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Ville Kuokkanen

UTILIZATION OF ELECTROCOAGULATION FOR WATER AND WASTEWATER TREATMENT AND NUTRIENT RECOVERY

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UTILIZATION OF ELECTROCOAGULATION FOR WATER AND WASTEWATER TREATMENT AND NUTRIENT RECOVERY

Techno-economic studies

Academic dissertation to be presented with the assent of the Doctoral Training Committee of Technology and Natural Sciences of the University of Oulu for public defence in Kuusamonsali (YB210), Linnanmaa, on 26 February 2016, at 12 noon

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Abstract

Electrocoagulation (EC) is an emerging technology that combines the functions and advantages of conventional coagulation, flotation, and electrochemistry in water and wastewater treatment. The aims of this work included doing an updated literary review of recent feasible applications of EC, which were found to be plentiful. Since the economic and practical operational key figures related to EC haven't been extensively mapped out before, this was a prime objective of this part of the work.

The aim of the next part of this work was to find new feasible applications for EC in the treatment of water and wastewater. The studied wastewaters included bio- and synthetic oil-in-water emulsions, various industrial nutrient-containing wastewaters, and peat bog drainage water containing humic substances (an interesting and topical problem, especially in Finland). These studies proved the feasibility of EC. In addition, larger-scale experiments were also conducted successfully, thus proving the scalability of the EC process. Extensive economic analyses of the studied EC applications were also done. The operational costs and energy consumption of EC were found to be very low—typically about 0.1–1.0 €/m^3 and 0.4–4.0 kWh/m^3.

It has been forecasted that in the future there will be a shortage of virgin phosphorus. Therefore, another essential purpose of this work was to conduct a preliminary study on the feasibility of using EC for nutrient (especially phosphorus, but also nitrogen) removal and recovery from different types of real wastewater. Specifically, it may be possible to use EC sludges containing notable amounts of phosphorus and nitrogen as additives in granulated bio ash-based fertilizer products for various applications. This is a novel idea and a "hot topic" in the waste utilization sector and in circular and bioeconomy.

Keywords: circular economy, electrocoagulation (EC), nutrient recovery, peat bog drainage water, scale-up studies, techno-economic analysis, water and wastewater treatment

Kuokkanen, Ville, Elektrokoagulaation hyödyntäminen vesien ja jätevesien käsittelyssä ja ravinteiden talteenotossa. Teknis-taloudellisia tutkimuksia
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Tiivistelmä

Elektrokoagulaatio (electrocoagulation, EC) on nosteessa oleva teknologia, joka yhdistää perinteisen koagulaation, flotaation ja sähkökemian hyödyt ja mahdollisuudet vesien ja jätevesien käsittelyssä. Tämän työn ensimmäisenä tavoitteena oli laatia kirjallisuuskatsaus EC:n viimeaikaisista käyttökelpoisista sovelluksista, joita löytyi runsaasti. Koska EC:n toiminnallisia ja taloudellisia avainlukuja ei ole kartoitettu kattavasti aiemmin, tämän tekeminen oli tämän osion tärkein tavoite.

Väitöstyön seuraavana tavoitteena oli löytää uusia sovellutuksia EC:lle vesien ja jätevesien käsittelyssä. Tutkittuja vesiä olivat bio- ja synteettisistä öljyistä valmistetut öljy-vesiemulsiot, erilaiset teolliset ravinnepitoiset jätevedet ja humusainepitoiset turvesoiden valumavedet (kiinnostava ja ajankohtainen ongelma, erityisesti Suomessa). EC todettiin käyttökelpoiseksi teknologiaksi näissä kokeissa. Suuremman skaalan kokeilla todistettiin lisäksi EC-prosessin skaalautuvuus. Lisäksi, em. EC-sovellutuksista suoritettiin kattavat taloudelliset analyysit. EC:n käyttökustannukset ja energiankulutus todettiin erittäin pieniksi, tyypillisesti ne olivat välillä 0.1–1.0 €/m^3 ja 0.4–4.0 kWh/m^3.

On ennustettu, että tulevaisuudessa on pulaa neitseellisestä fosforista. Tästä johtuen eräs tämän työn keskeisistä tarkoituksista oli suorittaa alustavia kokeita liittyen EC:n käyttökelpoisuuteen ravinteiden (erityisesti fosfori, mutta myös typpi) poistossa ja talteenotossa aidoista jätevesistä. Erityisesti jatkossa voisi olla järkevää hyödyntää runsaasti fosforia ja typpeä sisältäviä EC-sakkoja lisäaineina rakeistetuissa biotuhkapohjaisissa lannoitteissa eri sovellutuksissa. Tämä idea on uusi ja on jo herättänyt suurta kiinnostusta mm. kierto- ja biotaloussektoreilla.

Asiasanat: elektrokoagulaatio (EC), kiertotalous, ravinteiden talteenotto, skaalautuvuustutkimus, teknis-taloudellinen analyysi, turvesoiden valumavedet, vesien ja jätevesien käsittely

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I also wish to thank my fellow students, colleagues, and all of the department staff whom I have worked with through these years. Industrial and academic affiliates, especially partners at NBTec Oy, the Centre for Environment and Energy CEE (M. Sc. (Tech.) Juha Roininen and D. Sc. (Tech.) Pekka Tervonen), FA Forest Oy (PhD Mikko Räisänen), Turveruukki Oy (CEO Heikki Karppimaa), Rakeistus Oy (CEO Teemu Leskinen), Biotehdas Oy (CEO Kaisa Suvilampi and M. Sc. Eeli Mykkänen), Ekosata Oy (CEO Lauri Turpeinen), and Ekopine Oy (CEO Hannu Kokko), as well as M. Sc. Virpi Alenius (Luke) are also thanked for their interest in my work as well as material and other types of support.

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Oulu, August 2015 Ville Kuokkanen

Symbols and abbreviations

A_{eff}	effective (submerged) anode area [m^2]
ANOVA	analysis of variance
APC	alternating pulse current
BDD	boron-doped diamond
BOD	biological oxygen demand [mg/L]
BP	bipolar mode
CC	chemical/conventional coagulation
CCC	critical coagulation concentration
COD	chemical oxygen demand (chromium as oxidizer) [mg/L]
COD_{Mn}	chemical oxygen demand (manganese as oxidizer) [mg/L]
DC	direct current
DLVO	Derjaguin-Landau-Verwey-Overbeek
DOC	dissolved organic carbon [mg/L]
DPRW	digester plant reject water
DTA	differential thermal analysis
DWW	dairy wastewater
EC	electrocoagulation
ED	electrodialysis
EDL	electrical double layer
EEC	electrical energy consumption [kWh/m^3]
EF	electroflotation
E-F	electro-Fenton
EM	electromagnetic treatment
EMC	electrode mass consumption [kg/m^3]
EO	electro-oxidation
EPD	electrophoretic deposition
F	Faraday's constant (96,485 C/mol)
HRT	hydraulic retention time
HA	humic acids
HS	humic substances
i	current density [A/m^2]
IC	inorganic carbon
ICP	inductively coupled plasma
MCO	mineral oil-based chain oil
MO	synthetic motor oil

MP	monopolar mode
MWW	mining wastewater
NOM	natural organic matter
NTU	nephelometric turbidity unit
OC	operating costs [€/m^3]
OES	optical emission spectrometer
OFA	overland flow area
O/W	oil-in-water
PACl	poly aluminum chloride
PBDW	peat bog drainage water
PES-Na	polyethylene sodium sulphonate
PolyDADMAC	polydiallyldimethylammonium chloride
PVC	polyvinyl chloride
RO	reverse osmosis
RSM	response surface modeling
RSO	rapeseed oil
SDS	sodium dodecyl sulphate
SEC	supporting electrolyte consumption [kg/m^3]
SFO	sunflower oil
SS	stainless steel
SWW	synthetic wastewater
TC	total carbon
TGA	thermal gravimetric analysis
ThOD	theoretical oxygen demand [g/g]
TO	tall-oil based chain oil
TOC	total organic carbon [mg/L]
TS	total solids [mg/L]
TSC	total surface charge [µeq/L]
UV	ultraviolet
WWTP	wastewater treatment plant
XRD	X-ray diffraction

List of original publications

This thesis is based on the following publications, which are referred to throughout the text by their Roman numerals:

I Kuokkanen V, Kuokkanen T, Rämö J & Lassi U (2013) Recent applications of electrocoagulation in treatment of water and wastewater – a review. Green and Sustainable Chemistry 2: 89–121.

