Heikki Särkkä

ELECTRO-OXIDATION TREATMENT OF PULP AND PAPER MILL CIRCULATING WATERS AND WASTEWATERS

Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Auditorium in MUC, Mikkeli University Consortium, Mikkeli, Finland on the 30th of July, 2013 at noon.

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Interest in water treatment by electrochemical methods has grown in recent years. Electrochemical oxidation has been applied particularly successfully to degrade different organic pollutants and disinfect drinking water.

This study summarizes the effectiveness of the electrochemical oxidation technique in inactivating different primary biofilm forming paper mill bacteria as well as sulphide and organic material in pulp and paper mill wastewater in laboratory scale batch experiments. Three different electrodes, boron-doped diamond (BDD), mixed metal oxide (MMO) and PbO₂, were employed as anodes. The impact on inactivation efficiency of parameters such as current density and initial pH or chloride concentration of synthetic paper machine water was studied. The electrochemical behaviour of the electrodes was investigated by cyclic voltammetry with MMO, BDD and PbO₂ electrodes in synthetic paper mill water as also with MMO and stainless steel electrodes with biocides. Some suggestions on the formation of different oxidants and oxidation mechanisms were also presented during the treatment.

Aerobic paper mill bacteria species (Deinococcus geothermalis, Pseudoxanthomonas taiwanensis and Meiothermus silvanus) were inactivated effectively (>2 log) at MMO electrodes by current density of 50 mA/cm² and the time taken three minutes. Increasing current density and initial chloride concentration of paper mill water increased the inactivation rate of Deinococcus geothermalis. The inactivation order of different bacteria species was Meiothermus silvanus > Pseudoxanthomonas taiwanensis > Deinococcus geothermalis. It was observed that inactivation was mainly due to the electrochemically generated chlorine/hypochlorite from chloride present in the water and also residual disinfection by chlorine/hypochlorite occurred.

In real paper mill effluent treatment sulphide oxidation was effective with all the different initial concentrations (almost 100% reduction, current density 42.9 mA/cm²) and also anaerobic bacteria inactivation was observed (almost 90% reduction by chloride concentration of 164 mg/L and current density of 42.9 mA/cm² in five minutes). Organic material removal was not as effective when comparing with other tested techniques, probably due to the relatively low treatment times.

Cyclic voltammograms in synthetic paper mill water with stainless steel electrode showed that H₂O₂ could be degraded to radicals during the cathodic runs. This emphasises strong potential of combined electrochemical treatment with this biocide in bacteria inactivation in paper mill environments.
The results of the experiments showed that electrochemical oxidation could be used in paper mill waters for planktonic bacteria removal. Applying this technique together with some biocides can enhance the oxidation process, keeping the paper mill pipelines clean of slime formed by bacteria. Electrochemical oxidation is also a promising preliminary or tertiary treatment process in pulp and paper mill wastewater treatment, especially against refractory organic compounds which cannot be removed by biological processes.

**Keywords:** electrochemical oxidation, electrode, hydroxyl radical, hypochlorite, biocides, biofouling, cyclic voltammogram, hydrogen peroxide, pulp and paper mill wastewater

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In Mikkeli 24.6.2013,

Heikki
LIST OF PUBLICATIONS

The publications are listed in roman numerals in the text as follows:


Author’s contribution to publications I-IV

Planned and designed experiments with other co-authors, carried out all the experiments, analysed the data, interpreted the results and prepared the first draft of all the manuscripts.

Author’s contribution to publications V-VI

Participated in planning and designing experiments related to electrochemical oxidation part, participated in analysing the data, interpreting the results and commented the drafts of the manuscripts.
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HO$_2^*$ perhydroxyl radical
I current
M electrode surface
'OH hydroxyl radical
R organic pollutant
t time

Abbreviations

AOP advanced oxidation processes
AOX adsorbable organic halides
APC aerobic plate count
BDD boron-doped diamond
BOD biological oxygen demand
BSTFA bis(trimethylsilyl)trifluoroacetamide
CEH chlorination, extraction and hypochlorite bleaching
CFU colony forming unit
COD chemical oxygen demand
CV cyclic voltammogram
DAF dissolved air flotation
DO dissolved oxygen
DOC dissolved organic carbon
DSA dimensionally stable anodes
EC electrocoagulation
EF electroflotation
EO electro-oxidation
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
</tr>
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<tbody>
<tr>
<td>GC</td>
<td>gas chromatograph</td>
</tr>
<tr>
<td>GCE</td>
<td>general current efficiency</td>
</tr>
<tr>
<td>HFCVD</td>
<td>hot filament chemical vapor deposition</td>
</tr>
<tr>
<td>MB</td>
<td>methylene blue</td>
</tr>
<tr>
<td>MF</td>
<td>microfiltration</td>
</tr>
<tr>
<td>MMO</td>
<td>mixed metal oxide</td>
</tr>
<tr>
<td>MO</td>
<td>methyl orange</td>
</tr>
<tr>
<td>MS</td>
<td>mass selective</td>
</tr>
<tr>
<td>MTBE</td>
<td>methyl tert-butyl ether</td>
</tr>
<tr>
<td>NF</td>
<td>nanofiltration</td>
</tr>
<tr>
<td>NOM</td>
<td>natural organic matter</td>
</tr>
<tr>
<td>PAM</td>
<td>polyacrylamide</td>
</tr>
<tr>
<td>PCA</td>
<td>plate count agar</td>
</tr>
<tr>
<td>RO</td>
<td>reverse osmosis</td>
</tr>
<tr>
<td>ROS</td>
<td>reactive oxygen species</td>
</tr>
<tr>
<td>RSM</td>
<td>response surface methodology</td>
</tr>
<tr>
<td>SCE</td>
<td>saturated calomel electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SHE</td>
<td>standard hydrogen electrode</td>
</tr>
<tr>
<td>SPEF</td>
<td>solar photoelectro-Fenton</td>
</tr>
<tr>
<td>SPW</td>
<td>synthetic paper mill water</td>
</tr>
<tr>
<td>SS</td>
<td>stainless steel</td>
</tr>
<tr>
<td>TCF</td>
<td>totally chlorine free</td>
</tr>
<tr>
<td>TMCS</td>
<td>trimethylchlorosilane</td>
</tr>
<tr>
<td>TOC</td>
<td>total organic carbon</td>
</tr>
<tr>
<td>UF</td>
<td>ultrafiltration</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
</tbody>
</table>
1 INTRODUCTION

1.1. Pulp and paper mill circulating waters and wastewaters

1.1.1. General

The pulp and paper industry, like the primary metal and chemical industries, uses a great deal of raw water [1]. Water is needed at paper mills mainly for the pulp washing procedure and paper forming process in the wet end phase. Modern mills need 15 to 50 m³ of water to produce a ton of paper or cardboard [1,2] and consumption varies depending on the manufacturing process and country.

Pulp and paper mill circulating waters and wastewaters are a very complex mixture of different organic and inorganic compounds. Wastewaters from pulp making mainly contain lignin, resin acids, fatty acids and dissolved wood extractives [3-5]. After pulp bleaching inorganic chlorine and AOX compounds may also be present, depending on the bleaching procedure [4]. The wastewater generated from the paper making process contains particulate waste, organic compounds (e.g. fatty and resin acids), anions, inorganic dyes and biocides [6-9]. These substances can be highly toxic in natural waters causing fish death and negatively affecting the whole ecosystem [3].

1.1.2. Micro-organisms in the paper mill environment

A recent trend is the circulation of process waters, and purified wastewater may even be used again in the paper making process. Recycling of these waters is important to utilize as much fibers as possible in paper sheet making process [6]. This can reduce fresh water consumption but introduce other challenges, such as the neutralization of cationic retention chemicals, corrosion problems and the biofouling of pipelines by microbes. Biofouling is usually prevented by using chemicals (biocides), which are often relatively toxic to handle and the risk of negative effects in the receiving waters is
increased after wastewater treatment [6]. Some biocides can also retain in fibers and accumulate in the final paper product.

Because of the nutrient-rich, moist and warm paper mill environment, many microbes exist in paper mill circulating waters. Micro-organisms are constantly introduced into paper machines through raw materials, water, fibres and paper-making chemicals [10-12]. Microbial growth, if not controlled, can result in slime formation which can seriously disturb the paper making process and have a negative impact on the quality of the paper [11]. Free-living bacteria are not a major problem (some degrade fibre, for example), but when these species attach to the pipelines creating flocules or slime, the process is easily disturbed, causing breaks in the paper web [12]. Attached bacteria growing on a surface as a biofilm are not easy to remove by physical means such as washing. Mechanical cleaning is also a common method, though switching off the paper machine for cleaning the pipelines causes financial losses. Thus the paper industry uses biocides to control excessive bacterial growth [6,12,13,14]. Biocides are usually classified as either oxidizing or non-oxidizing and chlorine, hydrogen peroxide and peracetic acid are examples of oxidizing species used in mills.

Paper mill microbe communities vary a lot depending on the mill and paper making process used. Direct microscopic examination of slime deposits shows microbes with different shapes and sizes [11]. Filamentous organisms can be fungi or bacteria which are capable of accumulating large amounts of colourful slime. Many species have been isolated in these environments, such as Deinococcus, Pseudoxanthomonas, Meiothermus and Bacillus [12,14,15]. Väisänen et al. [12] isolated totally 390 strains of aerobic bacteria from printing paper machines. Deinococcus geothermalis was one of the species that could adhere to stainless steel surface only within one day. It is known for forming firm colored biofilms and for its persistence against cleaning and chemical treatments [13]. Some of these species can attach firmly to the surface of the pipelines and sometimes further species can attach to these, speeding up the biofouling process [16,17]. In favourable
conditions, microbes can also produce odorous and toxic compounds such as H$_2$S or cause localized corrosion under the biofilm deposits. Many strains also degrade paper-making raw materials, such as fibers and chemicals.

1.2. Wastewater treatment in the pulp and paper mills

1.2.1. General

The wastewater produced during paper-making process has to be purified before piping into natural waters or recycling back into process. The quality of the wastewater varies significantly depending on the processes and chemicals used for pulp and paper making operations. Some wastewater quality parameters for various pulp and paper processes are presented in Table 1 [3]. It can be concluded that the variation between wastewater parameters is significant in different processes, increasing the challenges for wastewater treatment processes at mills.
Table 1. Characteristics of wastewater at various pulp and paper processes [adapted from reference 3].

