cells was determined by incubation for 24 h at 37 °C and plate counts.

![Fig. 7-4: (a) Disinfection of \(E. coli\) in 0.154 M NaCl electrolyte with contact time of 2.3 s. (b) The logarithmic reduction and survival ratio as function of applied current. Unpublished data.](image)

The surviving \(E. coli\) indicated in Fig. 7-4a as colony forming units (CFU) per 100 mL rapidly decreased as a function of the applied current, and no living germs was found at 20 A (332 mA cm\(^{-2}\)). The logarithmic reduction showed a linear dependence on the applied current (Fig. 7-4b). In order to secure a log-3 reduction (99.9% killing) 9 A was needed at this very short contact time. From the active chlorine production capacity experiments, the concentration obtained in one passage at 9A can be calculated to 12.7 mg L\(^{-1}\) (9.4 mg A\(^{-1}\) min\(^{-1}\) \cdot 9A / 6.7 L min\(^{-1}\)). Compared to the pure chemical chlorination, 3.1 min (186 s) of contact time is needed in order to obtain the same disinfection efficiency using purely chemical means of chlorination as calculated using Selleck-Collins. Seen from another perspective, the calculated concentration of active chlorine could by use of the model only cause 24% killing ratio in the 2.3 s and not 99.9%.

Electrochemical disinfection is a very efficient technique, and electro-chlorination is as demonstrated much more efficient than common chemical chlorination. One reason why, is most probably the presence of other oxidizing species as the ROS generated in the electrochemical process as has been widely investigated. However, electro-chlorination has been shown also to be more efficient than chlorination even by use of anode materials, which
have been shown not to produce significant amounts of oxygen radical species. In this case, chlorine will still be the main disinfectant in play. Since the reaction between chloride and the electrode initially may be of radical nature, a proposed oxidizing species generated at the anode surface is the hydrated chlorine radical as proposed in Chapter 6. They may act as a powerful oxidant in the electro-chlorination process in the cell in the vicinity of the anode, but react further to residual active chlorine species and react as such in the bulk. However, the differences observed on electro-chlorination and chemical chlorination need much more study before the actual responsible mechanisms are revealed.

In addition to ROS production in chlorine free media, the production and efficiency of peroxodisulphate, peroxodicarbonate, and peroxodiphosphate by BDD has been examined as residual disinfectant, but the residual disinfection efficiencies of these oxidants are not as good as active chlorine. However, efficient disinfection of chloride free water has been obtained using BDD due to the ROS formation [135].

### 7.3 Implications of electrochemical disinfection

The practical implications of the efficient disinfection provided with the electro-chlorination process are many. Since disinfection typically can do with a single pass, the implementation of the technique is very easy compared to COD removal, where recirculation or some kind of cascade treatment with multiple cells has to be used. Watersafe has extensive experience in using in-line electro-chlorination for treatment and disinfection of salt water swimming pools, where the enhanced disinfection efficiency from the passing of the cells makes it possible to operate at much lower residual free chlorine concentrations (\(< 0.2 \text{ mg L}^{-1}\)) that again decreases the concentrations of disinfection by-products as trihalomethanes (THMs) and chloramines.

The market for drinking water disinfection is not currently relevant in Denmark (99% is based on good quality groundwater), but in southern Europe and most other parts of the world, where surface water constitutes the main source of drinking water, the opportunities are immense. The ease of operation of the electrochemical technique and the fact that it only needs electric power in order to operate may in addition provide great possibilities of exporting the technique to 3 world countries, where securing safe drinking water is of highest importance.

A coming market of much more relevance with regards to Denmark is due to the requirement that by 2016 the latest, all ballast water from ships has to be disinfected before discharge. The intension is to hinder the devastating effect of invasive species on local marine habitats, and electrochemical techniques and electro-chlorination has a great potential in offering a solution for this problem. The high conductivity of sea water (mainly due to high chloride concentration) promoting low cost and the small space requirements of the electrochemical technique are important advantages compared to competitive techniques. More companies have electrochemically founded solutions in the pipeline of approval, including Watersafe, and with more than 100,000 commercial ships in the world, the economically potential is very promising.
**Chapter 8**

**By-product formation during EO: Emphasis on halogenation of organics**

As has been demonstrated throughout this thesis, AOPs are able to mineralize organic substances to relatively harmless ions, carbon dioxide and other non-toxic compounds. Therefore, the overwhelming majority of studies on use of AOPs emphasize the benefits of the technology, i.e. detoxification of wastewater, decolourization and disinfection. However, in many cases more careful consideration is necessary. It is known that when any AOP is used for treatment of real water with organic pollutants, organic by-products may and can be formed, which can be more dangerous than the initial compounds as referred to in earlier chapters. Likewise, inorganic by-products as chlorite, chlorate, perchlorate, and bromate can be formed during the EO treatment if chloride and/or bromide are present, and common disinfection by-products (DBPs) as THMs and chloramines may also be of concern. Especially, inorganic by-product formation has so far often been neglected by equipment producers and users, but publications from different authors demonstrate considerably risk.