II Karhu M, Kuokkanen V, Kuokkanen T & Rämö J (2012) Bench scale electrocoagulation studies of bio oil-in-water and synthetic oil-in-water emulsions. Separation and Purification Technology 96: 296–305.

III Kuokkanen V, Kuokkanen T, Rämö J, Lassi U & Roininen J (2015) Removal of phosphate from wastewaters for further utilization using electrocoagulation with hybrid electrodes – techno-economic studies. Journal of Water Process Engineering 8: e50–e57.

IV Kuokkanen V & Kuokkanen T (2015) Removal of nutrients from hygienized anaerobic digester plant reject water by electrocoagulation for further utilization. Proceedings of the 5th International Conference on Environment (ICENV 2015), Penang, Malaysia, 18th-19th August 2015: 183–190.

V Kuokkanen V, Kuokkanen T, Rämö J & Lassi U (2015) Electrocoagulation treatment of peat bog drainage water containing humic substances. Water Research 79: 79–87.

The present author was the primary author of Publications I and III–V, and he mainly designed, conducted, and analyzed the results of all of the experiments related to these publications, with help from the other authors. He also prepared the first draft of the manuscripts for Publications I and III–V. He was also the second author of Publication II, in which he participated evenly with the primary author (D.Sc. (Tech.) Mirjam Karhu) in the design, laboratory, and analytical parts of the work and also assisted in the writing process.

In addition, the present author participated in the preparation of an abstract for the proceedings and poster “Bench scale electrocoagulation of bio oil-in-water emulsions” (both by Karhu M, Kuokkanen V & Kuokkanen T) at the IWA Regional Conference on Wastewater purification & Reuse, 28–30.3.2012, in Heraklion, Crete, Greece. These results are also partly discussed in this thesis.

Furthermore, a manuscript for a chapter titled "Water treatment by electrocoagulation" in a book titled “Sustainable Inorganic Chemistry”, which will be published by John Wiley & Sons, Ltd., has been written by Ville Kuokkanen. This manuscript, 37 pp., has been accepted for publication.

Contents

1 Introduction

Access to clean water is the most vital need for human life. However, fresh water accounts for only about 2–3% of all water on Earth, while the remaining volume of water is salt water (Kundzewicz 2008, Lohmann & Lorenz 2000, Ruini *et al.* 2013). Fresh water consists of ice, groundwater, and surface water and is furthermore divided unevenly between continents (Lohmann & Lorenz 2000). A vast majority of those who lack access to high-quality water live in rural areas, and today, nearly 800 million people lack safe drinking water globally (Unicef 2014).

On the other hand, billions of liters of various types of environmentally problematic industrial wastewater are generated daily on a global scale (Linares-Hernández *et al.* 2009). Simultaneously, laws and regulations related to the environment are constantly getting stricter (Chen 2004, Ebeling *et al.* 2005). This applies also to Finland. Taking all of the above into account, there is an urgent need to develop more effective water and wastewater treatment methods. This and its eco-friendliness have led to a significant global increase in interest in electrocoagulation (EC). During the last two decades, scientific literature has indeed seen a sharp rise in the annual amount of EC publications. (Chen 2004, Holt *et al.* 2002, Publication I) This has been particularly true in the most recent few years (Publication I).

As nutrients, P and N cause algae growth and lead to eutrophication when found abundantly in natural bodies of water. This, in turn, has harmful effects on aquatic life due to a decrease in the oxygen level in the water. (Bektaş *et al.* 2004, Zhao *et al.* 2009) Phosphorus is primarily present in wastewater in the form of orthophosphate compounds (commonly called phosphates). Municipal wastewater is a major source of nutrient-containing wastewater. Such wastewater is also generated in very large volumes in, e.g., mining, agriculture, food industry, and as effluents derived from various other industries (Akyol *et al.* 2013, Al-Zoubi & Al-Thyabat 2012, Giesen 1999, Kobya *et al.* 2010, Publication I, Sibrell *et al.* 2009).

Along with clean water, food is a basic vital need for mankind. It is common knowledge that at some time in the near future the value of virgin phosphorus will rise due to its shortage. This may lead to problems in the production of food (Childers *et al.* 2011). Therefore, finding alternate sources of phosphorus will be of great importance. EC may also play a part in this, namely through the utilization of nutrient-containing EC sludge for fertilization. This research topic is very interesting and important from the viewpoints of circular and bioeconom, both of which are currently extremely topical and essential in Finland, and also on

European and global levels (Ashby 2016, Ma *et al.* 2015, O'Brien *et al.* 2015, Scarlat *et al.* 2015).

2 Colloids

Pollutant particles contained by wastewater are often in colloidal form. Colloids are stable, charged aggregates of atoms and molecules, and they are extremely small in size (1–1000 nm). Since colloids are so small, their surface area to mass ratio is huge. The particle surface charges significantly affect the stability of colloids. (Sawyer *et al.* 2003, 360–362) Therefore, many of the water treatment technologies in use are based on changing the electrical properties of colloids. Surface charges may be formed in many ways, namely by ionization of functional surface groups, ion adsorption, dissolution of ionic solids, or isomorphous substitution due to lattice imperfections (Bratby 1980, 19–20).

2.1 The DLVO theory and the electrical double layer

According to the DLVO theory (named after its inventors: Derjaguin-Landau-Verwey-Overbeek), colloids interact with each other with two opposing forces. The particle associations are governed by the sum of these forces. Van der Waals forces along with London dispersion forces tend to pull the particles together to form larger aggregates. The attractive forces decrease very rapidly as the distance between the particles increases. (Benefield *et al.* 1982, 197, Bratby 1980, 37–38, Ohshima 2012, 27, Sawyer *et al.* 2003, 366)

Repulsive forces derive from the so-called electrical double layer (EDL). The EDL is an ionic cloud that surrounds a charged colloidal particle suspended in an electrolyte solution. Helmholtz first developed, and Gouy and Chapman replenished a model explaining the interface of a charged surface. These EDL models were later combined and further expanded by Stern in 1924. The EDL has a significant role in various interfacial electrical phenomena observed in a suspension of colloidal particles. These include, e.g., interactions between colloidal particles and electrokinetic phenomena, such as electrophoresis. The structure of the EDL is presented in Fig. 1, and the distribution of potential Ψ in the EDL, in Fig. 2. (Ohshima 2012, 3, Sawyer *et al.* 2003, 365–366, Scholz 2010, 3–9)

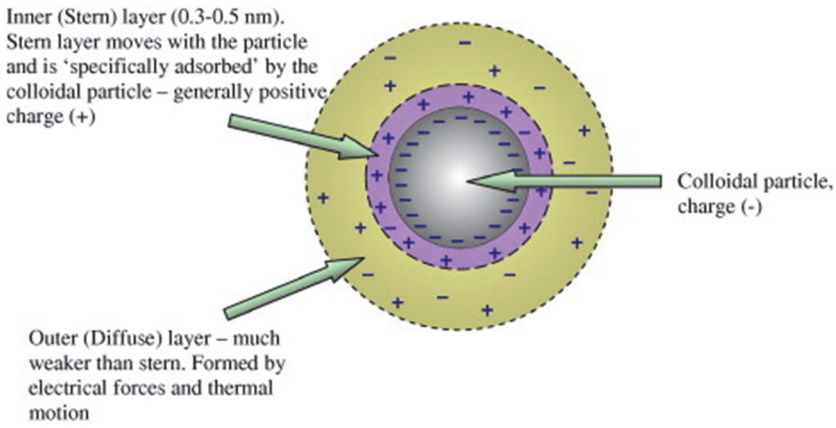

Fig. 1. The structure of the EDL. Adapted from Pritchard et al. (2010).

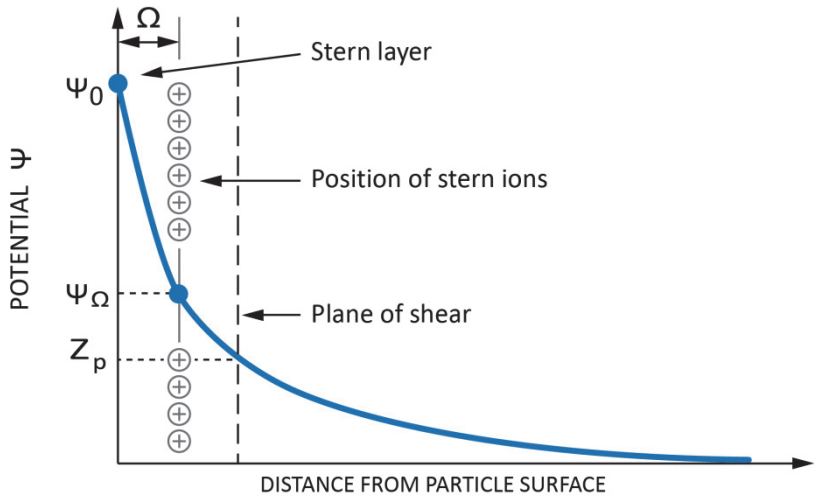

Fig. 2. Distribution of potential in the EDL.