<table>
<thead>
<tr>
<th>Process</th>
<th>pH</th>
<th>TS</th>
<th>SS</th>
<th>BOD₅</th>
<th>COD</th>
<th>Colour</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(mg/L)</td>
<td>(mg/L)</td>
<td>(mg/L)</td>
<td>(mg/L)</td>
<td>(Pt-Co)</td>
<td></td>
</tr>
<tr>
<td>Kraft mill</td>
<td>8.2</td>
<td>8260</td>
<td>3620</td>
<td>-</td>
<td>4112</td>
<td>4667.5</td>
<td>[18]</td>
</tr>
<tr>
<td>Bleached pulp mill</td>
<td>7.5</td>
<td>-</td>
<td>1133</td>
<td>1566</td>
<td>2572</td>
<td>4033</td>
<td>[19]</td>
</tr>
<tr>
<td>Pulp and paper mill</td>
<td>7.8</td>
<td>4200</td>
<td>1400</td>
<td>1050</td>
<td>4870</td>
<td>Dark Brown</td>
<td>[20]</td>
</tr>
<tr>
<td>Paper making</td>
<td>7.8</td>
<td>1844</td>
<td>760</td>
<td>561</td>
<td>953</td>
<td>Black</td>
<td>[21]</td>
</tr>
<tr>
<td>Paper mill</td>
<td>8.7</td>
<td>2415</td>
<td>935</td>
<td>425</td>
<td>845</td>
<td>Dark Brown</td>
<td>[22]</td>
</tr>
<tr>
<td>Paper machine</td>
<td>4.5</td>
<td>-</td>
<td>503</td>
<td>170</td>
<td>723</td>
<td>243</td>
<td>[19]</td>
</tr>
</tbody>
</table>

The main treatment process used at pulp and paper mills is primary clarification followed by biological treatment (secondary treatment). A tertiary process is needed e.g. for removing recalcitrant organic compounds or colour before water is circulated again into the process or to rivers or lakes (Fig. 1) [1]. Primary clarification can be achieved by either settlement or flotation, secondary
treatment by aerobic or anaerobic biological treatment and tertiary treatment for example by membrane processes, advanced oxidation processes or coagulation/flocculation.

Figure 1. Generalized schematic diagram of the plant for the treatment of paper mill effluent [adapted from reference 1]

1.2.2. Primary and secondary treatment

Sedimentation units usually achieve high removal rates for suspended solids, but little organic material (BOD and COD) is eliminated [1]. Flotation is also used for the removal of suspended solids [3]. Recently electrochemical techniques such as electroflotation (EF) have been applied in industrial
wastewater effluents as a primary or tertiary treatment [23,24]. Ben Mansour et al. [24] reported that the purification efficiency of suspended solids by combined coagulation/electroflotation process exceeded 95%.

Aerobic treatment is still the most popular secondary treatment technique for the removal of soluble biodegradable organic pollutants from pulp and paper mill effluents. There are numerous aerobic biological treatment systems available, but the most common is the activated sludge process, which can achieve high removal efficiencies for BOD and COD [1,3]. This process has certain disadvantages however, such as the production of sludges with very variable settlement properties, sensitivity to shock loading and toxicity, and limited capacity to remove poorly biodegradable toxic substances.

An anaerobic process has potential advantages over aerobic treatment, such as lower sludge production and chemical consumption [1]. It also produces methane which can be used for energy production. It also has its limitations, including potential hydrogen sulphide production in pulp and paper mill effluents due to the high sulphur content of wastewaters.

1.2.3. Tertiary treatment

Tertiary treatment of pulp and paper mill wastewaters is often needed to reach the target limit values set by the authorities for the further removal of residual COD, toxicity, colour and micro-organisms. Membrane-based techniques, advanced oxidation processes and physico-chemical processes are often used for this purpose [1,3].

Among the advanced treatment processes, membrane technology offers an alternative [25]. Membrane techniques include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Pizzichini et al. [26] pilot scale tested these techniques to remove salts, COD and total organic carbon (TOC) from the paper mill wastewater. MF followed by RO filtration could
recycle more than 80% of the original wastewater back into paper making process. Beril Gönder et al. [25] found out that biologically treated pulp and paper mill wastewater could be used again as process water using two-step NF. UF removed metals from totally chlorine free (TCF) wastewater and the process was enhanced by adding water-soluble polymeric ligands [27].

Chemical coagulation using alum, ferric chloride, ferric sulphate and lime have been used extensively in the treatment of different wastewaters [28]. Interest in the use of synthetic polyelectrolytes as flocculants for pulp mill wastewater treatment has grown recently [29]. The main advantage of polymeric flocculants is their ability to produce large, dense, compact and stronger flocules with good settling characteristics compared to those obtained by coagulation alone [28]. In particular polyacrylamide (PAM) flocculants have been used intensively in pulp and paper mill effluent treatment and proved their economic feasibility [28,29]. Coagulation/flocculation treatment can also be combined successfully with other techniques, such as heterogeneous photocatalysis [30].

Adsorption of organic pollutants from pulp and paper mill effluents is an alternative technique. Zhang and Chuang [31] compared the performance of styrene divinylbenzene copolymer and activated carbon for the acidic bleach plant effluent treatment. It was observed that resin is more effective than activated carbon in colour removal and that it is possible to regenerate resin by washing with sodium hydroxide solution.

Advanced oxidation processes (AOPs) for wastewater treatment have received significant attention in recent years. AOPs are based on the generation of very reactive non-selective oxidizing species such as the hydroxyl radicals [32]. These radicals can be formed by combining the following oxidizing agents: ozone (O₃), hydrogen peroxide (H₂O₂), ultraviolet (UV) radiation, ferrous and ferric salts (Fe²⁺ and Fe³⁺) and catalysts such as TiO₂. Catalkaya and Kargi [32,33] utilized these techniques in combination or individually to purify pulp mill effluents from colour, TOC and AOX compounds.
The results showed that TiO$_2$-assisted photocatalysis (UV/TiO$_2$) achieved the highest TOC and toxicity removals [32] and in another study [33] Fenton’s reagent utilizing H$_2$O$_2$/Fe$^{2+}$ resulted in the highest colour, TOC and AOX removals under acidic conditions compared to the other AOP’s tested. Solar photocatalysis [34] with Fenton reagent and TiO$_2$ and solar photo-Fenton [35] reactions have also been shown to be effective in the removal of refractory, organic compounds.

Catalysed ozonation has demonstrated promising results compared to conventional ozonation treatment. Homogeneous and heterogeneous catalysts have been used for the treatment of pulp and paper mill effluents [36,37]. Activated carbon together with ozonation treatment could increase the BOD$_5$/COD ratio from 0.11 to 0.28 and 87 % of colour was removed from chlorination, extraction and hypochlorite (CEH) bleaching effluent [36]. Fontanier et al. [37] used TOCCATA® catalyst in treating three different wastewaters from pulp and paper mills. It was shown that organic matter was removed through the steady conversion of organic carbon to carbon dioxide. Ozonation has also been applied to NF concentrate to increase its biodegradability [38].

Electrochemical techniques have been applied recently in pulp and paper mill wastewater treatment. Vepsäläinen et al. [39] investigated natural organic matter (NOM) removal by electrocoagulation (EC) together with chemical coagulation. The results indicated that the combined method was efficient in removing NOM even with small electric charges per litre. EC has also yielded promising results in sulphide and toxic pollutant removal from pulp and paper mill effluents [40,41].

Though several pulp and paper mill wastewater treatment techniques are available, many of these are still associated with high investment and running costs or lack of efficiency to remove refractory organic pollutants from effluents. It is important to maximize purification efficiencies and develop new, simple in situ techniques for treating pulp and paper mill effluents and circulating waters.
Strategies that promote lower energy use, reduce the amount of solid waste produced and increase efficient energy recovery are economically sustainable [42].

1.3. Electrochemical oxidation in water and wastewater treatment

1.3.1. General

Electrochemical techniques have been applied extensively to treat various wastewaters, disinfect drinking water or enhance polluted soils [43-52]. These include e.g. EC, EF, EO and electrokinetic treatment. Conventional water purification techniques, such as chemical coagulation, biological treatment or UV oxidation, are not effective against some toxic and refractory organic pollutants. Electrochemical techniques can offer a more efficient means of treating these pollutants.

Electrochemical techniques are innovative, inexpensive and effective methods for purifying wastewaters from many industrial processes before discharge into water systems or circulation back into processes [44]. They could also be called “green technology” methods because little or no chemicals are needed to facilitate water treatment. Electrochemical techniques can also be applied in sludge treatment. Tuan et al. [46] wrote a review about applying electro-dewatering to sewage sludge treatment. It was found that electro-dewatering has several potential benefits, such as lower energy and transportation costs and enhanced solid-liquid separation of sludge. Yet high operation costs still hinder the use of electro-dewatering in large scale applications.

Electrokinetic Fenton process is a promising technology for the remediation of low permeable soil [47,48]. It is effective for highly biorefractory contaminants, such as hexachlorobenzene. It is important to optimize parameters such as pH level at the cathode region or contact between the contaminant and the oxidant during the treatment, however [47,48].
Ultrasonically enhanced electrokinetics can increase pollutant removal from soils \[49,50\]. It has several advantages, such as lack of dangerous breakdown products and compact and transportable on-site treatment. Yet it still has technical limitations such as scaling up and physical effects such as noise.

EC is currently enjoying both increased popularity and major technical improvement \[44\]. It is a rather simple and robust technique and can be applied in many environments. However, it involves several chemical and physical phenomena which should be well understood before effective treatment. When “sacrificial” iron and aluminium anodes are releasing ions into water, EF occurs simultaneously by hydrogen and oxygen bubbles released at the electrodes, improving purification efficiency. Disadvantages of EC are the periodical need for replacement of anodes, electrode passivation and the lack of any systematic approach to reactor design and operation \[45\].

An important factor in EF treatment is the size of bubbles formed at the electrodes \[43\]. Smaller bubbles are more efficient in pollutant removal because of the larger surface area available for particle attachment. EF is a promising technique especially in oily wastewater treatment and it shows advantages over either DAF or settling.

EO treatment has received a great deal of interest in wastewater treatment and drinking water disinfection in recent years \[43\]. The technique is rather simple. Oxidants are produced during the treatment in situ either at the electrodes or indirectly by chemical compounds in the treated water. Unfortunately the lack of efficient and stable yet economical electrode material has hindered the large scale application of this technique to date.
1.3.2. Theory of electro-oxidation

Thermodynamically, the electrochemical degradation of any soluble organic compound in water should be achieved at low potentials, before the thermodynamic potential of water oxidation to molecular oxygen (1.23 V/SHE under standard conditions) as indicated in formula 1 [53]:

$$2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad (1)$$

In acidic media, water can be discharged on the electrode producing highly oxidative absorbed hydroxyl radicals (reaction 2):

$$\text{H}_2\text{O} + \text{M} \rightarrow \text{M}^{\cdot}\text{OH} + \text{H}^+ + \text{e}^- \quad (2)$$

where M means electrode surface.

These radicals are physisorbed on the anode surface where the organic pollutant R can be oxidized as follows (reaction 3):

$$\text{R}_{(aq)} + \text{M}^{\cdot}\text{OH}_{n/2} \rightarrow \text{M} + \text{Oxidation products} + \frac{n}{2}\text{H}^+ + \frac{n}{2}\text{e}^- \quad (3)$$

where $n$ is the number of electrons involved in the oxidation reaction of R. The reaction of organics with electrogenerated hydroxyl radicals (3) is in competition with the side reaction of the anodic discharge of these radicals to oxygen (reaction 4):

$$\text{M}^{\cdot}\text{OH} \rightarrow \text{M} + \frac{1}{2}\text{O}_2 + \text{H}^+ + \text{e}^- \quad (4)$$

Anodic activity by electrodes depends on their value of overpotential for oxygen evolution [43]. Platinum electrodes have much lower potential value for oxygen evolution reactions (1.3 V vs. SHE) than for example SnO$_2$ electrodes (1.9 V vs. SHE) or boron-doped diamond electrodes (Ti/BDD, 2.7 V vs. SHE). This signifies that anodic oxidation by hydroxyl radicals can take place on a Ti/BDD
electrode surface at a significantly higher current density with a minimal oxygen evolution side reaction.