In this chapter, some selected studies on the extent of formation of inorganic by-products during electrochemical disinfection and treatment are reviewed in order to outline the main issues in this area. However, the attention is focused on the risk of halogenation of PAHs during EO in chloride and bromide containing water. The latter issue has been studied in an array of experiments derived from the treatment process presented in Chapter 5, and the main implications will be presented and discussed. The full study is submitted for publication and is enclosed as paper V.

**8.1 Inorganic by-product formation during EO**

The main contributor underlining the need for awareness of the formation of inorganic by-products during use of EO is M.E.H. Bergmann from Anhalt University of applied Sciences, Germany. He and co-authors have in a number of papers demonstrated that especially the formation of perchlorate needs to be considered and included as an evaluation criterion, when new environmentally friendly AOPs are developed [147]. Especially, electrolysis by BDD of dilute chloride solutions promoted the formation of chlorate and perchlorate, due to the radical oxidation mechanisms. Perchlorate was also found by mixed oxide and Pt anodes, but in 3 orders of magnitude lower concentrations [148], observations which were confirmed by Polcaro et al. [149]. Chloride in the electrolyte was of course needed, but chlorate and perchlorate could be formed by electrolysis of hypochlorite and chlorite ions as well, and the formation mechanisms were showed to be very complex [150].
Another inorganic by-product, which can be formed during electrochemical disinfection using the natural chloride content of water, is chlorine dioxide gas. This molecule is in itself a highly efficient disinfectant, but Bergmann and Koporal [151] showed that it can be formed under several conditions and could be measured in the lower milligram per litre range. Once again they emphasize that technical cells should be designed and controlled better in order to ensure health safety. Despite efficient disinfection, it is not an applicable solution if inorganic by-products are formed, and for that reason BDD is not, compared to DSA and platinum anodes, suited for disinfection purposes.

8.2 Halogenation of PAHs during EO

The risk of formation of halogenated organic by-products is as clearly stated in this thesis a matter of concern for the further application of EO as a technique for pollution abatement. The many reactive species generated in the electrolysis process may induce unwanted side reactions besides the target oxidation reactions, and when electroactive halide ions are present in sufficient concentration the oxidized state may participate in substitution reactions with carbon bonded hydrogen on the organics leaving the by-products more toxic and recalcitrant to further oxidation. Halogens is from organic synthesis chemistry known to participate in especially electrophilic aromatic substitution reactions, and when already substituted on the organic, halogens are due to their electronegative nature weakly deactivating groups, which means that primarily mono halogenated organics can be expected to react slower to further oxidation than the parent compound.

In this way, halides often play a double role as the good and the bad guys in electrolysis. The rate of electrochemical mineralization of oxalic acid was significantly increased at a platinum anode due to the introduction of halides following the order $F^- > Br^- > Cl^-$ [26] and many other examples of this enhancement exists as presented in the prior chapters. Since fluoride in considerably concentrations is not found frequently in natural waters, bromide and chloride are the most interesting halides in relation to practical applications. However, several studies have documented the presence of residual refractory organic halogens (measured as adsorbable organic halogens (AOX)) after electrolysis in especially chloride media [23,152-155], and it must be emphasized that successful remediation of a waste is not achieved once the original contaminant has disappeared, if the reaction by-products are more toxic or persistent than the original contaminant.

The risk of AOX formation is in the published literature mainly connected to wastewater with a significant organic load, or in studies of model compounds in elevated concentrations. However, the extent of halogenation of a typical rather non-reactive micro pollutant found in quite low concentration in natural water was studied on the basis of the case of PAH contaminated sea water (presented in Chapter 5), using the same model compounds; naphthalene, fluoranthene and pyrene.