As illustrated in Fig. 1, the EDL model consists of an inner region called either the fixed layer (moves along with the particle) or the Stern layer/Helmholtz layer, and an outer diffusion region called the Gouy-Chapman layer. In the inner layer, the particle surface binds ions to itself. Conversely in the outer layer, ions may move due to diffusion. Ultimately, the EDL is formed by the separation of charges

on the particle surface—oppositely charged ions are attracted to the surface, and ions of the same charge are repelled from it. In other words, when two similar colloidal particles approach each other, their diffusion layers (see Fig. 1) come into contact with each other's sphere of influence. Consequently, the colloidal particles begin to repel each other as a function of the distance between them. The closer they come to each other, the stronger the repulsive force. (Bache & Gregory 2007, 6–7, Bratby 1980, 37, Sawyer *et al.* 2003, 366–367)

Generally, for particles approaching each other, the repulsive force is dominant over the attractive forces. For this reason, particle collisions and coalescence into larger particles is prevented. If, however, the attractive forces become strong enough to be dominant, and the so-called energy barrier can be exceeded and the particles will become irrevocably joined together. If there is an energy barrier detectable in the resultant curve, as illustrated in Fig. 3, then the colloid is stable. (Bache & Gregory 2007, 6, Bache & Gregory 2007, 37, Sawyer *et al.* 2003, 366)

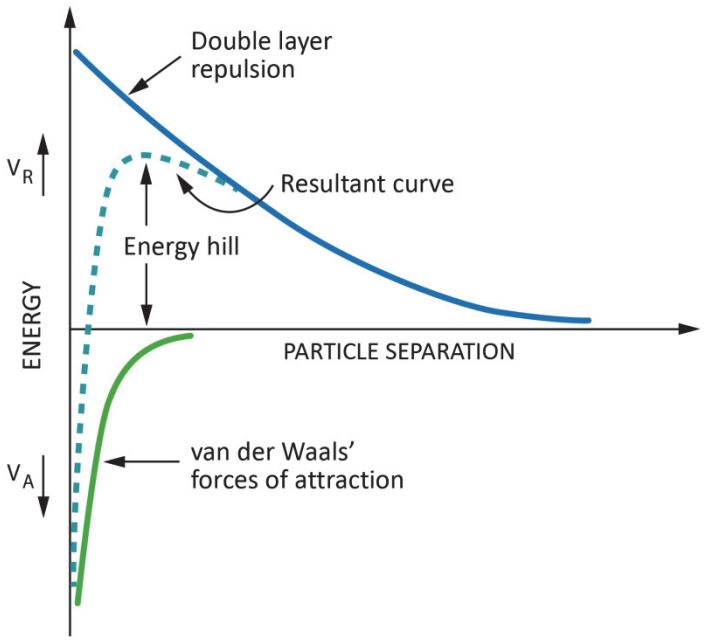

Fig. 3. Repulsive and attractive energies as a function of distance between particles.

2.2 Destabilization of colloids using coagulation

Stable colloids and are difficult to remove from water unless their size is grown. Due to their small mass, gravity has no effect on the settling of colloids. Instead, they will remain in suspension unless they are destabilized chemically. (Sawyer *et al.* 2003, 368) Chemical destabilization may be achieved using conventional coagulation (CC), which is a fundamental part of most modern water and wastewater treatment plants. Aluminum or iron (ferric) salts, such as aluminum sulfate (referred to as alum), ferric sulfate, and ferric chloride are typically used to promote coagulation. Additionally, coagulant aids and enhanced coagulants, both natural and synthetic, may be utilized. They have the ability to increase floc density and thus assist in their formation, promoting the growth of large, rapid-settling flocs. (Bratby 1980, 55–61, 79, Eckenfelder *et al.* 2009, 143–145) Nowadays, one of the most typically used organic polymers used to enhance coagulation in combination with a primary coagulant is polyaluminum hydroxychloride (PACl) (Ahmad *et al.* 2008). Partially prehydrolyzed, its use may significantly reduce sludge generation compared with conventional coagulants (Bratby 1980, 58).

The concepts of coagulation and flocculation are somewhat overlapped and are often mixed together. This is due to the fact that there are no completely unambiguous definitions for these concepts. According to general engineering practices, coagulation is an event where the EDL surrounding particles is affected so that repulsion between the particles decreases. Therefore, in coagulation, colloids coincide to microflocs as a result of destabilization. Flocculation, in turn, is an event in which particles that have already been destabilized come into contact with each other. Thus, they agglomerate into larger molecules. Flocculation can also be thought to comprise the entire process (agglomeration, aggregation) from the beginning to the end. (Benefield *et al.* 1982, 212, Bratby 1980, 5)

In coagulation, destabilization can take place by means of four different mechanisms. More than one of these mechanisms can simultaneously contribute to the formation of flocs. Possible destabilization mechanisms are: reduction of surface potential by compression of the EDL, inter-particle bridging of polymers, surface charge neutralization of the particles by the addition of counterions, and sweep coagulation (adsorption of pollutant particles inside flocs). (Benefield *et al.* 1982, 212–218, Sawyer *et al.* 2003, 368–371) Generally, the last two mechanisms may be considered to be the most important. Factors such as pH and coagulant dosage affect the relative importance of charge neutralization and sweep coagulation (Duan & Gregory 2003).

Critical coagulation concentration (CCC) is the minimum concentration of a coagulant that will allow rapid coagulation to occur. Related to this, the so-called Schulze-Hardy rule ($CCC \approx 1/z^n$) has been presented over a century ago. According to this empirical rule, the CCC is proportional to some inverse power of the counter-ion (ions of opposite charge to the charge on the colloid particles) valency (z). The exponent (n) has been calculated to vary between 2 or 6, and sometimes even over 6, thus showing a strong correlation. The first quantitative explanation of the Schulze-Hardy rule was the DLVO theory, which was thereby acknowledged as having prominent importance in colloid science. (Metcalfe & Healy 1990, Sano *et al.* 2000)

3 Electrocoagulation (EC)

3.1 History and current state of EC research

EC technology has been known for over a century and was first patented at the turn of the 20th century. Extensive EC studies were carried out in the latter half of the century in both the United States and the Soviet Union. However, EC remained practically unused in water and wastewater treatment until the 21st century. This was mainly due to the then-high investment and electricity costs. These economic facts gave other technologies an edge over EC. The prices of electricity as well as power sources have lowered substantially since, making EC again a viable alternative for water and wastewater treatment. Indeed, the environmental sector has recently shown great interest in EC as a research subject. (Chen 2004, Holt *et al.* 2005, Koren & Syversen 1995, Weintraub *et al.* 1983)

EC lies at an intersection of three more conventional technologies. It combines the functions and advantages of conventional chemical coagulation (CC), flotation, and electrochemistry in water and wastewater treatment. All of these are known technologies with decades of extensive research and development. However, the profound mechanism of interaction between these technologies, which is employed in an EC system, is still somewhat shrouded. More research on the core basis of EC is therefore needed to develop a better understanding of the technology as a whole. (Holt *et al.* 2005)

3.2 Principles of EC

As stated above (Chapter 3.1), EC is nowadays an established water treatment technology. It is based on *in situ* electrolytic dissolution of the anode metal material and may be readily automated. Simultaneously with the anodic reaction, gas bubbles are generated at the cathode surface, promoting electroflotation (EF). Usually, Al, Fe, and/or SS (stainless steel) are used as the electrode materials. (Chen 2004, Mollah *et al.* 2001, Sillanpää 2014, 81) The prevalence of these metals (Al, Fe) is due to their availability, inexpensive price, non-toxicity, and proven effectiveness (Chen *et al.* 2000, Kumar *et al.* 2004). Other metals, such as Mg, have also been used occasionally (Vasudevan *et al.* 2009a, Vasudevan *et al.* 2010). Inert aerated cathodes (air cathodes) may also be used. EC systems may contain either one or multiple anode-cathode pairs, and may be connected in serial or parallel, in

either a monopolar (MP) or a bipolar (BP) mode (Emamjomeh & Sivakumar 2009, Jiang *et al.* 2002, Khandegar & Saroha 2013).