Electrochemical oxidation may also occur by an indirect process where oxidants like chlorine, hypochlorous acid and hypochlorite [54-60] or hydrogen peroxide/ozone [61-64] are formed at electrodes by following reactions (5-11):

\[
\begin{align*}
2\text{Cl}^- & \rightarrow \text{Cl}_2 + 2e^- \quad (5) \\
\text{Cl}_2 + \text{H}_2\text{O} & \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad (6) \\
\text{HOCl} & \rightarrow \text{H}^+ + \text{OCl}^- \quad (7) \\
\text{H}_2\text{O} & \rightarrow \cdot\text{OH} + \text{H}^+ + e^- \quad (8) \\
2 \cdot\text{OH} & \rightarrow \text{H}_2\text{O}_2 \quad (9) \\
\text{H}_2\text{O}_2 & \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^- \quad (10) \\
\text{O}_2 + \cdot\text{O} & \rightarrow \text{O}_3 \quad (11)
\end{align*}
\]

At acidic pH, chlorine is present in the solution in the form of hypochlorous acid, which has a higher oxidation potential (1.49 V) than hypochlorite (0.94 V). Under alkaline conditions hypochlorite is a dominant species [55]. Under higher pH conditions more chlorate or perchlorate is also formed instead of chlorine/hypochlorite, which decreases oxidation efficiency. Higher initial chloride concentration in the electrolyte solution naturally encourages more chlorine/hypochlorite production [54-56]. A similar effect can be observed by lowering the temperature of the electrolyte solution, but this depends on the electrode material used [56]. Higher current density also increases chlorine production [55,56].
Electrochemical production of reactive oxygen species (ROS) such as ozone and hydrogen peroxide has proved effective in water disinfection without the mediation of active chlorine products [61]. In an electro-Fenton oxidation process, H₂O₂ is continuously generated in acidic solutions by the reduction of O₂ at the graphite cathodes or carbon felt [62]. When Fe²⁺ is introduced as the catalyst, a Fenton reaction takes place in the solution, generating hydroxyl radicals to decompose pollutants or disinfect bacteria. Chu et al. [63] recognized effective degradation of 4-nitrophenol by employing a dual-cathode system to generate H₂O₂ and Fe²⁺ simultaneously at two cathodes to encourage an electro-Fenton reaction in the solution together with anodic oxidation by hydroxyl radicals at the anode. Guinea et al. [64] achieved almost total mineralization of enrofloxacin solutions by solar photoelectro-Fenton (SPEF) treatment using an O₂-diffusion cathode. Some examples of indirect electro-oxidation studies are shown in Table 2.

Efficient organic pollutant removal can be achieved also by generating Fe²⁺ in situ by an EC process where an iron anode is dissolved into a solution, causing a Fenton reaction when hydrogen peroxide is added to the solution [65,66]. Martins et al. [65] could remove 95 % of nonylphenol polyethoxylate in five minutes (aqueous solution) and in ten minutes (wastewater), respectively.
Table 2. Indirect electro-oxidation of pollutants

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Pollutant, Colour</th>
<th>Anode material</th>
<th>Removal efficiency</th>
<th>Main oxidant</th>
<th>Current density (mA/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic dye wastewater</td>
<td>-</td>
<td>IrO₂-Ta₂O₅</td>
<td>-</td>
<td>Chlorine/hypochlorite</td>
<td>15</td>
<td>[56]</td>
</tr>
<tr>
<td>Synthetic water</td>
<td>-</td>
<td>IrO₂/RuO₂</td>
<td>-</td>
<td>Chlorine/hypochlorite</td>
<td>30</td>
<td>[57]</td>
</tr>
<tr>
<td>Synthetic dye wastewater</td>
<td>Colour</td>
<td>Ti anode covered by Ta, Pt and Ir thin film</td>
<td>100%</td>
<td>Chlorine/hypochlorite</td>
<td>5,10,14 and 20 A</td>
<td>[58]</td>
</tr>
<tr>
<td>Synthetic dye wastewater</td>
<td>Colour</td>
<td>Nb/D and Pt/Ti</td>
<td>up to 90%</td>
<td>Chlorine/hypochlorite</td>
<td>12-18 V (anode potential)</td>
<td>[59]</td>
</tr>
<tr>
<td>Synthetic water</td>
<td>E. Coli</td>
<td>BDD</td>
<td>under detection limit</td>
<td>Ozone, hydrogen peroxide</td>
<td>5.7 and 9 V (cell potential)</td>
<td>[61]</td>
</tr>
<tr>
<td>Synthetic water</td>
<td>Rotenone (COD removal)</td>
<td>Pt net</td>
<td>&gt; 97%</td>
<td>Hydrogen peroxide (EF)</td>
<td>10-60</td>
<td>[62]</td>
</tr>
</tbody>
</table>
### Table contd.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Pollutant</th>
<th>Anode material</th>
<th>Removal efficiency</th>
<th>Main oxidant</th>
<th>Current density (mA/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic water</td>
<td>4-nitrophenol (TOC removal)</td>
<td>Ti/SnO₂-Sb₂O₃-IrO₂</td>
<td>74.5 %</td>
<td>Hydrogen peroxide (EF)</td>
<td>-0.80 and -0.10 V/SCE</td>
<td>[63]</td>
</tr>
<tr>
<td>Synthetic water</td>
<td>Fluoroquinolone enrofloxacin (TOC removal)</td>
<td>Pt sheet and BDD thin film</td>
<td>Almost 100 %</td>
<td>Hydrogen peroxide (SPEF)</td>
<td>33</td>
<td>[64]</td>
</tr>
</tbody>
</table>

#### 1.3.3. Electrodes

Several electrodes have been used for water treatment by electrochemical oxidation. Anodes used for water and wastewater treatment include lead and lead dioxide [67-70], DSA electrodes [71-74], graphite [75-77] and boron-doped diamond electrodes [70,78-85].

Lead and lead dioxide have been used as anodes because of their stability, low cost and high oxygen evolution potential which delays O₂ evolution in favour of Cl₂ evolution [67]. Hamza et al. [68] completely mineralized 1,3,5-trimethoxybenzene in acid media at a Ta/PbO₂ anode. They discovered that all oxidation products were finally oxidized to CO₂ by the intermediary of carboxylic acids. Awad and Abo Galwa [69] found out that the electrocatalytic activity of a lead dioxide electrode depends on the conductive electrolyte. They concluded that in the presence of H₂SO₄ electrolyte electrode poisoning occurred, since an adherent film was formed on the anode surface. The dissolution of toxic Pb²⁺ ions also hinders the use of lead and lead dioxide as anodes [43].
DSA are catalytic oxide electrodes which can effectively generate active hydroxyl radicals and active chloride species [72]. They also have a relatively high overpotential for oxygen evolution. Efficient degradation of paper mill wastewater was achieved using three-dimensional electrodes (Ti/Co/SnO₂-Sb₂O₃) combined with activated carbon treatment [72]. This was mainly due to the fact that the conversion rate within an electrochemical reactor can be increased substantially due to its large specific surface area in comparison to conventional two-dimensional electrodes. So-called “non-active” electrodes such as SnO₂ form hydroxyl radicals on their surface more easily, which can result in the complete oxidation of the organic molecules to CO₂ [74]. With “active electrodes”, such as RuO₂ and IrO₂, only selective oxidation of the organic species in the solution occurs.

Effective removal of COD (> 96 %) was achieved when the electrochemical degradation process was catalysed by transition metals (Co and Cu) [76] or molybdenum and phosphate (Mo-P) modified kaolin with graphite as the anode and cathode [77]. Pollutants were adsorbed on the surface of the kaolin where they were oxidized by hydroxyl radicals produced at the graphite cathode by the reaction of hydrogen peroxide and transition metals [76]. This process is similar to the electro-Fenton process.

Recently the potential of conducting diamond films for water treatment has been recognised. They have an inert surface with low adsorption properties, remarkable corrosion stability even in strong acidic media and an extremely wide potential window in aqueous and non-aqueous media [79,81]. They also have the highest oxygen evolution overpotential value [43,79] meaning that more hydroxyl radicals are formed on the anode surface during treatment. BDD electrodes can also degrade refractory organic pollutants completely and the nature of the pollutant does not affect the efficiency of the process significantly [80]. It is also known that besides hydroxyl radical formation on the electrode surface, diamond electrodes also increase mediated oxidation by other electrochemically
formed compounds such as persulphate, perphosphate, percarbonate or hypochlorite depending on the electrolyte used.

The low pressure conversion of carbon to diamond crystals has made it possible to grow a thin layer of diamond film on suitable substrates such as silicon, niobium, tungsten, molybdenum, and titanium [82]. Hot filament chemical vapour deposition (HFCVD) technique has been applied primarily to fabricate active and stable BDD electrodes, mainly using titanium as a substrate material [82,84,85]. Migliorini et al. [85] used an additional H2 gas flux passing through a bubbler containing a solution of B2O3 dissolved in CH3OH with a B/C ratio of 30,000 ppm during the HFCVD coating of diamond films. Two different fluxes were used to produce heavily boron-doped diamond films. Figure 2 shows the top view of scanning electron microscope (SEM) images of the deposited diamond films. The images present well-facetted microcrystalline diamond surfaces for both coatings and a significant increase in the smallest diamond grain population for E2 because as the boron content increases, the diamond grain size decreases.

Figure 2. SEM images of E1 and E2 BDD films [85]
The main advantages and disadvantages of different electrodes in EO treatment are presented in Table 3.