At first, the molecular structures of the halogenated PAH compound to search for in the electrolysis experiments were identified by an array of chemical hypochlorination experiments.
of elevated PAH concentrated solutions in order to maximize the potential for by-product formation. No halogenations or PAH degradation was observed in alkaline media, but analogous to organic synthesis chemistry formation of chlorinated and brominated PAHs were found in acidic chloride and bromide media, where the acidic conditions catalyzed the substitution reactions. High concentrations of active chlorine were used in order to promote as much by-product formation as possible. Especially naphthalene, as the most reactive PAH, was halogenated. In a chloride solution both mono-, di-, and tri-chloro-naphthalene could be found, whereas in a bromide solution only mono- and di-bromo-naphthalene were identified. Of the four ring structured PAHs only pyrene was halogenated as mono- and tri-chloro-pyrene and mono-bromo-pyrene.

Once identified, PAH solutions using concentrations just below the natural solubilities were electrolyzed at pH 6 by the Watersafe Ti/Pt90-Ir10 anode in order to examine the fate of the by-products during electrolysis. In general, the parent PAHs were degraded during the electrolysis in accordance to what was prior observed in Chapter 5. In a chloride electrolyte primarily mono-chlorinated naphthalene was formed during electrolysis, peaking at 45 min, and subsequently degraded at the extended electrolysis time. Small peaks representing di-chloro-naphthalene was the only other halogenated PAH found and no pyrene or even fluoranthene halogenation were observed.

In relation to electrolysis of sea water, the presence of bromide in the electrolyte is very interesting. An important observation from the study was that in a sea water simulated chloride electrolyte (0.10 M) with small amounts of bromide present (1.0·10⁻³ M corresponding to 80 mg L⁻¹) chlorination of naphthalene was significantly depressed in comparison to bromination, and peak concentrations of both mono-halogenated compounds were found already after 15 min, corresponding to a slightly more rapid removal of the parent naphthalene compound (Fig. 8-1a).

![Fig. 8-1: (a) the evolution in brominated and chlorinated byproducts measured as relative counts during EO in mixed 0.0010 M KBr and 0.10 M NaCl electrolyte at 25 mA cm⁻² and pH 6. (b) Concentration comparison of parent naphthalene and mono halogenated naphthalene species. Submitted for publication in paper V.](image-url)
Compared on a molar basis, the sum of mono-chloro- and mono-bromo-naphthalene at the peak concentration comprised 30% of the initial concentration of naphthalene so the halogenation is considerably (Fig. 8-1b).

Bromide is in itself an electroactive ion and can analogous to chloride be anodically oxidized to molecular bromine, which can participate in the electrophilic aromatic substitution reaction with naphthalene. However, it is known from chlorination chemistry that when active chlorine species are present, hypobromous acid is rapidly formed due to bulk oxidation of bromide ions.

$$HOC\ell + Br^- \rightleftharpoons HOBr + Cl^- \quad (8.1)$$

In reality, hypobromous acid is therefore expected to be the primary oxidizing species present in the “sea water” electrolyte during electrolysis. Hypobromous acid ($E^\theta=1.33V$) is thermodynamically a comparable strength oxidant as hypochlorous acid ($E^\theta=1.48V$), and as observed, it next to oxidation appears also to be willing to participate in organic halogenations reaction. The presence of bromide has in this way turned out to be the real reason of concern in treating sea water media.

A positive observation was that despite the persistent behavior towards EO of both the chloro- and the bromo-naphthalene compounds, extended electrolysis time was indicated to be sufficient to completely remediate the solutions through this mean of treatment. As a final comment it can be added that a comparative experiment was conducted using BDD as anode, which showed the same pattern of by-product formation and removal.

### 8.3 Important implications

The implications of this study and the other published results on the by-product issue are very important for a responsible further use of EO as an environmentally friendly remediation technique. In the case of halogenation of the parent compounds as documented in this chapter, the by-products typically form common volcano shaped curves with formation followed by degradation. When electrolyzing water with higher initial COD, formation of lower carbon chained halogenated organic oxidation products in the form of halogenated acetic acids (HAA) represent a more difficult problem [156], since some compounds have been documented to be refractory to further oxidation on active anodes and even on BDD [154].

An overall parameter as AOX or other means of by-product analysis should in future studies of the applicability of electrolysis, as means of treatment of a harmful wastewater always be implemented in the final evaluation in order to establish the feasibility and the needed electrolysis time. In addition, ecotoxicity tests would be relevant to conduct. It is however important to notice that when refractory organics are seen, the concentrations are usually very low compared to the starting point. If they still exceed the discharge limits, a final active carbon adsorption polishing step may be necessary.
A way to minimize the halogenations of the treated organics during treatment will be to run to the electrolysis under alkaline conditions, where chemical chlorination of PAHs was not observed in the present study (Paper V) - in line with what is also suggested in this paper by Gotsi et al. [82].