Utilization of so-called sacrificial anodes is the main difference between EC and practically all other water purification technologies based on electrolysis. These technologies are namely EF, electro-Fenton (E-F), electro-oxidation (EO), electrodialysis (ED), electrofiltration, electrophoretic deposition (EPD), etc. (Brillas *et al.* 2009, Chang *et al.* 2009, Chen 2004, Sadrzadeh *et al.* 2007, Yang & Li 2007). Furthermore, in other electrolysis-based technologies, the (electro)chemical reactions mainly take place only on the electrode surfaces.

3.2.1 Electrolytic reactions in an EC cell

The main electrolytic electrochemical reactions that take place in the EC process are presented in Eqs. (1)–(5) (Chen 2004, Mollah *et al.* 2001, Publication V):

At the anode:

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^- \quad E_0 = +1.66 \text{ V} \tag{1}$$

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \quad E_0 = +0.44 \text{ V} \tag{2}$$

$$Fe(s) \rightarrow Fe^{3+}(aq) + 3e^- \quad E_0 = +0.04 \text{ V} \tag{3}$$

$$2Fe^{2+}(aq) + ½O_2(g) + H_2O(l) \rightarrow 2Fe^{3+}(aq) + 2OH^- \tag{4}$$

At the cathode:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^- \quad E_0 = -0.83 \text{ V} \tag{5}$$

In principle, as presented in Eq. (3), iron may oxidize directly to Fe^{3+} at the anode. This reaction is nevertheless highly unfavorable (E_0 = +0.04 V) compared with oxidation to ferrous (Fe^{2+}) iron (E_0 = +0.44 V), as presented in Eq. (2). As presented in the sum reaction Eq. (4), dissolved oxygen in solution may cause oxidation of the electrogenerated Fe^{2+} to Fe^{3+} (Zodi *et al.* 2009).

In addition to the main reactions presented above, a variety of minor side effects, such as direct reduction of metal ions on the cathodes, may also take place in an EC cell, (Mollah *et al.* 2004, Sillanpää 2014, 83, Zongo *et al.* 2009). Due to these side reactions, specifically OH^- ion production, as presented in Eq. (5), the EC process may typically neutralize the water treated. Thus, after EC treatment, the

effluent's pH will be increased for acidic influent but decreased for alkaline influent. The increase in solution pH has also been found to be greater when Fe anodes are used, compared with Al anodes. The decrease in solution pH is suggested to be due to the formation of aluminate ($Al(OH)_4^-$), which is an alkalinity consumer. The change in pH occurs at a significantly greater rate in the beginning of an EC experiment than toward its end, where a steady state is typically reached. (Chen 2004, Katal & Pahlavanzadeh 2011, Publications II and V, Sillanpää 2014, 84–85, Zongo *et al.* 2009)

3.2.2 Hydrolyzation of the dissolved anode metal

In EC, after the anode metal has been dissolved into the liquid media, it will immediately undergo rapid hydrolyzation. In these spontaneous reactions various hydroxides and/or polyhydroxides are produced. For aluminum, species such as, e.g., $Al(OH)^{2+}$, $Al(OH)_2^+$, and $Al(OH)_4^-$ and $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{4+}$, and $Al_{13}(OH)_{34}^{5+}$ have been suggested. These species will then finally transform into $Al(OH)_3$ according to complex precipitation kinetics. (Mollah *et al.* 2004, Rebhun & Lurie 1993) The most important and best-known polymeric form of aluminum is the so-called Keggin cation $(Al_{13}O_4(OH)_{24})^{7+}$, which is regarded as the main unit of larger precipitated and soluble complexes. It is commonly known as the Al_{13} ion. The Keggin structure (radius of about 2.5 nm) consists of a tetrahedral AlO_4 unit at the center of the cluster, which is surrounded by 12 octahedral AlO_6-units in which H_2O groups are attached to the vertexes of the octahedras. The Al_{13} ion has been found to achieve the highest charge neutralization compared with other aluminum species. Thus, it is denoted as the most effective and stable polymeric Al species for water and wastewater treatment. (Gao *et al.* 2005, Sarpola 2007, 56)

Correspondingly for iron, after the electrogeneration of ferric ions, monomeric ions, ferric hydroxocomplexes with OH^- ions, and polymeric species may be formed. These species include (but are not limited to), e.g., $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$, $Fe(OH)_4^-$, $Fe(H_2O)_5OH^{2+}$, $Fe(H_2O)_4(OH)_2^+$, $Fe(H_2O)_8(OH)_2^{4+}$, and $Fe_2(H_2O)_6(OH)_4^{2+}$. As with aluminum, these species will further react to form $Fe(OH)_3$ (Akbal & Camcı 2010, Kobya *et al.* 2003). One of the main factors effecting the formation of the metal complexes is solution pH. The dominant species in solutions with a pH value above 9 are $Al(OH)_4^-$ and $Fe(OH)_4^-$. (Akbal & Camcı 2010) This can be seen from Fig. 4, in which the relative proportions (mole

fractions) of dissolved hydrolysis products in equilibrium with amorphous hydroxides (for Al and Fe) are presented.

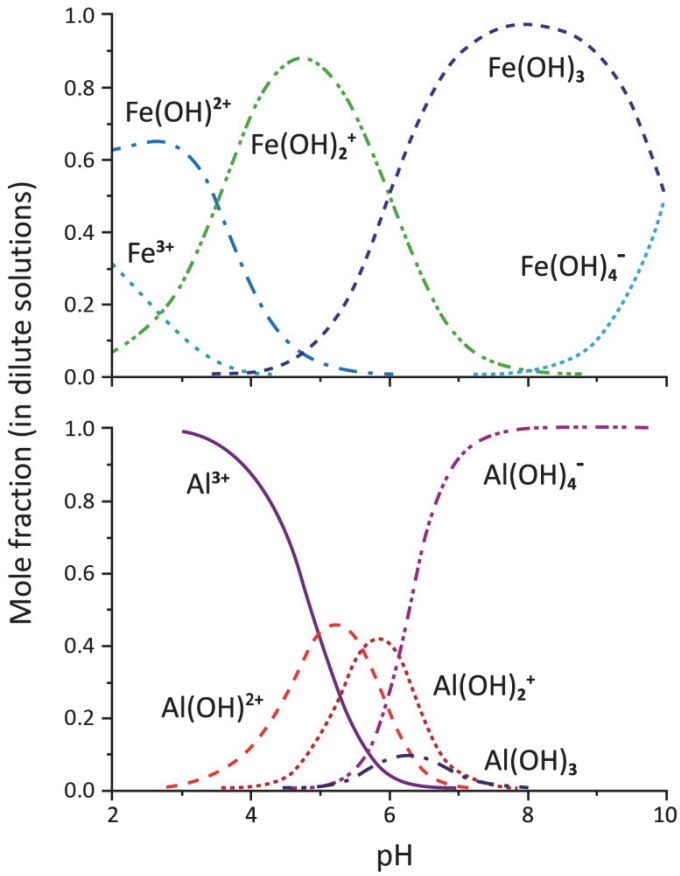

Fig. 4. Mole fractions of dissolved hydrolysis products in equilibrium with amorphous hydroxides for Fe(III) and Al(III).