Table 3. Comparison of electrodes in EO treatment

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Compared to other electrodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Stable</td>
<td>Passive, expensive</td>
<td>Poor efficiency in anodic oxidation of organic compounds</td>
</tr>
<tr>
<td>Pt</td>
<td>Inert, low oxygen evolution overpotential</td>
<td>Expensive</td>
<td></td>
</tr>
<tr>
<td>PbO₂</td>
<td>Good current efficiency, cheap, effective in oxidizing pollutants, high oxygen evolution overpotential, easy to prepare</td>
<td>Corrosive, toxic Pb²⁺-ions could be released</td>
<td></td>
</tr>
<tr>
<td>DSA electrodes</td>
<td>Supports indirect oxidation, good current efficiency, high oxygen evolution overpotential, lower cost, higher availability</td>
<td>Short lifetime, lack of electrochemical stability</td>
<td></td>
</tr>
<tr>
<td>BDD</td>
<td>Inert in tough conditions, high oxygen evolution overpotential and electrochemical stability, good current efficiency, high corrosion stability, good conductivity</td>
<td>Very expensive</td>
<td>Higher activity</td>
</tr>
</tbody>
</table>
1.3.4. Treatment of different wastewaters

EO treatment has been applied in various wastewaters. The treatment of highly refractory dyes has yielded especially promising results [86-89]. Ma et al. [86] found out that 96.47% of COD could be removed from methylene blue (MB) containing wastewater assisted by Fe_2O_3-modified kaolin with graphite plate electrodes. The performances of the Ti-Pt/β-PbO_2 and BDD electrodes were investigated in Reactive Orange 16 dye treatment [87]. Total decolourisation was achieved by both electrodes but BDD electrode was more effective with lower energy consumption. A study by Tsantaki et al. [88] showed that complete decolourisation of textile dyehouse effluents was achieved by BDD electrodes in 180 minutes. Song et al. [89] observed that the decolouring efficiency of the azo dye C.I. Reactive Red 195 increased whereas the mineralization efficiency decreased with increasing concentrations of NaCl signifying that oxidized active chlorine at the anode favours the oxidation cleavage of the azo bond.

Ramirez et al. [90] degraded methyl orange azo dye in a recirculation flow plant system. BDD electrodes gave an optimum decolourization efficiency of about 94% with a flow rate of 12 L/min and response surface methodology (RSM) was used to describe the EO treatment behaviour.

Coupling ozone and EO treatment significantly improved COD removal from industrial wastewater [91]. The coupled process was efficient at a relatively low current density so the synergistic effect was easily recognized. Xu et al. [92] and Park et al. [93] presented the innovative approach of combining membrane filtration techniques such as NF and MF with EO treatment. It was observed that the concentration polarization and membrane fouling were effectively restrained by electroosmosis, electrophoresis and EO treatment [92]. During electrochemical degradation of municipal wastewater the simultaneous production of hydrogen fuel was observed [93]. MF after EO
treatment achieved significant TOC and turbidity removals, with a clear reduction in membrane fouling.

EO treatment together with biological oxidation was investigated in individual, combined and integrated methods [94]. It was observed that the combined process performed rather better than the individual, but took longer. It was concluded that combined processes can be improved by optimizing process parameters and experimental design. A study by Gonçalves et al. [95] presented the positive performance of a two-step process consisting of anaerobic digestion followed by EO in olive mill wastewater treatment.

A novel catalyst prepared by Chen et al. [96] showed excellent catalytic activity in the electrochemical treatment of 1-naphthylamine wastewater. Kinetic experiments with EO resulted in the complete removal of iohexol and showed great agreement between the experimental results and the kinetic model [97].

EO treatment of reverse osmosis concentrate revealed that in the presence of high chloride ions concentrations of persistent halogenated by-products will be formed [98]. Another study by Bagastyo et al. [99] showed that effective dissolved organic carbon (DOC) removal could be achieved without chlorine mediated oxidation and by-products. Toxic by-products hinder the use of the EO technique in wastewater treatment and other water purification techniques are needed for removing by-products before water will be recycled back into the process or released into natural waters.

Some comparison in the treatment of different wastewaters and pollutants has been presented in Table 4.
Table 4. EO treatment of different pollutants

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Pollutant</th>
<th>Electrodes</th>
<th>Removal efficiency</th>
<th>Current densities used (mA/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic dye wastewater</td>
<td>COD</td>
<td>Graphite</td>
<td>96.47 %</td>
<td>69.23</td>
<td>[86]</td>
</tr>
<tr>
<td>Synthetic dye wastewater</td>
<td>Colour</td>
<td>Ti-Pt/β-PbO₂, BDD</td>
<td>100 %</td>
<td>10-70</td>
<td>[87]</td>
</tr>
<tr>
<td>Synthetic dye wastewater</td>
<td>Colour</td>
<td>BDD</td>
<td>100 %</td>
<td>4-50</td>
<td>[88]</td>
</tr>
<tr>
<td>Synthetic dye wastewater</td>
<td>Colour</td>
<td>Ti/SnO₂-Sb/PbO₂</td>
<td>100 %</td>
<td>5-40</td>
<td>[89]</td>
</tr>
<tr>
<td>Olive mill wastewater</td>
<td>COD, colour</td>
<td>Ti/TiRuO₂</td>
<td>100 %</td>
<td>60</td>
<td>[100]</td>
</tr>
<tr>
<td>Olive mill wastewater</td>
<td>Colour, phenols</td>
<td>Ti/IrO₂</td>
<td>100 %</td>
<td>50</td>
<td>[101]</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Paracetamol</td>
<td>BDD</td>
<td>&gt; 98 % of TOC decay</td>
<td>33-150</td>
<td>[102]</td>
</tr>
<tr>
<td>Tannery wastewater</td>
<td>COD, ammonia, Cr, sulphides</td>
<td>Ti/Pt-Ir, Ti/PbO₂, Ti/PdO-Co₃O₄, Ti/RhO₂-TiO₂</td>
<td>Satisfactory with all anodes</td>
<td>20 and 40</td>
<td>[103]</td>
</tr>
<tr>
<td>Pulp bleaching effluent</td>
<td>Pentachlorophenol</td>
<td>Graphite</td>
<td>100 %</td>
<td>6</td>
<td>[75]</td>
</tr>
<tr>
<td>Paper mill effluent</td>
<td>Organic material: COD</td>
<td>Lead</td>
<td>&gt; 96 %</td>
<td>2.2-11</td>
<td>[67]</td>
</tr>
<tr>
<td>Dye wastewater</td>
<td>Anthraquinone dye</td>
<td>BDD</td>
<td>100 %</td>
<td>30</td>
<td>[83]</td>
</tr>
</tbody>
</table>
Table contd.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Pollutant</th>
<th>Electrodes</th>
<th>Removal efficiency</th>
<th>Current densities used (mA/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic wastewater</td>
<td>Phenol</td>
<td>Ti/SnO₂-Sb, Ti/RuO₂, Pt</td>
<td>100 %</td>
<td>20</td>
<td>[104]</td>
</tr>
<tr>
<td>Coking wastewater (TOC)</td>
<td>Organic pollutants</td>
<td>BDD</td>
<td>almost 100 %</td>
<td>20-60</td>
<td>[105]</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>2,4-dichlorophenol</td>
<td>Ti-based oxide electrode</td>
<td>almost 100 %</td>
<td>- 1.5 to 1.5 V (anodic potential)</td>
<td>[106]</td>
</tr>
<tr>
<td>Domestic wastewater</td>
<td>Sulphide</td>
<td>Ta/Ir, Ru/Ir, Pt/Ir, SnO₂, PbO₂</td>
<td>77-85 %</td>
<td>10</td>
<td>[107]</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Ketoprofen</td>
<td>BDD and Pt</td>
<td>100 %</td>
<td>4.4, 8.9 and 13.3</td>
<td>[108]</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>1,4-dioxane</td>
<td>BDD</td>
<td>&gt; 95 %</td>
<td>5,15 and 25</td>
<td>[109]</td>
</tr>
<tr>
<td>Landfill leachate</td>
<td>Ammonium</td>
<td>BDD</td>
<td>100 %</td>
<td>15-90</td>
<td>[110]</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Surfactants (TOC)</td>
<td>BDD</td>
<td>82 %</td>
<td>4-20</td>
<td>[111]</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>4,6-dinitro-α-cresol</td>
<td>BDD</td>
<td>100 %</td>
<td>33-150</td>
<td>[112]</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Triclosan</td>
<td>BDD</td>
<td>&gt; 99 %</td>
<td>6-15</td>
<td>[113]</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Progesterone</td>
<td>BDD</td>
<td>Almost complete</td>
<td>15-100</td>
<td>[114]</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Sulfamethoxazole</td>
<td>BDD</td>
<td>to below 0.1 μg/L</td>
<td>15-100</td>
<td>[115]</td>
</tr>
</tbody>
</table>
Table contd.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Pollutant</th>
<th>Electrodes</th>
<th>Removal efficiency</th>
<th>Current densities used (mA/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic wastewater</td>
<td>Chlorpyrifos</td>
<td>BDD</td>
<td>100 %</td>
<td>15 and 30</td>
<td>[116]</td>
</tr>
<tr>
<td>Citric acid wastewater</td>
<td>Organic pollutants</td>
<td>Ti/RuO₂-IrO₂</td>
<td>Almost 100 %</td>
<td>9 V (cell potential)</td>
<td>[117]</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Chloroxylenol</td>
<td>Pt, BDD</td>
<td>100 % (with BDD)</td>
<td>33, 100, 150</td>
<td>[118]</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Diclofenac</td>
<td>Pt, BDD</td>
<td>100 %</td>
<td>150</td>
<td>[119]</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Atrazine</td>
<td>BDD</td>
<td>up to 94 %</td>
<td>100</td>
<td>[120]</td>
</tr>
</tbody>
</table>

EO treatment achieved 100 % removal of colour from olive mill wastewaters by DSA electrodes [100,101]. In both cases indirect oxidation by active chlorine took place. Also, bulk electrolysis of wastewater showed that degradation proceeded through partial oxidation reactions to intermediates that are eventually mineralized to carbon dioxide and water [101].

The effect of experimental parameters on oxidation results has been investigated in several papers. Commonly increasing the pH improves pollutant degradation efficiency [106,108,111]. Contrarily, the opposite has also been observed [112]. Higher current density [105,108,111,112], temperature [105,109,112] and initial pollutant concentration also increase the removal rates [111,112].

Based on the results in Table 4, it can be concluded that BDD electrodes are highly efficient for the removal of different organic pollutants. Degradation current efficiencies can vary significantly,
however, and it is important to achieve the required removal efficiency by adjusting the applied current density together with the removal time and energy consumption of the process [109].

One novel approach is to use solar photo-assisted EO treatment for organic pollutant degradation [121,122]. It allows more rapid mineralization of carboxylic acids [121] and photovoltaic solar EO is a self-sustaining wastewater treatment process [122]. The main benefits can be summarized as follows: there is no need for energy storage systems and sun energy can be directly supplied to the treatment process [122].

Comparison of different AOP’s (such as EO, ozonation and Fenton oxidation) shows that all technologies can reduce the organic content of wastewaters but with different performances [123,124]. EO was the most efficient in mineralization of enrofloxacin but not as effective as ozonation in COD removal [123]. Removal of organic material also seems to depend greatly on the addition of an electrolyte salt in EO treatment [124]. The differences in purification efficiencies can be explained mainly in terms of the contribution of hydroxyl radicals and other oxidation mechanisms involved in each technology.