Finally, the gases produced during the electrolysis have to be evaluated before a practical application can be considered fully environmentally friendly. Chloroform has been documented as the main organic compound in the evolved gases in a study on electrochemical phenol oxidation in chloride media [23], and this is very likely to apply for treatment of other organics too, and will require either good ventilation or polishing of the discharge air dependent on the concentrations observed.
Chapter 9
XPS anode surface analysis: Pre and post electrolysis

Watersafe are experienced in using and producing platinum based metal alloys as anode material in their electrolysis product portfolio, and the cell used for the studies presented in this thesis has an anode consisting of a titanium core coated with platinum alloyed with 10% iridium as presented in Chapter 3. This type of anode is by the theory of EO of organics classified as primarily an active anode. Since higher oxidation states are possible on both platinum and iridium, a strong interaction between the discharge water molecule and the anode surface is considered to result in formation of a chemical bond of covalent nature creating metal oxides.

Using X-ray photoelectron spectroscopy (XPS), it is possible to identify which atoms are present at a surface and their most pronounced chemical oxidation states. In this chapter a study is presented, where the platinum alloy used by Watersafe has been investigated before and after electrolysis in the search for surface metal atoms in higher state of oxidation, which in the EO terminology is referred to as the higher oxide as presented in chapter 2. Their existence has been documented only recently by atomic oxygen labeling on iridium oxide anodes [17,18], but if their presence can be documented by XPS analysis, it will be a strong support for the general EO theory. The study is published in a joint book chapter and is enclosed as paper IV.

9.1 Analytic principle in XPS

Photoelectron spectroscopy is an analytical technique in which a sample is irradiated with high energy photons and emitted photoelectrons are studied [157]. Applying the principle of energy conservation, the kinetic energy of the emitted photoelectrons, $E_{kin}$, can be estimated from the incoming photon energy, $hv$, and related to the binding energy of the photoelectrons, $E_B^i$, via (9.1):

$$
hv = E_B^i + E_{kin}^i
$$

The binding energy is the difference of the total energy of the atom in its initial state in the specific molecule, and the energy in the final state (now as an ion) after an electron is emitted. In this way, the difference between the photon energy in the beam (which we determine) and the kinetic electron energy (which we measure) is in rough terms the binding energy of the electron in the orbital, from which the electron is emitted. An XPS spectrum is thus a graphical picture of the binding energies versus the number of electrons emitted in a given sample.

For each element, there will be a characteristic binding energy associated with each core atomic orbital, i.e. each element will give rise to a characteristic set of peaks in the photoelectron spectrum. Singlet or doublet peaks arise dependent on the coupling between the magnetic field of spin and angular momentum of the electron in an orbital, termed the spin-orbit splitting.
For each element, specific core level electrons have been shown to be particular useful in XPS, for oxygen and carbon it is the electrons in the $1s$ orbital (electrons from $s$ orbitals give rise to a single peak), whereas it for the larger atoms platinum and iridium are the electrons in the $4f$ orbital (which give rise to doublet peaks with total angular momentums of $5/2$ and $7/2$). The binding energy for the core level electrons in an element is modified, when constituted in a molecule and depend on the species, to which it is bonded. These chemical shifts of the core level binding energy contain important information regarding the electronic structure of the bonded atoms. When the energy spectra are analyzed, the experimental data can be fitted with one or more peaks assigned to electrons with different surroundings. The chemical shift of the binding energies has a close connection to the effective charge for an atom in a molecule, and partial positively charged atoms lead to shift in core levels to higher binding energies associated with increased coulombic attraction between the core electrons and the nucleus. Consequently, atoms in a high formal oxidation state will yield XPS peaks at high binding energy relative to the same atom in a low oxidation state. [157]

XPS is very surface sensitive and reach a depth of only 5 nm. However, bulk analysis can be conducted by sputtering, where the outer layer of material is removed by a high intensity electron beam.