3.2.3 Faraday's law

Theoretically, the mass of the dissolved anode metal [g] can be calculated using Faraday's law, which is presented in Eq. (6):

$$m_{metal} = \frac{ItM}{zF} \tag{6}$$

where I is the applied current [A], t is the treatment time of the EC process [s], M is the molar mass of the anode metal [g/mol], z is the valence number of ions of the substance ($z_{Al} = 3$, $z_{Fe} = 2$), and F is Faraday's constant (96,485 C/mol). As Eq. (6) implies, the amount of dissolved metal may be directly adjusted simply by altering the applied current. This facilitates the automation of EC. (Mollah *et al.* 2001, Mollah *et al.* 2004, Sillanpää 2014, 84)

3.2.4 Superfaradaic efficiencies and pitting corrosion

The theoretical amount of anodic dissolution is commonly exceeded in many real EC applications with varying results. This phenomenon is referred as to superfaradaic efficiencies. Case-specifically, the experimental variance of superfaradaicity in the EC studies found in scientific literacy has typically been between 105–190% of the theoretically expected value. (Kobya *et al.* 2011, Kongjao *et al.* 2008, Mouedhen *et al.* 2008, Şengil & Özacar 2009, Terrazas *et al.* 2010, Yetilmezsoy *et al.* 2009)

Superfaradaic efficiencies have been proposed to be due to pitting corrosion (Mameri *et al.* 1998, Shen *et al.* 2003). Naturally, long-term submerging of the electrodes may also cause slow dissolution. Furthermore, cathodic metal dissolution, specifically of aluminum, may also occur due to the localized decrease in pH on the cathode surface. This is due to OH^- formation, according to Eq. (4), or the consumption of hydronium ion/protons. (Picard *et al.* 2000, Sillanpää 2014, 84)

Pitting corrosion can occur as a result of exposure to certain environments. It is a localized form of corrosion, which is typical for metals, whose corrosion resistance is based on the so-called protective passive oxide film. Such films are present, e.g., on the surface of unprotected aluminum or SS, consisting of a thin oxide film. Generally, pitting occurs most notably in solutions where chloride is present, e.g. from NaCl. (McCafferty 2003, Refaey *et al.* 2004, Szklarska-Smialowska 1999)

In such cases, if the anode potential is sufficiently high, active chlorine species may form. These species, such as Cl_2, HClO, and OCl^-, may then both oxidize pollutants and simultaneously chemically oxidize the anode material. This may, however, enhance the performance of an EC reactor. (Publication V)

3.3 Process economy and ecology of EC

The dissolved metal material and electricity costs are largely regarded as the main cost components of the EC process, excluding fixed costs such as sludge processing and labor, as presented in Eqs. (7) and (8). Therefore, it should be noted that the economic values of a particular EC process calculated using Eqs. (7) and (8) are only estimates.

$$OC = aEEC + bEMC + cSEC \tag{7}$$

$$EEC = \frac{UIt}{60V} \tag{8}$$

In Eq. (7) OC is operating cost [€/m^3]; a, b, and c are the current market prices of electricity [€/kWh], electrode materials [€/kg], and supporting electrolyte [€/kg], respectively; EMC [kg/m^3] is electrode material consumption; and SEC [kg/m^3] is supporting electrolyte consumption. In this work, a, b, and c were estimated (Publication V) to be approximately 0.09 €/kWh (in Finland in February 2015, including electrical energy, distribution of electricity, and taxes), 1.60 €/kg$_{Al}$, 0.42 €/kg$_{Fe}$ (steel), and 0.06 €/kg$_{NaCl}$, respectively. The numerical values of a, b, and c may fluctuate over time, but during the course of this work, this fluctuation has only been slight. In Eq. (8) EEC is electrical energy consumption [kWh/m^3], U is the applied voltage [V], t = treatment time [min], and V is the volume of the treated water [dm^3]. (Kobya *et al.* 2007, Publications I and V)

To facilitate additional economic analyses and comparisons with other water purification methods, EEC and OC per kg of pollutant (e.g. chemical oxygen demand, COD)—derived from Eqs. (7) and (8)—may also be readily evaluated. To do this, the initial/final concentrations of the pollutants in the solution must be known. Also, the effect of superfaradaicity on the EC process economy should be taken into account case-specifically when analyzing the economics of a given EC application. (Publications I and V)

It is generally thought that, compared with CC, EC is more economical and in many ways “greener”. Still, the ecological effects of EC are rather obscure and should be addressed in more detail. Furthermore, this, and the OC of the two processes have not often been compared with each other in the literature. (Vepsäläinen 2012, 38, 47) In some parts of the world, conventional coagulants may be obtained as industrial by-products. For example, in Southern Finland, ferrous sulfate is derived as a by-product from the industrial production of titanium dioxide. This can make the use of CC favorable due the lower prices of the

coagulants. However, the prices of prehydrolyzed coagulants are usually relatively higher (Vepsäläinen 2012, 47). The price of aluminum in PACl is up to about fourfold higher than the price of aluminum metal (Vepsäläinen 2012, 47, Gebbie 2001).

The production of metals results in the formation of emissions. Thus, unwanted solids, liquids, and gases are generated both directly (during mining and processing) and indirectly. Even though the production of metallic Al and Fe is extremely energy-consuming and they are more costly (per kg) than the corresponding metal salts, the fact that they are purely metal and do not contain, e.g., crystallization water must be taken into account. (Norgate *et al.* 2007) Also, recycling of metals substantially reduces energy demand, pollution, and environmental impact caused by, e.g., aluminum production versus the use of virgin metal materials. This has become commonplace nowadays. (Vepsäläinen 2012, 47) This is a very important point indeed, because in the overall supply chain of material needs in metal production, mineral resource extraction and processing are particularly critical stages in terms of potential emissions release (Norgate *et al.* 2007).

Additionally, it is also noteworthy that the use of coagulation chemicals may significantly lower the pH of water (Sillanpää 2014, 84). However, in contrast to this, and as stated in Chapter 3.2.1, in EC a neutralization effect of water typically occurs. Also, the EC process itself doesn't usually require other "chemicals" than the electron (Khandegar & Saroha 2013).

3.4 Comparison of EC with conventional methods

A profound question may be asked: why electrocoagulation? As stated before in Chapter 2.2, conventional coagulation is an essential part of most modern water and WWTPs (wastewater treatment plant). Other potential methods for water and wastewater treatment may include physical processes (e.g. filtration, screening, and sedimentation/flotation), physicochemical processes (e.g. coagulation, adsorption, and ion exchange), various biological processes, membrane processes, disinfection methods (e.g. chlorination, ozonation, or ultraviolet processes), etc. (AWWA 1999, Eckenfelder *et al.* 2009). Naturally, their feasibility depends on the application in question. However, EC has several advantages over CC (and also other technologies), which may naturally be seen as its main competition. Then again, EC, like any other technology, has its downsides.

3.4.1 Advantages of EC

Firstly, the advantages of EC over conventional coagulation include economic aspects. Investment costs for EC systems are low due to their small size. No large mixing or sedimentation pools are usually needed. EC systems may be automated, hybridized with other methods, and rather simple in design and therefore their maintenance costs are low. This is also true for the energy and treatment costs related to EC. Compared with CC, using EC significantly lowers the volume of sludge produced. In addition to practicality, this is also an important point related to the economy of the process, since sludge generated using any water treatment method must be further treated. Furthermore, EC sludge is also of better quality (lower water content, much larger and more stable flocs with better settlability). This is thought to be particularly true for Fe-EC (Publication IV, Zodi *et al.* 2009, Zodi *et al.* 2011). (Chen *et al.* 2002, Mollah *et al.* 2001, Mollah *et al.* 2004, Publication I)

One of the main advantages of EC is the avoidance of chemical additions (excluding possible NaCl additions), which makes EC "a green technology". Indeed, the electron may be considered to be the only "chemical" used, thus preventing secondary pollution. This is also a logistical advantage, and since the dosaging of chemicals is avoided, no problems due to pumping them (e.g. freezing) will occur. The functional pH range of EC is wide, and water and wastewater may even be neutralized using EC (Chen *et al.* 2000, Chen *et al.* 2002). Conversely, as mentioned in Chapter 3.3, the pH of the treated solution decreases significantly using CC. This is due to hydrolysis of Al/Fe. EC has been found to have similar or slightly better treatment efficiency compared with CC, applying similar metal dosaging (Ryan *et al.* 2008). However, the presence of simultaneous EF is beneficial. Response surface modeling (RSM) has been shown to be applicable in several EC studies, which may significantly help the design of a given EC application (Aleboyeh *et al.* 2008, Chavalparit & Ongwandee 2009, Kumar *et al.* 2009, Kushwaha *et al.* 2010, Tir & Moulai-Mostefa 2008, Vepsäläinen *et al.* 2009, Zodi *et al.* 2010). (Mollah *et al.* 2001, Publication I)

The applicability of EC in treating cold water is an important techno-economical point (Publication V). Due to their rather low electricity consumption, some EC systems may also be designed to utilize, e.g., windmills or solar electricity, the price of which is currently in significant decline globally. Due to these facts and the compact size of EC systems, decentralized treatment may be viable case-specifically, even in rural areas with no access to power grids. (Khandegar &

Saroha 2013, Mollah *et al.* 2001) Furthermore, since the EC process can be started by turning on the switch, it requires minimal startup time (Khandegar & Saroha 2013).