1.3.5. Disinfection of wastewater and drinking water

Electrochemical oxidation has also been used in disinfection of drinking water and various wastewaters. Jeong et al. [125] applied EO to disinfect Escherichia coli in drinking water. They found that the main mechanism was inactivation of bacteria by hydroxyl radicals produced by water discharge, also involving direct oxidation at the electrode surface. ROS can also cause effective inactivation [61,126-128]. It was observed that different electrodes have different abilities to produce radicals, e.g. BDD electrodes prefer to form hydroxyl radicals and DSA electrodes activate chlorine, depending on the electrolyte solution used [127]. Also, inactivation of E. coli at BDD and Pt electrodes was mainly achieved by the reaction of hydroxyl radical and the direct electron transfer...
reaction, respectively. Ma et al. [128] noticed that a hemin/graphite electrode was preferable to produce ROS compounds, such as $\text{H}_2\text{O}_2$ and $^\cdot\text{OH}$, at the cathode surface when applying low potentials without any addition of chloride. A sterilizing rate as high as 99.9% could be obtained after 60 minutes of inactivation. Fang et al. [129] and Drees et al. [130] also observed effective bacteriophage MS2 inactivation in drinking water. Yet the inactivation rate for bacteriophage MS2 was much lower than for $\textit{E. coli}$ demonstrating that bacteria are more sensitive to electrochemical inactivation than bacteriophages [130]. Electrochemically generated oxidants were a major cause of inactivation within the electrochemical cells.

EO has also been applied in $\textit{Legionella}$ bacteria disinfection of germinated brown rice circulating waters and cooling tower waters [131]. Disinfection was attributed to the synergistic effects of the oxide anode, the electric field and the radicals formed during the treatment. This observation strongly suggests that electrochemical oxidation could be applicable to the disinfection of waters from other sources. The technique has shown its potential also in the treatment of municipal wastewaters [132] and for disinfection in seawater desalination systems where biofouling of the desalination plant membranes can be prevented without using chlorination [133]. Total removal of coliform bacteria was achieved with very different raw wastewaters and the main disinfectants produced depended on the applied current density, the concentration of chlorides and the concentration of non-oxidized nitrogen in the electrolyte [132].

Though EO has shown promising results in wastewater purification from organic pollutants and disinfection of drinking water, it has its drawbacks. For example some disinfection by-products, such as perchlorates or bromates, can be produced during the treatment. Oh et al. [134] observed that this phenomenon occurred during the desalination treatment of seawater and bromate concentrations were some orders of magnitude higher than the USEPA regulation. It was strongly indicated that the application of electrochemical treatment to seawater desalination cannot be recommended without the
control of bromate by-product formation. It is also possible to find nitrite, ammonia and monochloramine residues in drinking water disinfection depending on the treatment conditions and original water quality parameters [135].

EO has been applied also to ballast water treatment in the disinfection of *Artemia salina* [136] and for algae removal using *Chlorella vulgaris* as a model organism [137]. A current density of 135 mA/cm² and a treatment time of around 1 minute could achieve 100 % mortality of *A. salina*, the main oxidant being chlorine together with direct oxidation at the anode surface [136]. Total inactivation of *C. vulgaris* was achieved by EO when 100 mg/L of chloride was present in the solution so the main mechanism killing the algae was long life oxidants electrogenerated at the anode surface [137].

Some studies of electrochemical disinfection of different microbes are presented in Table 5.

Table 5. EO treatment in disinfection of different waters

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Microbe</th>
<th>Anode</th>
<th>Removal efficiency</th>
<th>Current densities used (mA/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic water</td>
<td><em>Escherichia coli</em></td>
<td>Pt</td>
<td>90 %</td>
<td>0-100</td>
<td>[125]</td>
</tr>
<tr>
<td>Tap water</td>
<td><em>Escherichia coli</em></td>
<td>BDD</td>
<td>5 log reduction</td>
<td>24 and 216</td>
<td>[126]</td>
</tr>
<tr>
<td>Synthetic water</td>
<td><em>Escherichia coli</em></td>
<td>BDD, Ti/RuO₂, Ti/IrO₂, Ti/Pt-IrO₂, Pt</td>
<td>2.4 log reduction (BDD)</td>
<td>17-167</td>
<td>[127]</td>
</tr>
<tr>
<td>Synthetic water</td>
<td><em>Escherichia coli</em></td>
<td>Graphite felt</td>
<td>almost 100 %</td>
<td>-0.6 V vs. SCE (anodic potential)</td>
<td>[128]</td>
</tr>
</tbody>
</table>

38
<table>
<thead>
<tr>
<th>Matrix</th>
<th>Microbe</th>
<th>Anode</th>
<th>Removal efficiency</th>
<th>Current densities used (mA/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic water</td>
<td>Bacteriophage MS2</td>
<td>Ti pellet with a thin layer of IrO₂-Sb₂O₃-SnO₂</td>
<td>8 log reduction</td>
<td>0.20 A</td>
<td>[129]</td>
</tr>
<tr>
<td>Synthetic water</td>
<td><em>Escherichia coli</em>, <em>Pseudomonas aeruginosa</em>, bacteriophages MS2 and PRD1</td>
<td>Pt-tipped copper wire</td>
<td>even 4 log reduction (<em>P. aeruginosa</em>)</td>
<td>5-350 mA</td>
<td>[130]</td>
</tr>
<tr>
<td>Germinated brown rice</td>
<td><em>Legionella</em></td>
<td>Ti/RuO₂</td>
<td>100 %</td>
<td>1.0 and 1.5 kV (cell potential)</td>
<td>[131]</td>
</tr>
<tr>
<td>circulating water and</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cooling tower water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Municipal wastewater</td>
<td><em>Escherichia coli</em></td>
<td>BDD</td>
<td>100 %</td>
<td>1.3-13</td>
<td>[132]</td>
</tr>
<tr>
<td>Sea water</td>
<td><em>Bacillus sp.</em></td>
<td>-</td>
<td>100 %</td>
<td>110</td>
<td>[133]</td>
</tr>
<tr>
<td>Tertiary treated wastewater</td>
<td><em>Escherichia coli</em></td>
<td>BDD</td>
<td>100 %</td>
<td>2.1</td>
<td>[138]</td>
</tr>
<tr>
<td>Saline secondary effluent</td>
<td>Coliform bacteria</td>
<td>Ti/RuO₂/TiO₂</td>
<td>99.9 %</td>
<td>0-30</td>
<td>[139]</td>
</tr>
<tr>
<td>Biologically treated</td>
<td>Coliform bacteria</td>
<td>BDD</td>
<td>4 log reduction</td>
<td>2.5-120</td>
<td>[140]</td>
</tr>
<tr>
<td>wastewater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthetic water</td>
<td><em>Escherichia coli</em> K-12</td>
<td>BDD</td>
<td>100 %</td>
<td>5-40</td>
<td>[141]</td>
</tr>
</tbody>
</table>
Table contd.

<table>
<thead>
<tr>
<th>Synthetic water</th>
<th><em>Escherichia coli</em> K-12</th>
<th>BDD</th>
<th>Almost 100 %</th>
<th>20</th>
<th>[142]</th>
</tr>
</thead>
</table>

2 OBJECTIVES OF THE STUDY

The overall objective of this study was to investigate the inactivation of biofilm forming bacteria present in a paper mill environment by electro-oxidation (EO). The main goal was to discover electrochemical behaviour and the efficiency of different electrode materials during the treatment. Another focus of the research was the applicability of EO to sulphide and organic material removal in real paper mill wastewaters. The enhancement of treatment together with biocides (such as hydrogen peroxide) was a further research interest.

The specific aims of the study were:

1. Investigating the electrochemical behaviour of some electrode materials in paper mill water and their inactivation efficiency against primary biofilm forming bacteria *Deinococcus geothermalis*, *Meiothermus silvanus* and *Pseudoxanthomonas taiwanensis* and discovering the main inactivation mechanisms. Studying the influence of parameters, such as current density and initial pH or chloride concentration of paper mill water on the inactivation efficiencies (Papers I and II).
2. Studying the efficiency of the EO treatment in sulphide removal from paper mill wastewaters and inactivation of sulphide forming anaerobic bacteria (Paper III)
3. Studying the electrochemical behaviour of electrodes combined with biocides in paper mill water and discovering the oxidation and radical formation mechanisms. Finding the synergistic effects when combining biocides with polarization treatment (Paper IV).
4. Investigating EO in the degradation of methyl orange dye in synthetic wastewater and studying effect of key operative parameters on degradation efficiency. Discovering the oxidation mechanism (Paper V).
5. Discovering the purification efficiency of EO compared to some other common
physico-chemical treatment methods used in pulp and paper mill wastewater treatment (Paper VI).
3 MATERIALS AND METHODS

3.1. Reactors and electrodes

The electrochemical treatment system used for electro-oxidation of *Deinococcus geothermalis* bacteria in paper I is shown in Fig. 3.

Figure 3. Electrochemical oxidation reactor used in Paper I

1. Sample tank (V= 5 L)  
2. Electro-oxidation reaction tank (V= 75 mL)  
3. Electrodes (A= 1 cm²)  
4. Tube (diameter = 8 mm)  
5. Reference electrode (Saturated calomel electrode, SCE)

P: Tube pump pumping a water sample from the sample tank to the reaction tank

For the experiments in papers II, III, IV and V a sterile beaker was used as a reaction chamber. Volumes, electrode materials and current densities used for the experiments in this study are presented in Table 6. SCE was selected as the reference electrode.
<table>
<thead>
<tr>
<th>Paper</th>
<th>Volume</th>
<th>Reaction chamber and volume</th>
<th>Pollutant</th>
<th>Anode material</th>
<th>Cathode material</th>
<th>Current densities used (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>75 mL</td>
<td>Paper I</td>
<td>Deinococcus geothermals E50051</td>
<td>PbO₂, MMO and BDD</td>
<td>Pt wire</td>
<td>25-75</td>
</tr>
<tr>
<td>II</td>
<td>250 mL</td>
<td>Paper II</td>
<td>Deinococcus geothermals E50051, Pseudoxanthomonas taiwanensis JN1109, Meiothermus silvanus B-R2A5-50.4</td>
<td>MMO</td>
<td>Stainless steel rod</td>
<td>5-65</td>
</tr>
<tr>
<td>III</td>
<td>500 mL</td>
<td>Paper III</td>
<td>Sulphide, anaerobic bacteria</td>
<td>MMO</td>
<td>MMO</td>
<td>14.3 – 42.9</td>
</tr>
<tr>
<td>IV</td>
<td>500 mL</td>
<td>Paper IV</td>
<td>MMO, stainless steel 2343</td>
<td>MMO</td>
<td>MMO</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>200 mL</td>
<td>Paper V</td>
<td>Methyl orange dye</td>
<td>MMO, BDD</td>
<td>Stainless steel plate</td>
<td>30 and 50</td>
</tr>
</tbody>
</table>
Table contd.