9.2 Survey scans and identification of distinct platinum peaks

In order to create an overview, survey scans of the material surface were conducted to clarify the diversity of elements present (Fig. 9-1a). Scans of the raw surface revealed contamination (Na, Cl, and C peaks) and noise peaks, which were removed by cleaning. Sputtering of the material revealed the true composition of the alloy with very well defined doublet peaks of platinum and small doublet peaks assigned to iridium. The oxygen peak was almost completely removed by sputtering and analysis of the bulk material, and the Pt doublet peaks found in this sample could be assigned to metallic Pt(0).
Fig. 9-1: (a) Survey spectra of the Watersafe anode with indications of identified elements. (b) Detailed spectrum of the Pt 4f 7/2 and 5/2 peaks, and deconvoluted into two doublets. Published in paper VI [158], reprinted with permission from Nova Science Publishers, Inc.

Using mixed Gaussian-Lorentzian mathematical functions, the detailed spectrum of the platinum doublets was deconvoluted into four single peaks applying the XPS Peak Fitting software developed by Dr. Kwok [159]. The dominant peaks, 1 and 1’ are assigned to the presence of surface Pt(0), whereas the peaks 2 and 2’ was assigned to bulk Pt(0) after careful examination of quite contradictory literature reportings (Fig. 9-1b). Some authors propose the presence of peaks 2 an 2’ to be due to Pt(II) chemical states in PtO or Pt(OH)₂, but the arguments assigning them to bulk Pt(0) was most convincing in addition to the fact that the sputtering procedure just exposed the bulk material to analysis by the x-ray beam.

Due to the lack of intensity of the iridium peaks from the samples, it was decided to focus only on the platinum peaks in the continued study.

9.3 Analysis of platinum oxidation states: Oxygen versus chlorine evolution

In order to investigate if more single peaks would appear in the raw spectra of platinum, which could be assigned to platinum atoms in higher oxidation states bonded in metal oxides, detailed spectra were obtained after 30 and 60 min of galvanostatic electrolysis. Two different electrolytes were investigated, a 0.10 M sodium sulphate electrolyte in order to promote oxygen evolution as the primary anodic reaction and 0.10 M sodium chloride in order to promote chlorine evolution.

As reference, samples submerged in the respective electrolytes for 60 min and then dried were analyzed. The reference samples were despite generally lower intensities deconvoluted in the same manner as Fig. 9-1, so no blind oxidation of the surface occurred without applied voltage. In both electrolytes the spectra changed appearance due to the electrolytic processes, and introduction of more single peaks, 3 and 3’, were necessary in order to obtain proper fits of the experimental data (Fig. 9-2). The peaks 3 and 3’ can definitely be assigned to oxidized chemical
states of platinum as Pt(II) or Pt(IV). Since Pt(IV) has a greater binding energy than Pt(II), the chemical shift can be used to specify valence. The chemical shift between Pt(0) and Pt(II) (in PtO) is ≈3 eV and ≈1.6 eV (in Pt(OH)₂) and between Pt(0) and Pt(IV) (in PtO₂) ≈ 4 eV [160]. The spectra indicated chemical shifts between 1-3 and 1'-3' of 2.6-3 eV suggesting that platinum in the formed oxide layer was in the +2 chemical state, but strongly implying that the oxide layer was composed of mixed platinum oxide and hydroxide [161].

Differences were observed on the spectra after 30 and 60 min of electrolysis in the different electrolytes. The analysis indicated that the formation of the oxide layer was stronger in the chloride electrolyte, since the 3 and 3’ peaks increased in area compared to the sulphate electrolyte, where they seemed to return to the initial state with a spectrum similar to the reference. One can speculate that this is a demonstration of the very corrosive environment in especially the chloride electrolyte, but the experiments needs to be repeated before more can be concluded. There were no visual indications of differences on the surfaces from the samples.

### 9.4 Implications and further experiments

The demonstrated formation of an oxidized layer on platinum during aqueous electrolysis supported the model proposed for EO, where platinum based electrodes were characterized as utilizing chemisorbed oxygen for the oxidation of organic pollutants, and that platinum oxide rather than metallic platinum are involved in oxidation in aqueous solution. However, if the
platinum peaks 3 and 3' can be directly assigned to the higher oxide proposed in the theory of EO or “just” to common Pt(II) oxide is still not clear. However, the oxide layer, $MO$, is formed at the initial metallic Pt(0), $M$, during electrolysis from discharge of water so in this sense it fits with the suggested theory presented in Chapter 2.

$$M + H_2O \rightarrow M(OH^+) + H^+ + e^- \rightarrow MO + 2H^+ + 2e^- \quad (9.2)$$

More experiments confirming the reported observations and investigating of classical DSA type iridium oxide anodes needs to be performed in order to derive more clear conclusions. A positive identification of the higher oxide by XPS will require it to be really stable, since this analysis is made ex situ.