3.4.2 Disadvantages of EC

The most obvious disadvantage of EC is the need to periodically replace the electrodes. Another main disadvantage of EC is the need for adequate water conductivity. (Mollah *et al.* 2001) Industrial wastewater often has high enough conductivity due to its high ion concentration. However, e.g. natural water and lightly polluted wastewater lack this feature. Thus, their conductivity must be raised by using a supporting electrolyte. Due to its low price, availability, and non-toxicity, NaCl is the most common supporting electrolyte used, but others, such as Na_2SO_4 have also been used occasionally (Cañizares *et al.* 2007). Furthermore, toxic chlorinated organic compounds may form from water containing chlorides (e.g. from NaCl) and organic substances (Mollah *et al.* 2004).

No widely accepted mathematical/kinetic model for EC exists. However, this is more of an academic issue, and adsorption kinetics for multiple case-studies have been modeled successfully, as presented in Publication II. Furthermore, as stated in Chapter 3.4.1, RSM has also been used successfully with EC. Uneven anode dissolution may hinder the effectiveness of EC. Electrode passivation, specifically when Al-EC is used, may occur due to slow oxide film development on electrode surfaces (Osipenko & Pogorelyi 1977). This inhibits electron exchange and metal dissolution, increasing electrical energy consumption. Even though there is no universal solution to this problem yet, using alternating pulse current (APC) has been found very promising (Eyvaz *et al.* 2009, Keshmirizadeh *et al.* 2011, Vasudevan *et al.* 2011). Also, periodic cleaning of the electrodes may prevent electrode passivation. (Holt *et al.* 2005, Kabdaşlı *et al.* 2012, Mollah *et al.* 2004)

On a theoretical level, and in practice on a theoretical level only, the hydrogen gas produced could be explosive. Furthermore, laboratory-scale recollection of hydrogen gas has been studied with success (Phalakornkule *et al.* 2010a). Treatment costs are subject to change if the prices of electricity and metal change significantly. On the other hand, this also applies to other water treatment methods.

Excessive residual aluminum concentrations in the environment must be prevented. Aluminum may cause neurological disorders such as the Alzheimer's disease, and thus has a bad environmental reputation (Crapper-McLachlan 1986, Polizzi *et al.* 2002). On the other hand, if needed, iron can be used as the soluble

anode material. However, particularly if overdosed, iron may cause coloration of water (Gao *et al.* 2010, Kobya *et al.* 2006, Li *et al.* 2008, Zaied & Bellakhal 2009).

4 Aims of this work

In the beginning of this study, the focus was set on updating knowledge on recent global EC literature, because EC is currently under vigorous research globally. The aim of this part of the work (Publication I) was to survey the optimal process conditions of the studied feasible EC applications, and specifically their economic key figures. Even though the economy of a given water/wastewater treatment technology is of utmost significance when comparing different technologies, the economics of EC have been estimated very little in the scientific literature until now. This is also true regarding the scalability of EC. Indeed, most of the EC studies in the scientific literature have been conducted using only laboratory-scale EC systems. From a practical point of view, this is a major design challenge concerning the large-scale feasibility of almost any real-life industrial process.

The aim of the next part of this work (Publications II–V) was to find new feasible applications for EC in the treatment of water and wastewater. Treatment of peat bog drainage water (PBDW) by EC was of particular interest, since proper treatment of PBDW may even be considered to be a key question affecting the future of the entire Finnish peat industry. Both synthetic and real wastewaters were used in the experiments conducted in this work. The main process parameters affecting the performance of EC were optimized as necessary. The aim of these studies was also to conduct larger-scale EC experiments to prove the scalability of EC, as discussed above. Furthermore, an important objective of these studies was to perform extensive economic analyses of the EC applications in question and also study the superfaradaic and Joule effects related to the EC process.

It has been forecasted that in the future there will be a shortage of virgin phosphorus. This will lead to serious global agricultural problems. Therefore, another important aim of this work (Publications III–IV) was to conduct a preliminary study on the feasibility of using EC for nutrient removal and recovery from different types of wastewater. In this way, EC could possibly be used simultaneously as a wastewater treatment method and as a means to obtain valuable nutrients for fertilization use. Specifically, it may be possible to use EC sludges containing notable amounts of phosphorus and nitrogen as additives in granulated bio ash-based fertilizer products (so-called symbiosis pellets). This is a novel idea and a “hot topic” in the waste utilization sector. It also fits well into the extremely topical and essential themes of circular and bioeconomy.

5 Materials and methods

5.1 Research principles

It is generally acknowledged that the main parameters influencing the efficiency of the EC process are the electrode materials used and solution chemistry, including the conductivity and initial pH of the solution and its chemical composition. The applied current density i [A/m^2], see Eq. (9) below, and treatment time (t) are naturally of utmost significance, since they determine the dosaging of the anode metal:

$$i = \frac{I}{A_{eff}} \tag{9}$$

where A_{eff} [m^2] is the submerged (effective) area of the anode metal. The solution temperature, type of salt possibly used to raise conductivity, presence of chloride (e.g. from NaCl), electrode gap, passivation of the anode, mixing speed, and flow conditions—all of the aforementioned also have an impact on the removal efficiency and process economy of a given EC application. Therefore, in this work (in Publications II–V), the effect of altering the aforementioned main process parameters on the EC treatment efficiency of the water and wastewater types studied was investigated. The removal efficiencies of pollutants ($R\%$) presented in Publications I–V have been calculated with Eq. (10):

$$R\% = \frac{c_0 - c_1}{c_0} * 100 \tag{10}$$

where c_0 and c_1 are pollutant concentrations before and after EC treatment, respectively. The economic analyses were conducted using Eqs. (7) and (8), as presented in Chapter 3.3. Also, the generation (Publication II) and composition (Publications III–IV) of particular EC sludges were analyzed in this work. This was done to help evaluate the amounts of sludge generated by EC and the possibility of their further utilization.

Publication I differs from the other papers of this dissertation, since it is a review of recent applications of EC in water and wastewater treatment in the scientific literature. However, in Publication I, the main scrutiny was directed at generating an overview of optimum values of the main process parameters for specific EC applications. Other practically important key figures of the EC studies

in question were also mapped out, and new innovations related to EC were discussed.

In a small part of the papers addressed in Publication I, the authors did not present economic values and/or current densities in optimum conditions, but they could be approximated by using numbers given in the article. These numbers/values included, e.g., total submerged anode surface area, applied current and voltage or current density, volume of the wastewater treated, treatment time, initial concentration, removal efficiency, etc. It should be pointed out that these approximation calculations were rather simple. They were based on Eqs. (6)–(10). Furthermore, it should be very strongly emphasized that they were done only when the authors of the corresponding research papers had not presented the numbers themselves but had clearly stated the values needed for the calculations. Additionally, such values could be easily deduced in some cases.

5.2 EC systems and other equipment used in this work

Three different EC systems were used during the course of this work. All of the EC systems used direct current (DC) and operated in a batch mode. An electrode gap of 7 mm between the anode and the cathode was set as a constant in this work (unless stated otherwise, see Publication III), and was thus used in all three EC systems.

5.2.1 Bench-scale EC apparatus

The first EC apparatus used in this work was a bench-scale EC system and it had minimum and maximum working volumes of about 17 L and 35 L, respectively. The bench-scale EC system was used solely in the experimental part of Publication II, and also in Publication III, in the scale-up part of that particular work. As stated above, this EC system also operated in a batch mode, however with continuous recirculation of the water. The bench-scale EC apparatus is presented in Fig. 5. In addition, the process instrumentation diagram of the system has been presented in Publication II.

Fig. 5. Bench-scale apparatus (before SS basin reconstruction) used in the experimental parts of Publications II–III. Modified from Publication II.

As presented in Fig. 5, the EC cell was composed of a basin (65 cm x 27 cm x 5 cm) made of austenitic steel with molybdenum (SS 316), and 6 Al bars (58 cm x 8 cm x 1 cm). The Al bars were rectangular and the gaps between them were about 2.5 cm. A flow barrier made of SS was installed at the end of the basin and consequently the height of the water column in the overflow end (see Fig. 5) of the EC cell was raised variably to 17/25 mm and 110 mm in Publications II and III, respectively. Thus, in Publication II, the aluminum bars were not fully submerged. However, an EC basin made of SS was reconstructed in Publication III, and the Al bars were subsequently fully submerged to an average (due to slight declination of the EC basin) depth of 18 mm.