<table>
<thead>
<tr>
<th>Reaction chamber and volume</th>
<th>Pollutant</th>
<th>Anode material</th>
<th>Cathode material</th>
<th>Current densities used (mA/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper VI</td>
<td>3 L</td>
<td>COD, resin acids</td>
<td>BDD, MMO</td>
<td>BDD, MMO 4.7 and 9.5</td>
</tr>
</tbody>
</table>

Figure 4 shows the experimental apparatus of the electrochemical system in paper VI. The reactor was equipped with circulation. Two types of electrodes were tested as anodes and cathodes; BDD electrodes and MMO electrodes. The surface area of the BDD anode was 644 cm\(^2\) and the current density used was 4.7 mA/cm\(^2\). The surface area of the MMO anode was 315 cm\(^2\) and the current density used was 9.5 mA/cm\(^2\). Stream velocity was adjusted to 1 L/min and the volume of the water sample was three litres. The recycling time was 60 minutes and the samples were taken at variable time intervals.
3.2. Chemicals

3.2.1. Wastewaters used for the experiments

Synthetic paper mill waters were used for the experiments in papers I, II and IV. The composition of the synthetic paper mill water is presented in Table 7 and was developed by Peltola et al. [13]. More detailed compositions are represented in published papers I, II and IV. In paper III real paper mill wastewater was used (Table 8). Methyl orange was used as a pollutant for the experiments in paper V. Finally, in paper VI wastewater samples (Table 9) were obtained from three Finnish pulp and paper mills which produce peroxide bleached mechanical pulp. These mills are hence called mill A, mill B and mill C. Samples were collected after the primary clarifier and biological process.
Table 7. Composition of synthetic paper mill water [13]

<table>
<thead>
<tr>
<th>Substance</th>
<th>mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$HPO$_4$(3H$_2$O)</td>
<td>10</td>
</tr>
<tr>
<td>FeSO$_4$(7H$_2$O)</td>
<td>5</td>
</tr>
<tr>
<td>Al$_2$(SO$_4$)$_3$(16H$_2$O)</td>
<td>200</td>
</tr>
<tr>
<td>CaCl$_2$(2H$_2$O)</td>
<td>100</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>700</td>
</tr>
<tr>
<td>Mg(CH$_3$COO)$_2$.4H$_2$O</td>
<td>61</td>
</tr>
<tr>
<td>MnCl$_2$</td>
<td>3</td>
</tr>
<tr>
<td>HCOONa</td>
<td>100</td>
</tr>
<tr>
<td>Starch</td>
<td>100</td>
</tr>
<tr>
<td>C$_3$H$_3$NaO$_3$</td>
<td>100</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>10</td>
</tr>
<tr>
<td>C$_2$H$_3$NaO$_3$</td>
<td>100</td>
</tr>
<tr>
<td>AKD-glue</td>
<td>50</td>
</tr>
<tr>
<td>Humic acid</td>
<td>3</td>
</tr>
</tbody>
</table>
Table 8. Paper mill wastewater characteristics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.5-7.0</td>
</tr>
<tr>
<td>Conductivity (µS/cm)</td>
<td>1500-1700</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>60-115</td>
</tr>
<tr>
<td>Sulphate (mg/L)</td>
<td>660</td>
</tr>
<tr>
<td>COD (mg O₂/L)</td>
<td>1500</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>270-350</td>
</tr>
<tr>
<td>Redox-potential (mV)</td>
<td>-200 – -300</td>
</tr>
<tr>
<td>Dissolved oxygen (mg/L)</td>
<td>0.5-2</td>
</tr>
<tr>
<td>Sulphide (mg/L)</td>
<td>4-32</td>
</tr>
</tbody>
</table>
Table 9. Wastewater characteristics of Finnish pulp and paper mills

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Mill A</th>
<th>Mill B</th>
<th>Mill C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>After primary clarifier</td>
<td>After biological process</td>
<td>After primary clarifier</td>
</tr>
<tr>
<td>pH</td>
<td>6.7</td>
<td>5.9</td>
<td>6.4</td>
</tr>
<tr>
<td>COD, mgO₂/L</td>
<td>1550</td>
<td>45</td>
<td>1029</td>
</tr>
<tr>
<td>DOC, mg/L</td>
<td>488</td>
<td>11</td>
<td>390</td>
</tr>
<tr>
<td>Colour</td>
<td>826</td>
<td>-</td>
<td>660</td>
</tr>
<tr>
<td>Turbidity, FAU</td>
<td>74</td>
<td>-</td>
<td>101</td>
</tr>
<tr>
<td>Lignin, mg/L</td>
<td>255</td>
<td>16</td>
<td>257</td>
</tr>
<tr>
<td>Cl-, mg/L</td>
<td>38</td>
<td>-</td>
<td>177</td>
</tr>
<tr>
<td>Abietic acid, mg/L</td>
<td>12.4</td>
<td>nd</td>
<td>1.1</td>
</tr>
<tr>
<td>Oleic acid, mg/L</td>
<td>7.7</td>
<td>nd</td>
<td>14.3</td>
</tr>
<tr>
<td>β-sitosterol, mg/L</td>
<td>2.4</td>
<td>nd</td>
<td>1.7</td>
</tr>
<tr>
<td>Conductivity, mS/cm</td>
<td>1.2</td>
<td>-</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Remarks:
nd = not detected
- = not analysed
3.2.2. Biocides

The following biocides were tested in combination with polarization in paper IV: hydrogen peroxide p.a. (Merck); peracetic acid, 15 % equilibrium solution (Kemira Chemicals, Oulu, Finland); formic acid, 85 % (Kemira Chemicals, Oulu, Finland); sodium percarbonate, ECOX (Kemira Chemicals, Helsingborg, Sweden); Omacide IPBC 100, 3-Iodo-2-propynyl-n-butylcarbamate (Arch Chemicals, UK); and Fennosan GL10, 50 % glutaraldehyde; Fennosan M9, 9 % methylene bisthiocyanate (MBT); Fennocide BIT20, 20 % benzisothiazolinone (BIT); and Fennodispo 315, a naphthalene sulphonate containing anionic dispersant, all from Kemira Chemicals, Vaasa, Finland.

3.3. Bacterial strains

The bacterial strains used in this study were Deinococcus geothermalis E50051, Pseudoxanthomonas taiwanensis JN1109 and Meiothermus silvanus B-R2A5-50.4. They were selected on the basis of being common primary paper mill bacterial strains [143-145] and were received from the Hambi Collection (Department of Applied Chemistry and Microbiology, Faculty of Agriculture and Forestry, University of Helsinki, Finland) and stored in glycerol freezer stocks (-22 ºC). Fresh bacteria were taken for each of the experiments. All bacteria were inoculated into Petri dishes (R2A-agar) and incubated for 3 days (45 ºC). After this bacteria were inoculated into five test tubes which had 5 ml of R2 stock solution (composition [per litre]: yeast extract 0.5g, beef extract 0.25g, meat peptone 0.25g, tryptone 0.5g, starch [soluble] 1.0g, K2HPO4 0.3g, MgSO4*7 H2O (dried) 0.05g, Na-pyruvate 0.3g). Test tubes were incubated for 24 hours (45 ºC, 70 rpm) until cultivated bacteria was ready to use.
3.4. Analyses

3.4.1. Bacteria

Amounts of each bacteria species were determined as total aerobic plate counts (APCs) according to the standard method [146] before and after the electro-oxidation treatments (Papers I and II). The bacterium was cultured on PCA agar and incubated at 30 °C for 72 ± 3 h. After the incubation period, bacterial colonies were counted and the results calculated as CFU/mL. In Paper III the method was similar but for measuring bacteria an anaerobic atmosphere was created in anaerobic jars (Oxoid Ltd., Hampshire, England) using anaerocults.

3.4.2. Oxidants

Measurement of total oxidants (chlorine/hypochlorite, ozone and hydrogen peroxide) was performed according to the standard method [147].

3.4.3. Cyclic voltammograms

In paper I and paper IV the electrochemical behaviour of the electrodes was investigated by cyclic voltammetry. In paper I, cyclic voltammograms (CV’s) were performed with stirred solutions at scan rates of 25 mV/min by potentiostat (delivered by Savcor Forest Oy). In paper IV a Princeton ParStat 2273-Potentiostat/Galvanostat was used for CVs. Anodic CVs were run by range 0 – 1.6 V vs. SCE (up = from 0 V to 1.6 V and down = from 1.6 V to 0 V) and cathodic curves by range 0 – -1.9 V vs. SCE (up = from 0 V to -1.9 V and down = -1.9 V to 0 V) at a scan rate of 25 mV/s.

3.4.4. Other analyses

The conductivities of the synthetic and real wastewater samples were measured by conductivity meter (VWR EC300, VWR International) and pH values and redox potentials by pH meter using different probes (VWR pH100, VWR International). Dissolved oxygen (DO) measurements were done by DO
meter (VWR DO200, VWR International). Sulphide, sulphate and chloride concentrations were measured directly without filtration by HACH Lange photometer (DR 2800 VIS Spectrophotometer) using Lange Cuvette tests. DOC values of the samples were measured by TOC-analyzer (Shimadzu, Model TOC-5000A) and COD values by the standard method [148]. DOC samples were filtrated before analysis through 0.45 μm membranes.

Wood extractives were analysed adapting a method from Örså and Holmbom [149]. Four millilitres of the sample were measured in a screw capped test tube and the pH was adjusted to 3.5 with 0.05 M or 0.5 M H₂SO₄, depending on initial pH of the sample. Bromocresol green was used as an indicator. Two millilitres of methyl tert-butyl ether (MTBE), containing 20 μl/ml of heneicosanoic acid and botulin, were also added. The sample was mixed vigorously for two minutes and centrifuged at 4500 rpm for five minutes. A clear organic layer was carefully pipetted off. The extraction was repeated twice with two millilitres of MTBE (without ISTD) and mixed for one minute. The combined MTBE layers were evaporated in a nitrogen stream. The residue was silylated adding 80 μL of bis(trimethylsilyl)trifluoroacetamide (BSTFA) and 40 μl of trimethylchlorosilane (TMCS). The silylation was carried out in an oven at 70 °C for 20 minutes.

A Hewlett Packard 6890 gas chromatograph (GC) coupled with a 5973 Mass Selective Detector GC-MS equipped with a standard capillary column (25 mm x 0.32 mm I.D. x 0.17 μm film thickness) containing polydimethylsiloxane was used for measuring resin acids. The initial oven temperature was 120 °C and the temperature was programmed to 190 °C at a rate of 10 °C/min from which it was raised to 340 °C at a rate of 3°C/min. The final temperature was held for 10 minutes. The inlet temperature was 260 °C. Helium was used as a carrier gas. All the samples were added by splitless injection with a sample volume of 1 μl. Identification and quantification were performed using heneicosanoic acid as the internal standard for resin acids.
Dye concentration was determined on a UV-visible spectrophotometer at the maximum visible wavelength of 465 nm (PerkinElmer Lambda 45). Wastewater mineralization was monitored by the removal of TOC (Shimadzu, Model TOC-5000A).
4 RESULTS AND DISCUSSION

4.1. Cyclic voltammograms

To find out the oxygen evolution overpotentials, CV’s were recorded for three different electrodes (Paper I). Figure 5 presents CVs recorded in the synthetic paper mill water (SPW). According to the CVs, BDD has the highest oxygen evolution overpotential (2.5 V vs. SCE) of the electrodes, suggesting that instead of molecular oxygen, hydroxyl radicals are formed on the surface of the anode. In addition, PbO2 has a higher oxygen evolution overpotential than the MMO electrode which belongs to DSA electrodes. This has been reported also by Chen [43].