At this first attempt, it was chosen to run the experiments without organics in the electrolyte, in order to promote as much formation of metal oxide as possible and limit the reduction caused by the organics. But, the presence of the platinum in higher oxidation states does not directly mean that it is taken part in organic oxidation, and the next successive XPS studies will focus on the change of the surface with the presence of an organic pollutant in the solution and thus concurrent organic oxidation, which might promote a regeneration of the initial dominating Pt(0) surface or show distinct chemically bonded carbon, different from the carbon just adsorbed to the surface.
Chapter 10
Conclusions

EO has in the many different applications studied in this thesis been demonstrated as a powerful technique for degradation of toxic and recalcitrant organic pollutants of different kinds and origins. Direct oxidation of organics through EOTR does occur at the Ti/Pt_{90}-Ir_{10} anode, but this process has shown in general to be more efficiently carried out using the BDD, due to a higher production of hydroxyl radicals capable of TOC removal. Instead, the Ti/Pt_{90}-Ir_{10} anode has showed strengths for use in the indirect electro-chlorination process, where several different applications as disinfection and bleaching can be pursued. In treatment of real water matrices both oxidation pathways are commonly in play, and if the natural chloride concentration in water is significant and the target organics are amendable to indirect chlorine oxidation, the Ti/Pt_{90}-Ir_{10} anode may be the preferable choice. However, other very important factors as material costs, durability and accessibility can be even more deciding than performance differences for which anode and type of cell to choose. Here the Ti/Pt_{90}-Ir_{10} anode may have additional advantages, but these parameters have not been considered in this work.

The most crucial issue of electro-chlorination and EO is formation of harmful by-products, and the Ti/Pt_{90}-Ir_{10} anode is according to the literature not as disposed to form inorganic by-products as chlorate and perchlorate ions as the BDD. However, formation of halogenated organics has been showed in halide electrolytes, which needs to be considered, when evaluating the performance of EO. Most frequently, the by-products are further degraded after prolonged electrolysis times as observed in our research, but formation of refractory organics has been documented elsewhere in the literature.

The specific conclusions, which can be drawn from the research presented in this thesis, are:

- EO can be efficiently used for degradation of organo-phosphoric pesticides in polluted groundwater, and for treatment of PAHs from sea water from a sediment removal process.
- The Ti/Pt_{90}-Ir_{10} anode is capable of bleaching p-nitrosodimethylaniline, which was used to demonstrate the importance of the presence of chloride for the EO performance. The compound was also used to demonstrate the efficiency of electro-chlorination versus chemical chlorination, and addition of a hydroxyl radical scavenger demonstrated clearly the theoretically suggested difference on oxidation mechanisms for Ti/Pt_{90}-Ir_{10} and BDD anodes.
- Formation of halogenated PAHs during EO in bromide and chloride electrolytes was documented. Only naphthalene species were formed in detectable amounts, with bromated naphthalene as the most pronounced when bromide is present even in small
concentrations. Indications were that the by-products could be completely removed at longer electrolysis time.

- XPS revealed that before electrolysis, platinum was presence as metallic Pt(0), whereas after electrolysis the chemical state of platinum shifted to at least Pt(II) in a mixed oxide layer. The oxidized states of platinum (and most probably iridium) are likely the one responsible for direct EOTR of organics in aqueous solution using the Ti/Pt90-Ir10 anode, and these observations supports the theoretical suggested formation of chemisorbed higher oxides at this type of anode.

Electrochemical oxidation as a technique for degradation of organics in advanced water treatment does definitely possess a promising potential for industrial use and increasing dissemination as the preferable AOP, when facing problems with toxic, refractory, bio-incompatible organics. But, continuing efforts have to be invested in research aiming at providing a full understanding of the fate of by-products and the derived consequences. In this way the technique is still just on the edge of reaching the necessary level of maturity, which can clear the field for industrial break through.
Chapter 11
Reflections on the perspectives in the future use of EO

As a chemical engineer doing research in the field of environmental chemistry and technology, the last three years of work with EO in various different applications - and with introductory test runs on several different types of wastewaters (fish curing wastewater, diary wastewater, pharmaceutical production wastewater, pectin production wastewater, beer brewing wastewater etc.) besides the detailed studies presented in this thesis - has revealed a strong and powerful oxidation technique, reasonably easy to operate and handle, but very complex with regards to the chemistry. However, one major advantage with electrolysis in general is the control of the reactions in the sense that you might not be able to completely decide which reactions you want to happen, but you can fully control if you want reactions to occur or not - just by a click of a switch. This added to the fact that you in general, with some limitations, can adjust the reaction rates according to your needs make the process very attractive and safe to operate.