In Publication II, the submerged area of the SS basin was 1840 cm^2 (without the flow barrier) and 1960 cm^2/2100 cm^2 (with the flow barrier) when the height of the water column was 17 mm/25 mm, respectively. In Publication III, the submerged area of the SS basin was 3600 cm^2. For the Al anode bars, A_{eff} was 1190 cm^2 when the height of the water column was 25 mm (Publication II) and 6200 cm^2

when the bars were fully submerged (Publication III). The water volume in the electrolytic cell was 1.8 L/2.9 L when the height of the water column was 17 mm/25 mm, respectively, and 15 L (hydraulic retention time, HRT = 2.5 min) after the reconstruction of the SS basin. After every experiment using this EC apparatus, the EC cell was carefully mechanically cleaned using hydrochloric acid. Hot tap water was then circulated in the apparatus for 20–30 minutes to remove any remaining sludge from the pipes.

5.2.2 Laboratory-scale EC apparatus

A smaller, laboratory-scale EC system was also designed, built, and used in Publications III–V. This EC system is presented in Fig. 6. Electrode plates made of Al, Fe, and stainless steel SS were manufactured and used in this EC system. The dimensions of the plates were 10 mm x 50 mm x 50 mm. After each experiment, the electrodes and the glass EC cylinder were rinsed with hot tap water and submerged in 1.5 M nitric acid solution for a short time. The electrodes were then mechanically cleaned and rinsed thoroughly with deionized water. After this, a precision scale was used to weigh the oven-dried anode plates. A magnetic stirrer was used to mix the water in the glass cylinder.

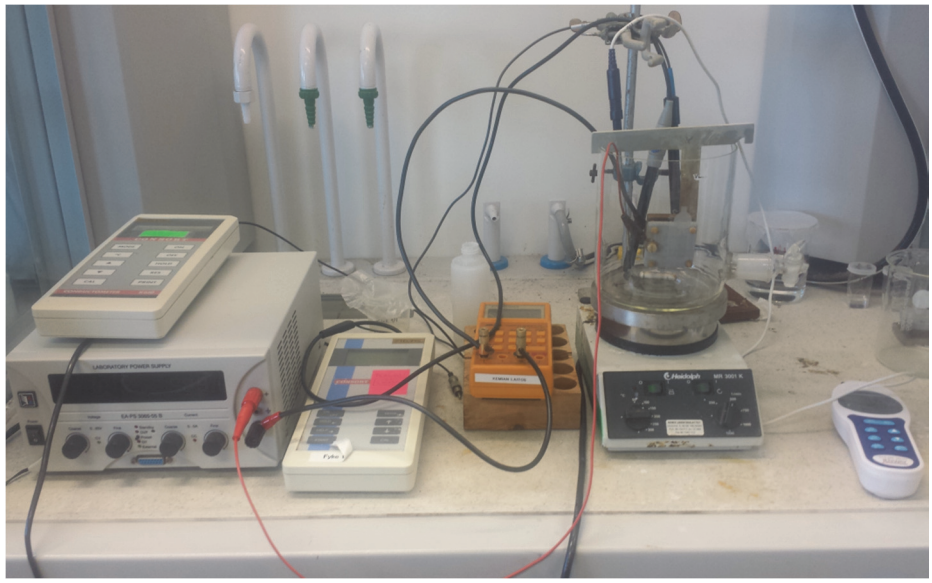

Fig. 6. Laboratory-scale EC system used in the experimental parts of Publications III–V.

5.2.3 Large-scale EC system

A large-scale EC system, which was based on the laboratory-scale EC system, was designed and built in this work. The large-scale EC system was used in the experimental part of Publication V to experiment with scaling up the EC process. The working volume of this EC system was about 1 m^3, otherwise it was very similar to the (smaller) laboratory-scale EC system. A motorized overhead stirrer was used to mix the solution in the EC vessel. The electrodes and the EC vessel were cleaned thoroughly with hot tap water between the experiments. The large-scale EC system and real peat bog drainage water (PBDW) used in the experimental part of Publication V are presented in Fig. 7.

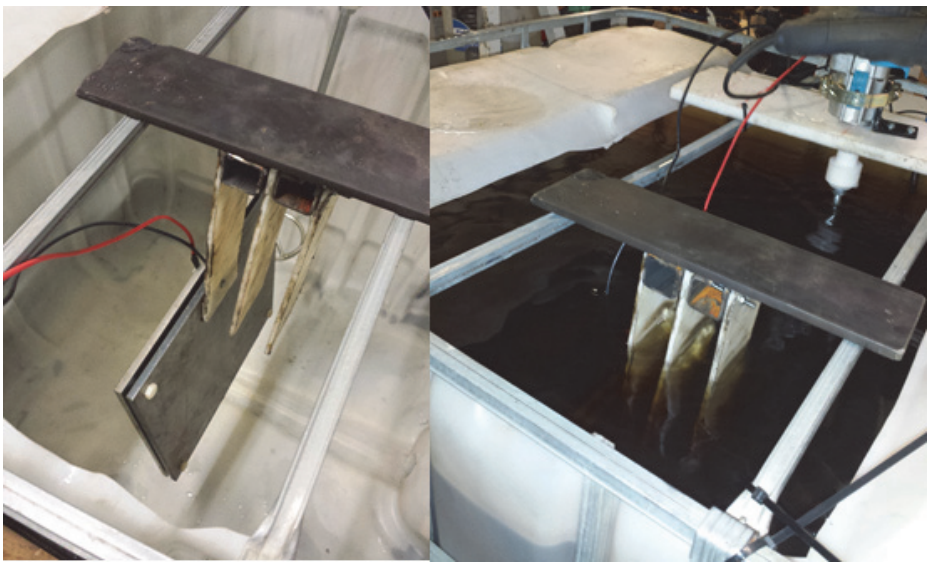

Fig. 7. Large-scale EC system and real PBDW used in the experimental part of Publication V.

5.2.4 Analytical sensors and other equipment

In this work, electrical current was measured with an Amrel 3200 Multimeter, while voltage could be read directly from the DC power source (Publication II: GW Instek GPR-1810H, 18V/10A, Publications III–V: EA-PS 3065-05 B, 65V/5A or EA-PS 3016-40 B, 16V/40A). Water temperature was measured with a TES-1300 Type K

Thermometer (Publication II) and a Jenway Enterprise Portable Model 370 pH/mV meter (Publications III–V). Solution pH values were measured using a WTW inoLab pH 720 (Publication II) and a Jenway Enterprise Portable Model 370 pH/mV meter, Consort C931 pH meter, or Mettler Toledo S20 SevenEasy pH meter (Publications III–V). In Publications II–III, water flow in the bench-scale EC apparatus was measured electromagnetically with a combination of a Toshiba LF470 detector and a Toshiba LF420 converter. The conductivity of the oil-in-water (O/W) emulsions (Publication II) was measured with either a YSI 600 OMS-sonde with a YSI 650 MDS or a WTW Multiline P4 Universal meter. In Publications III–V, solution conductivity was measured using a Consort Conductometer K610.

5.3 Water and wastewater samples

Synthetic wastewater (SWW) solutions containing O/W emulsions, phosphate, and humic acids were used in Publications II, III, and V, respectively. The synthetic solutions containing phosphate (KH_2PO_4, Merck Millipore) or humic acids (Aldrich H16752 Humic acid sodium salt) were prepared simply by diluting an appropriate amount of the desired (commercial) model components into deionized water. In Publications III–V, real wastewaters were also used. Namely, these were apatite mining wastewater (MWW) and dairy wastewater (DWW) derived from Finnish industry (Publication III), hygienized digester plant reject water (DPRW) from Biotehdas Oy, Vampula (Publication IV), and PBDW from three northern Finnish peat bogs (Publication V). The characteristics of the aforementioned water samples are presented in the corresponding subsections of this Chapter.

In Publication II, multiple types of O/W emulsions were prepared by using bio oils (rapeseed oil, RSO; sunflower, SFO; and tall oil-based chain oil, TO) and synthetic oils (motor oil, MO;, and chain oil based on recycled industrial oils, MCO). The RSO had been cold pressed in Ilmajoki at Seinäjoki University of Applied Sciences, School of Agriculture and Forestry (Vauhkonen *et al.* 2011). The SFO was a commercial product of Rainbow from Finland, the TO was a product of Ekopine Oy, and the MO was commercial Mobil Super 3000 5 W-40. The other synthetic oil used in Publication II, Metsuri chain oil (MCO), was a mineral oil-based chain oil produced from recycled industrial oils by Ekokem Oy Ab, Finland. The O/W emulsions were prepared by mixing 7.5 L of tap water, oil, anionic surfactant (sodium dodecyl sulphate, SDS, needed for emulsification and homogenization), and NaCl in a plastic bucket using a whisk-equipped Heidolph RZR 1 overhead stirrer for 20 min at a rate 280–900 rpm. SDS was added to

emulsify and homogenize the O/W emulsion. Real oily wastewaters are known to contain surfactants (Publication II). The surfactant type and amount were determined by preliminary experiments according to COD and total surface charge (TSC) measurements as well visual inspection. The prepared O/W emulsions were colored and turbid.