![Voltammograms of the anode materials MMO, PbO2 and BDD obtained at a scan rate of 25 mV/min in SPW at room temperature and pH = 7 (Data from paper I)](image)

In Figure 6 are presented CV’s for three electrodes without chloride salts in SPW. BDD seems to have still the highest oxygen evolution overpotential, but the difference between BDD and PbO2 is not significant. This means that PbO2 can form more hydroxyl radicals on its surface in this SPW than in ordinary SPW containing chloride salts.
To achieve one of the main objectives of this study, electrochemical properties of electrodes in paper mill water were investigated. The main idea was to observe how well electrochemical treatment can enhance the radical formation reactions in paper mill waters where biocides are already present. If more oxidative radicals can be formed, more efficient biofilm prevention will be also achieved.

Combination of CVs for the MMO and stainless steel SS 2343 electrodes with H₂O₂ concentrations of 50 mg/L are shown in Figures 7-8 (Data from Paper IV). CVs without H₂O₂ additions showed good reproducibility through the runs. It can be seen that the added biocide has a clear effect on the surface of the SS 2343 electrode by increasing the currents (between 0.7 – 1.4 V vs. SCE) even before the oxygen evolution reactions occur. This was also seen on the cathodic side when hydrogen peroxide caused a current increase during the experiment on the SS 2343 electrode at -1.0 V vs. SCE (reduction of H₂O₂) which was also observed by Patra and Munichandraiah [150]. Thus different radical reactions may occur with hydrogen peroxide. On the MMO electrode, the current also increased between 0.2 – 1.1 V vs. SCE. Probably the radicals were formed at the beginning of the run until formation stopped after 1.1 V vs. SCE. A clear current increase was also observed on the
cathodic side after starting the run on the MMO electrode, indicating radical formation also on this side. On the cathodic side, curves returning back to initial stage show that currents are smaller on both SS 2343 and MMO electrodes. This means that hydrogen peroxide has been degraded during the run to water. More reactive behaviour of SS 2343 electrode must be due to its surface structure. On the cathodic side it can be also seen that hydrogen peroxide has degraded almost completely because it has a similar curve to the SS 2343 electrode without biocide (Fig. 8). It is a clear proof that on the cathodic side, hydrogen peroxide has a capacity to form different radicals in combination with electrical treatment until degraded to water. The proposed radical production mechanism could be as follows (reactions 12-13):

\[
\begin{align*}
\text{H}_2\text{O}_2 & \rightarrow \cdot\text{OH} + \cdot\text{OH} \\
\cdot\text{OH} + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^\cdot + \text{H}_2\text{O}
\end{align*}
\]  

(12)  

(13)

Patra and Munichandraiah [150] suggested that following reactions will occur in direct reduction of H$_2$O$_2$ in a slightly acidic medium (pH = 5.8) (reactions 14-18):

\[
\begin{align*}
\text{H}_2\text{O}_2 \text{ (bulk)} & \rightarrow \text{H}_2\text{O}_2 \text{ (surface)} \\
\text{H}_2\text{O}_2 \text{ (surface)} + e^- & \rightarrow \text{OH}_\text{ad} + \text{OH}^- \\
\text{OH}^- + \text{H}^+ & \rightarrow \text{H}_2\text{O} \\
\text{OH}_\text{ad} + e^- & \rightarrow \text{OH}^- \\
\text{OH}_\text{ad} + \text{H}^+ + e^- & \rightarrow \text{H}_2\text{O}
\end{align*}
\]  

(14)  

(15)  

(16)  

(17)  

(18)

Reaction 14 followed by electron transfer steps (reactions 15 and 17) is expected to result in the CV peak current [150] which we observed at -1.0 V vs. SCE (Fig. 8).
It is also known that hydrogen peroxide is relatively stable at pH<9 [151] which proofs that H₂O₂ was not degraded by itself. Many other biocides were also tested in this study but they did not give any response (oxidation or reduction peaks) for radical formation with electrical treatment (Paper IV). Peltola et al. [13] showed that removal of *Deinococcus geothermalis* biofilm was enhanced by cathodically weighted pulsed polarization in the presence of oxidizing biocides. ROS compounds were successfully generated during the experiments for biofilm removal from stainless steel surfaces which supports also results of this study.

Figure 7. Cyclic voltammograms of hydrogen peroxide in synthetic paper mill water (cPMW) on the anodic side (Data from Paper IV)
4.2. Electrochemical inactivation of bacteria

4.2.1. Aerobic bacteria in synthetic paper mill water

Figure 9 shows the electrochemical inactivation of *Deinococcus geothermalis* in synthetic paper mill water (SPW) as the current density varied from 5 to 65 mA/cm² (Paper II). It can be seen that the effective inactivation (>2 log) of bacteria was reached when current density was higher than 25 mA/cm² and the time taken was at least three minutes. The inactivation also increased with higher current density which has also been observed in other studies [152,153]. Differences in inactivation in the range of 25 to 65 mA/cm² were minor, signifying that above the threshold value (25 mA/cm²) most of the electric energy used in the experiments was spent to form oxygen. In addition, it can be seen from Figure 10 that different oxidants were formed during the EO. With higher current density it is possible to form more oxidants. The amounts of oxidants produced are in accordance with the
inactivation rate. In three minutes it was possible to reach a sufficient inactivation level, which means that the concentration of oxidants needed is about 3 mg/L. The amount of oxidant was smaller at a current density of 65 mA/cm² than at 50 mA/cm². This can be explained by the higher oxygen evolution reaction and hydroxyl radical production at this current density.

Figure 9. Inactivation of *Deinococcus geothermalis* in SPW using an MMO electrode and different current densities during galvanostatic electrolysis (pH=7) (Data from Paper II)

Log (N/N₀) vs. Time (min)
Figure 10. Amounts of oxidants electrochemically generated on an MMO electrode during galvanostatic electrolysis using different current densities at pH=7 (Data from Paper II)

Figure 11 indicates that the pH of SPW did not have a significant influence on the inactivation efficiency of Deinococcus geothermalis. Almost equal amounts of total oxidants were formed during the experiments (Figure 12). However, less oxidants were produced at lower pHs. Similar inactivation efficiency can be explained by higher oxidation potential of hypochlorous acid formed (reaction 6) at acidic pH. Hypochlorous acid has higher oxidation potential than hypochlorite present at neutral or alkaline pH (reaction 7) [55]. It was also observed that generation of chlorine is more or less same under the fixed current density [54]. However, in this study also other oxidants than chlorine/hypochlorite could be formed by higher pH.
Figure 11. Inactivation of *Deinococcus geothermalis* in SPW using an MMO electrode at different pH values during galvanostatic electrolysis (current density 50 mA/cm²) (Data from Paper II)

Figure 12. Amounts of electrochemically generated oxidants on MMO electrode during the galvanostatic electrolysis using different pH values (current density 50 mA/cm²). (Data from Paper II)
The effect of different chloride concentrations on inactivation efficiency is shown in Figure 13. It is evident that electrochemically generated chlorine/hypochlorite has a significant influence on the inactivation of *Deinococcus geothermalis* (indirect oxidation). This can also be seen from Figure 14. A 6 log inactivation could be reached in five minutes when the chloride concentration was 130 mg/l in SPW. However, most likely anodic oxidation by direct electron transfer reaction occurred simultaneously, as well as oxidation by ROS generated from water discharge [125]. It has been also shown that oxidation may occur by peroxodisulfates generated from sulphate ions [141] in SPW but they were not measured in this study. Chemical composition of SPW is very heterogeneous mixture including many different anions which can be oxidized to more reactive form to inactivate bacteria.

Figure 13. Inactivation of *Deinococcus geothermalis* using an MMO electrode and different initial chloride concentrations during galvanostatic electrolysis (pH=7, current density 50 mA/cm²) (Data from Paper II)
Because it was obvious that chlorine/hypochlorite played a significant role in inactivation, the effect of residual chlorine on *Deinococcus geothermalis* was investigated. Electrical treatment was switched on for one minute and then switched off. A bacteria sample was taken immediately after switching on and then every minute. Figure 15 shows that with a chloride concentration of 130 mg/L it was possible to achieve a reasonable inactivation level in five minutes. Figure 15 shows also inactivation was faster when the initial chloride concentration in SPW was higher.

*Deinococcus geothermalis* has been showed to be an efficient primary biofilm former in paper machine water [12,16,17] and it forms thick biofilms on which secondary biofilm bacteria can further attach [16]. It is known to be highly resistant towards radiation and desiccation so results in our study show that EO treatment can produce effective oxidants to inactivate it. In addition, when *Deinococcus*
will be inactivated, it also decreases capability of other potential biofilm formers to attach pipe lines because they cannot adhere on the surfaces without *Deinococcus*.

Figure 15. Inactivation of *Deinococcus geothermalis* using an MMO electrode and different initial chloride concentrations during galvanostatic electrolysis, effect of residual chlorine/hypochlorite (pH=7, current density 50 mA/cm²) (Data from Paper II)

Three different paper mill bacteria species (*Deinococcus geothermalis, Pseudoxanthomonas taiwanensis* and *Meiothermus silvanus*) were compared to discover possible differences in inactivation efficiency. These species have been recognized as pertinent, primary biofilm formers in the wet-end of paper machines and they can cause colourful spots to final product [154]. Experiments were conducted as before (each species was treated separately) and responses to all oxidants (SPW) and oxidants without chlorine/hypochlorite (SPW without chloride salts) were measured. The residual effect of chlorine/hypochlorite on the inactivation efficiency of these three bacteria species was also investigated.
Figure 16 shows how electrochemical inactivation affected these three bacteria species. The inactivation order was *Meiothermus silvanus* > *Pseudoxanthomonas taiwanensis* > *Deinococcus geothermalis*. *Meiothermus silvanus* could be inactivated quite effectively (1.5 log) in one minute. The resistance of other bacteria to oxidants was somewhat higher.

Figure 16. Inactivation of *Deinococcus geothermalis*, *Pseudoxanthomonas taiwanensis* and *Meiothermus silvanus* using an MMO electrode during galvanostatic electrolysis (chloride concentration 65 mg/L, pH=7, current density 50 mA/cm²) (Data from Paper II)

The same experiments were conducted without chloride salts in SPW (chloride concentration = 0 mg/L) to compare their influence. Figure 17 indicates that the inactivation order was different to that with chlorine/hypochlorite. Thus bacteria have different abilities to withstand different oxidants. It was also observed that *Deinococcus geothermalis* was more sensitive to other oxidants than chlorine/hypochlorite. On the other hand, *Pseudoxanthomonas taiwanensis* was more resistant to these oxidants than to chlorine/hypochlorite. Also *Meiothermus silvanus* was inactivated with a
slower response. Li et al. [142] observed that oxidants with high oxidation-reduction potential, such as hydroxyl radical, will damage cell structure more due to strong oxidation ability. For weaker oxidants, such as chlorine, reactions with the cell wall are quite limited and then there is little cell surface deformation. Oxidation with the enzymes in the cell plasma might be the lethal reason. As a conclusion, sensitivity of different bacteria species to different oxidants varies a lot.