The two biggest challenges for a bright future for dissemination of EO for use in the water treatment sector is the case dependent by-product formation and the in general high treatment costs, but that hold true for almost all of the AOPs. EO has to be evaluated as an AOP and considered as such, when costs and the areas of applications are considered. There is no need to compete with biological treatment if the wastewater is biodegradable, since this principle is at present the cheapest and most environmentally compatible option. But in the right context and compared to the rest of the AOPs, EO has a lot of benefits as presented in Chapter 1.

This chapter will present how the author sees the future of EO, how it can develop from a promising laboratory scale technique to an industrially implemented technique - with some supporting literature references. The issue with by-products will not be discussed further in this chapter, since this subject has been thoroughly presented in the thesis and is an obvious area of more research.

Sustainability, carbon footprint and life cycle analysis etc. are principles and procedures, which due to the recent focus on and awareness of climate change issues, have started to be more and more considered and evaluated, when deciding on remediation strategy and treatment principles in environmental engineering. In this context, EO has a potential to provide yet almost unexplored advantages, which might be important for the future dissemination of the technique.

11.1 Implementation of EO in pilot or full scale industrial use

The implementation of EO for disinfection purposes is, as discussed in Chapter 7, in principle rather straight forward using inline electrolysis, when the conductivity of the water media is sufficient or otherwise through addition of electrolyte as salts or brine solution. For disinfection, typically a single pass of the electrochemical cell is sufficient, when the applied current is high
enough to reach the aimed killing ratio. For oxidation of organics, recirculation of the waste stream through the electrochemical cell is needed in order to obtain the target degradation levels, and this stipulates some other requirements. In general two continuous treatment approaches are conceivable, recirculation through the cell from a reservoir in a semi batch process or cascade treatment with multiple single passes of the waste stream in cells connected in series. Watersafe has so far in their industrial installations used the semi batch approach in different alignments utilizing both direct treatment of the waste stream in the cells and indirect chemical oxidation through addition of an electrochemically produced oxidant. Not many scientific studies are published on pilot and/or full scale treatment of wastewater by EO, but the ones that are, to the authors knowledge, all use the semi batch approach, and this design principle does also seem as the one most easy to implement. A combined approach using semi batch treatment in two connected stages is also seen [6].

In many situations, wastewater contains both solid and dissolved pollutants, biological degradable and toxic and refractory organic compounds. In these cases, EO cannot stand alone as a universal solution, but needs to be combined with other treatment principle for the most optimal performance. This can be combined with other AOPs in sequential or simultaneous treatment, but most frequently a separation step is needed prior to EO in order to remove the solid particulate waste. In addition, the combination of EO with the cheaper biological treatment is obviously an approach to minimize treatment cost. This combination is frequently stressed as promising and the way forward, since EO pre-treatment can enhance the BOD/COD ratio of the wastewater and convert toxic and recalcitrant organics to highly oxidized biodegradable carbon source compounds, which are rapidly metabolized by microorganisms. However, EO as pretreatment requires quenching of any residual oxidant that will provide a disaster if entering the biological treatment stage. The concept of integration of AOPs as pre-treatment to bio-degradation post treatment has been illustrated by Comninellis et al. [2], which consider the rate of C-C bond scission by chemical and biological means versus the molecular size of the organics (Fig. 11-1).

As seen, AOPs in general provide the fastest degradation rates when the organics have larger size, whereas a breakpoint appears beyond which biological treatment becomes more attractive than chemical oxidation in terms of rate and consequently efficiency of the treatment.

Another combined approach is to use EO for tertiary polishing of wastewater before discharge, either for disinfection purposes, but also for oxidation and removal of pollutants not affected by the preceding treatment stages or to complete the COD removal or other parameters to comply with the discharge limits. An example of this approach is published by Chrysafopoulou et al. [162], who treated biologically processed wastewater in a pilot unit consisting of an electrolytic oxidation step and a flotation and coagulation/precipitation step. The results were reported as promising with complete discoloration, disinfection, removal of suspended solids and reduction of COD and BOD. 1 m³ h⁻¹ was continuously treated in the setup, with the recirculation flow rate being 7.5 m³ h⁻¹, but it was recommended to use higher recirculation rate in future installation. The effluent from the pilot unit complied with the guidelines for agricultural water reuse or aquifer recharge in Greece.