Figure 17. Inactivation of *Deinococcus geothermalis*, *Pseudoxanthomonas taiwanensis* and *Meiothermus silvanus* using an MMO electrode during galvanostatic electrolysis without chloride salts (chloride concentration 0 mg/l, pH=7, current density 50 mA/cm²) (Data from Paper II)

Figure 18 shows the influence of residual chlorine/hypochlorite on the inactivation efficiency of bacteria species. As expected, the inactivation order was the same as in Figure 16. An efficient inactivation result was achieved with *Pseudoxanthomonas taiwanensis* and *Meiothermus silvanus* bacteria in three minutes. *Deinococcus geothermalis* bacteria were more persistent against residual chlorine/hypochlorite. Thus the effective oxidation noted during the experiments was mainly due to indirect electrochemical oxidation through chlorine/hypochlorite produced on the anode. This
mechanism has also been reported in many other studies [127,129,132,140,155-157]. The main achievement of the current study is to show that residual disinfection efficiency by chlorine/hypochlorite can keep the circulating waters clean enough to avoid biofilm formation on the pipeline surfaces.

We did not measure in this study hydroxyl radicals which have also important role in disinfection [125,152]. In general, inactivation mechanisms in EO are very complex and depend on many factors, such as electrolyte composition, bacteria species, electrodes and operating conditions during the treatment. For example, in disinfecting germinated brown rice circulating water and cooling tower water containing *Legionella* bacteria it was concluded that electrochemical disinfection was due to synergistic effect of the oxide anode, pulsed electric field and the hydroxyl radicals formed during the electrochemical treatment [131]. Li et al. [139] did similar observation in electrochemical disinfection of saline wastewater effluent.

![Graph of bacterial inactivation](image)

Figure 18. Inactivation of *Deinococcus geothermalis*, *Pseudoxanthomonas taiwanensis* and *Meiothermus silvanus* using an MMO electrode during galvanostatic electrolysis, effect of residual
chlorine/hypochlorite (chloride concentration 65 mg/L, pH=7, current density 50 mA/cm²) (Data from Paper II)

4.2.2. Anaerobic bacteria in paper mill wastewater

The reduction of sulphate to sulphide by anaerobic bacteria is a serious problem for pulp and paper mills so it was worth of investigating the inactivation efficiency of EO against them (Paper III). Real paper mill wastewater was used for the experiments. Figure 19 shows that inactivation was less effective with chloride concentration (in this case 62 mg/L) originally present in the wastewater. Thus, it was justifiable to increase the initial chloride concentration of the wastewater by adding NaCl to the wastewater. With chloride concentrations of 164 mg/L and 281 mg/L it was possible to inactivate anaerobic bacteria effectively in five minutes, so electrochemically produced chlorine species accelerated inactivation. Yet many studies have shown that electrochemical disinfection can be effective against bacteria and viruses without the generation of chlorine species [125,128,130,141,152,158]. Jeong et al. [125] observed that in chloride-free phosphate buffer solution E. Coli inactivation occurred in two distinct stages. The first step was direct anodic oxidation at anode’s surface and another step oxidation by hydroxyl radicals generated from water discharge. It is also evident that oxygen evolution reaction killed part of the bacteria in this study. Li et al. [141] also showed in their study that oxidants produced in the electrolysis of SO₄²⁻ (such as S₂O₈²⁻) improved the disinfection process. This phenomenon cannot be ignored in this study either because paper mill wastewater had high concentration of sulphate as well as SPW. Chlorine containing organic and inorganic by-product formation is also expected [134] during electrochemical treatment, but investigation into this was beyond the scope of the present study. However, applying lower current densities could help to avoid formation of hazardous compounds [132].
4.3. Electrochemical oxidation of sulphide

Figure 20 shows the change in sulphide concentration in paper mill wastewater by EO. It was clearly seen that the oxidation of sulphide occurred in all cases. It was possible to achieve an almost 100% reduction with all the different initial sulphide concentrations. Yet at a lower initial concentration (4.0 mg/L) the adequate level of sulphide in wastewater was achieved with a smaller electric charge.

The effect of current density on sulphide removal efficiency is shown in Figure 21. The initial sulphide concentration was ca. 20 mg/L in all the experiments. The best electric charge efficiency was achieved with the lowest current density. Other current densities were not as effective and it was noted that the energy consumption of the effective treatment was higher. Other experiments of this study showed that pH did not change much during the experiments and the redox potential as well as dissolved oxygen values raised which proofs that oxidation of sulphide was mainly occurred by electrochemically generated oxygen.
Figure 20. Electrochemical oxidation of sulphide in pulp and paper mill wastewater using an MMO electrode and different initial sulphide concentrations (current density 42.9 mA/cm$^2$) (Data from Paper III)

Figure 21. Electrochemical oxidation of sulphide in pulp and paper mill wastewater using an MMO electrode and different current densities with initial sulphide concentration of ca. 20 mg/L (Data from Paper III)
In earlier studies EO has been used for the oxidation of sulphide containing waters [159-160]. It was found that sulphides were oxidized to elemental sulphur and sulphate during electrochemical treatment [159].

4.4. Electrochemical oxidation of organics in pulp and paper mill bleaching effluent

In paper VI the MMO and BDD electrodes were employed in electrochemical oxidation of the pulp and paper mill bleaching effluents. The method was rather effective in resin acid degradation in the treatment of the mill B effluent by MMO electrode. At a constant pH of 7.0 and 60 minutes of treatment time, the removal of abietic acid, β-sitosterol and oleic acid were 51 %, 83 % and 76 %, respectively. About 28 % of COD could be removed. Compared to other techniques used in the study (such as chemical precipitation), removal rates were rather low. However, in this study continuous circulation of the wastewater was used through the experiments. Comparable study has shown better purification results for COD [161] but it was done in batch mode. This study showed also that MMO electrode was more effective in degradation efficiency of organic material than BDD electrode most likely due to active chlorine produced during the treatment. Jeong et al. [127] also observed that active chlorine was produced more on DSA electrodes than on BDD electrode. Yet electrochemical oxidation seems capable of removing wood extractives which are hazardous in a biological wastewater treatment process. If the method is used as a pre-treatment, potential inhibition of the biological treatment can be eliminated due to reduced toxicity in the primary effluent.

4.5. Electrochemical degradation of methyl orange dye

Textile industry dye was selected as a refractory organic compound for further analysis to see effectiveness of MMO and BDD electrodes. Methyl orange (MO) was selected as the model azoic dye since it is persistent and highly soluble in water; therefore its removal is also a subject of major
importance in environmental protection. It was necessary to gain insight the electrochemical mineralization of MO in relatively high initial concentrations on BDD and MMO electrodes.

It was observed that MO dye degradation was more effective on a BDD electrode than on an MMO electrode (Paper V). For instance, at a current density of 50 mA/cm², the colour was almost completely removed on BDD after 90 minutes of treatment, while for the MMO electrode the removal ratio was less than 15 %. It was noticed that the BDD electrode has higher onset potential for oxygen evolution than the MMO electrode which indicates that the former has a much higher current efficiency.

The degradation on two electrodes presented different trends on the operative parameters. High current density enhanced the decolourization on both electrodes, but the promotion was not as significant on MMO as on BDD, leading to a sharp increase in specific energy consumption. The decolourization of MO was more successful under acidic conditions for both electrodes but the pH dependence was not as obvious on BDD as on MMO. The presence of NaCl favoured the indirect oxidation of active chlorine on the MMO electrode, which greatly improved the decolourization rate. The presence of NaCl promoted the decolourization also on BDD electrode, as also combustion rate of dye on both electrodes. The formation of active chlorines seemed to be more efficient on the MMO electrode. Oxygen evolution potential on BDD is much higher than on MMO electrode, which prevents the side reactions and greatly improves the current efficiency for hydroxyl radical formation [43,162]. High initial concentration enhanced the general current efficiency (GCE), though the COD and TOC removal efficiency was reduced.

In general, EO treatment of MO dye was more effective by BDD electrode in tested conditions. BDD performed better in relative wide concentration ranges and effect of pH was not so important for
decolourization efficiency of dye. Moreover, BDD demonstrated more economical way for dye mineralization from the technical point of view, even absence of NaCl.
5 CONCLUSIONS AND FURTHER RESEARCH

Electrochemical oxidation was an effective method for inactivation of different biofilm and sulphide forming bacteria species in pulp and paper mill circulating waters and wastewaters. Paper mill bacteria (*Deinococcus geothermalis, Pseudoxanthomonas taiwanensis* and *Meiothermus silvanus*) were inactivated effectively (>2 log) at the MMO electrode with a current density of 50 mA/cm² and contact time of three minutes and the oxidation was mainly due to indirect electrochemical oxidation (electrochemical formation of chlorine/hypochlorite).

Increasing current density and initial chloride concentration of synthetic paper mill water speeded up inactivation. The initial pH value of the synthetic paper mill water did not have a significant impact on the inactivation rate. Bacteria species varied in response to different oxidants. Optimising the operative parameters is important in finding the best current efficiency for inactivation.

Electrochemical oxidation showed promising performance in oxidizing the sulphide present in paper mill wastewater. Inactivation of the anaerobic bacteria present in the wastewater was also observed. This supports strongly use of technique in oxidizing sulphide containing wastewaters or preventing sulphate reduction by anaerobic bacteria.

Based on the CV runs it was observed that hydrogen peroxide could be degraded to radicals with cathodic potentials used in this study in the synthetic paper mill water. The stainless steel electrode was more reactive than the MMO electrode on cathodic treatment. More reactive behaviour of SS 2343 electrode must be due to its surface structure which would offer great opportunity for biofilm prevention on stainless steel pipe lines at paper mills.

EO treatment of organics in bleaching effluent gave rather good results for resin acid degradation but COD removal was not as effective most likely due to continuous flow system used in the study. Electrochemical oxidation seemed capable of removing wood extractives which are hazardous in a
biological wastewater treatment process. If the method is used as a pre-treatment, potential inhibition of the biological treatment can be eliminated due to reduced toxicity in the primary effluent.

EO treatment of MO dye (colour removal) was more effective by BDD electrode in tested conditions than by MMO electrode. It was observed that the BDD electrode had higher onset potential for oxygen evolution than the MMO electrode which indicated that the former had a much higher current efficiency for dye degradation.

The efficiency of the EO process largely depended on cell configuration, electrode material, electrolyte composition, the micro-organism or pollutant, and other experimental parameters, such as current density or the temperature of the treated water. Effective EO treatment of primary biofilm forming bacteria species will offer an alternative to biocides. In addition, combined treatment with hydrogen peroxide will produce powerful oxidants (radicals) which are effective but still environmentally friendly in paper mill environment. In future studies, it would be important to measure different radical reactions at the surface of the anode and by-products formed after the treatment.

Finding an effective and stable yet economical electrode material would speed up the use of EO technique in wastewater treatment. It would also be important to develop some novel electric power source for the system, such as solar energy. Combining treatment with current tertiary techniques would enhance the purification results. Also economical calculations of EO technique in treatment of different pulp and paper mill circulating waters and wastewaters would be needed.
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