Several other combinations of EO and other treatment techniques have been proposed and studied in smaller scale with some of them showed in Fig. 11-2.


Particular the combination of membrane filtration and EO will be explored in my future research, since the use of reverse osmosis (RO) or other membranes can reduce the capacity requirement to the EO, generating a concentrated stream of not only suspended but also soluble pollutants to be EO treated, which is good to enhance the mass transfer in the cell. This combination has in particular been studied within leachate treatment. However, all of the presented treatment schemes in Fig. 11-2 have been evaluated with promising results [163], and development of a sustainable process based on the integration of efficient technologies is often stressed as one of the key obstacles that have to be overcome before full scale implementation of EO can be expected in large scale. Another important upscale issue is to better understand
the behavior of EO described by mathematical models and parameters. As presented in section 2.6, we are close by, but the model has been reported to show deviations when dealing with complex mixtures, where the presence of electro-generated oxidants also contributes to the oxidation. Others models that describe the combined contribution of both mechanisms have been developed, but still lack thorough validation, and the many competitive reactions on the anode and the different species interacting creates a very complex system as clearly stressed in this thesis. Future research areas are definitely scaling up issues of EO from the laboratory studies to pilot and full scale treatment in combination with separation and other advanced oxidation techniques.

11.2 Use of on-site renewable energy and pure electrons during remediation

Green and sustainable remediation is principles, which are believed to become more and more in focus in the near future. Already within the technical area of remediation of contaminated sites, software tools have been developed, where the total impact of different remediation strategies can be evaluated based on carbon footprint analysis etc., with the overall aim of minimizing the impact on the surrounding ecosystem from our otherwise good intentions of taken care of and restoring the environment. Electrochemistry and EO as a technique for degradation of organics have features, which render it promising as part of such strategies. Many of the competing techniques for the abatement of refractory pollutants involve transportation and storage of reactants, which compared to EO induce increased emission of carbon dioxide that is not generated by EO, since the primary reactant is the electron itself produced on-site and addition of chemicals is not necessary if used under the right circumstances. If the needed electrical power can be produced by on-site renewable means from e.g. wind or solar energy, then we are really on the right track. These arguments are in line with the idea of on-site production of oxidant for ISCO applications as presented in Chapter 5.

As input to the inclusion of carbon dioxide emission in the mindset, when exploring possibilities with different remediation technologies, a very interesting study published by Serikawa et al. [6] deserves to be mentioned. Results from more than 100 runs with thirty different industrial wastewaters were gathered and compared, and an obtained average of 97% of COD removal was reported with an average power consumption of 53 kWh kg-COD⁻¹. If only the wastewaters with initial COD above 5000 mg L⁻¹ was considered (too disregard mass transfer limitations) 30 kWh kg-COD⁻¹ was used in average. One wastewater was chosen to be evaluated in a six months pilot scale run, using BDD electrodes with polarity reversal, treated in two semi batch stages using two stacks of electrodes operated at different current densities. Most interestingly was that for achieving the same level of COD removal, despite the energy consumption of 420 kWh m⁻³, the emission of carbon dioxide was calculated to be roughly 50% less than the emission generated by the normal incineration process of the waste using fossil fuels, primarily due to the water content in the waste. However, the calculation cannot be considered general and is country and wastewater dependent, but the study illustrates that despite what looks like operating costs never feasible in practical use, environmental and
economically benefits can arise other places in the total account of wastewater treatment costs – in this case since the tax paid for carbon dioxide emission can be lowered.

Another obvious environmental benefit, which still needs to be explored in coming research, is the fact that the main anodic oxidation always in water electrolysis is corresponded by the cathodic hydrogen evolution, and a promising potential is to couple this hydrogen production with fuel cells, which can use the hydrogen to generate electrical power as a co-source for the EO treatment unit. For this combination to be feasible other than in drawings, the efficiency and several other parameters of the fuel cell technology needs to be appropriately developed. The full status of current research on this subject is by the author unknown, but a paper of Soler et al. [164] studies some introductory step for this combined hydrogen production and waste removal, and it is known by the author that other practical steps have been taken to utilize the hydrogen produced during electrolytic swimming pool treatment.

Lots of exciting work and research still have to be done implying engineers and scientists in multiple technical fields and specialized areas in order to continue the promising development of EO. But EO possess a lot of promising features as a strong water treatment solution to be included in our arsenal of technologies needed to defeat our increasing pollution problems and help us to preserve our environment for the benefits of all.
Chapter 12
References


References