In this work, all of the synthetic solutions' initial pH values were adjusted using 0.1 M HCl and NaOH. In Publication IV, due to the strong buffering effect of the real wastewater used (DPRW), 12 M HCl and 3.75 M NaOH were used to adjust its pH. Also, the initial pH values of the real phosphate-containing wastewaters (MWW and DWW) in Publication III were adjusted using 1 M HCl and NaOH. Also, if necessary, sodium chloride (NaCl, L.T. Baker) was added to the synthetic wastewaters to increase their conductivity. The real industrial wastewaters used in this study had high conductivity, and thus no NaCl was added to them.

5.3.1 Characteristics of the oil-in-water emulsions (Publication II)

The initial COD, TOC, TSC, and turbidity values of the O/W samples used in Publication II varied greatly (even for the same type of O/W emulsions). Respectively, they were in the range of 2,210–26,800 mg/L, 220–1,510 mg/L, (-600)–(-10,470) μeq/L, and 110–1,760 NTU (nephelometric turbidity unit). The variance between similar O/W samples might have been a result of several factors, such as differences in sample preparation (amount of free oil in the surface layer) and sampling for analytics. However, this did not affect the EC process itself: repeatable results were achieved. Furthermore, it should be noted that considerable variation in parameter values may also exist when dealing with real oily wastewaters.

5.3.2 Characteristics of the phosphate-containing wastewaters (Publication III)

The SWW used in Publication III contained 15–30 mg/L phosphate and 1 g/L NaCl (to raise its conductivity). The quality of the studied apatite MWW was reported to fluctuate significantly over time (at the apatite mine); its pH and phosphate content may vary between 6–12 and 4–16 mg/L, respectively. The characteristics of the real phosphate-containing MWW (n = 9) and DWW (n = 8) samples used in Publication III are presented in Table 1. No NaCl additions to the real wastewaters were needed due to their high conductivities.

Table 1. Characteristics of the real MWW and DWW samples used in Publication III.

Wastewater type	Color	pH	Conductivity [mS/cm]	Pt_{ot} [mg/L]	Nt_{ot} [mg/L]	As [µg/L]	COD [mg/L]	TOC [mg/L]	Turbidity [NTU]
MWW	light yellow	11.7–11.8	1.4–1.8	4.6–5.1	12–18	22–26	<40	7–11	n.d.
DWW	milky white	4.5–5.5	5.4–5.7	130–140	120–140	n.d.[2]	2,000–2,300	630–810	145–154[1]

[1] Unmodified pH value 4.5–5.5 (turbidity values of 267–298 NTU and 22–34 NTU were measured with modified initial pH values of 6 and 8, respectively), [2] n.d. = Not determined.

5.3.3 Characteristics of the hygienized anaerobic digester plant reject water (DPRW, Publication IV)

The characteristics of the DPRW (with a modified initial pH of 5.0) used in Publication IV are presented in Table 2. It should be noted that in addition to a slight color change (probably due to dissolution of organics), the main difference between the raw DPRW sample and the pH-altered one was the amount of dissolved phosphorus and nitrogen—the relative content of both increased significantly. From Table 2 it can be seen, that the DPRW was highly polluted and contained abundant nutrients (especially N). Raw DPRW had a high conductivity of about 26 mS/cm.

Table 2. Characteristics of the DPRW (modified initial pH of 5.0) used in Publication IV.

P_{tot} [mg/L]	N_{tot} [mg/L]	COD [mg/L]	DOC [mg/L]	Al [mg/L]	Fe [mg/L]	TS [mg/L]
37.8	3,000	4,700	380	4.42	45.4	2,400

5.3.4 Characteristics of the humic-containing wastewaters (Publication V)

The SWW used in Publication V was brown in color and contained 100 mg/L of a commercial humic acid (Aldrich H16752 Humic acid sodium salt) and 0.5 g/L NaCl. The COD_{Mn} and DOC values of the SWW were about 38–43 mg/L and 27–32 mg/L, respectively. Its natural pH varied between 7.0 and 8.0.

In the experimental part of Publication V, real PBDWs containing HS from three northern Finnish peat bogs were also treated. Their characteristics are presented in Table 3. Due to their low conductivity (about 60–160 µS/cm for all three), 0.5 g/L NaCl was added to them prior the EC experiments.

Table 3. Characteristics of the real PBDW samples used in Publication V.

Wastewater type	Color	pH	P_{tot} [µg/L]	N_{tot} [mg/L]	COD_{Mn} [mg/L]	DOC [mg/L]	Al [µg/L]	Fe [mg/L]	TS [mg/L]
PBDW1	brown	6.4–7.0	60–110	1.5–1.7	27–28	23–25	~130	~4.3	n.d.[2]
PBDW2	brown	6.6–6.8	60–70	1.1	17	14–15[1]	380–410	3.7–3.8	~12
PBDW3	brown	6.1–6.4	35–60	1.9–2.0	20–21	~17[1]	330–660	5–14	~13

[1] Analyzed as TOC, [2] n.d. = Not determined.

5.4 Water sample analytics

5.4.1 Main analytical parameters and practices

The main parameters measured to control water purification in this work were, depending on the publication: COD/COD_{Mn}, TSC, total organic carbon/dissolved organic carbon (TOC/DOC), biological oxygen demand (BOD), turbidity, P_{tot}, N_{tot}, and total solids (TS). Additionally, Al and Fe were measured to obtain knowledge about residual metal concentrations in the water. Solution pH and conductivity were also monitored during the experiments. In Publication II, laser diffraction was also used by the authors to prove the forming and subsequent breaking of O/W emulsions by EC treatment.

Most of the water analytics of this work were done at an accredited test laboratory, Ahma ympäristö Oy, Oulu, Finland. However, in Publication II, all analytics were conducted by the authors. Also, in Publication III, elementary analyses of synthetic wastewater were conducted by the staff of the Trace Element Laboratory at the University of Oulu using inductively coupled plasma with optical emission spectrometry (ICP-OES). Thus, based on the above, the following chapters (5.4.2–5.4.6) describe the analytics performed/supervised by the author of this work.

5.4.2 Laser diffraction analytics

In Publication II, laser diffraction measurements were conducted using an LS 13320 Laser Diffraction Particle Size Analyzer (Beckman Coulter). Particle size measurement (range: 0.017–2000 µm) using this apparatus was based on measurement of light (780 nm light source) scattering from the laser-lit particles, using silicon photo-detectors, according to the ISO standard 13320-1 (ISO 2009).

The intensity of light at each detector is measured as a function of angle, and is then analyzed mathematically using a complex inversion matrix algorithm.

5.4.3 Turbidity and total surface charge analytics

In this work, water turbidity was determined (Publication II) with a Hach Ratio XR Turbidity meter or (Publication III) an Oakton T-100 Turbidity meter. Turbidity is determined based on the concentration of suspended particles in a water sample by capturing incident light scattering from the sample with a photodiode, according to the ISO standard 7027 (ISO 1999). Mütek PCD 03 pH (Mütek Analytic Gmbh) was used (Publication II) to measure TSC, using polydiallyldimethylammonium chloride (PolyDADMAC, BTG Instruments GmbH) and polyethylene sodium sulphonate (PES-Na, BTG Instruments GmbH) as titrants. Using this apparatus, TSC determination is based on measurement of the so-called streaming potential and polyelectrolyte titration. The sample is titrated with an oppositely charged polyelectrolyte of known charge density to identify the zero value at streaming potential (0 mV), and the titrant consumption is the actual measured value. Finally, the TSC value is calculated by the apparatus on the basis of titrant consumption.

5.4.4 TOC analytics (Publication II)

TOC measurements (Publication II) were conducted using a Sievers 900 Portable TOC Analyzer (GE Analytical Instruments). The operating principle of this device is based on oxidation of organic compounds chemically and photochemically (ultraviolet, UV) into carbon dioxide (CO_2). The amount of CO_2 is then measured based on the conductivity of the solution, which has passed a CO_2-selective membrane. Continuing, other inorganic carbon (IC) fractions and total carbon (TC) content of the sample are also determined. These are done by first lowering the sample's pH to about 2, and then oxidizing the organic content of the sample, respectively. TOC may then be calculated (TOC = TC-IC).

Before measuring TOC, the samples had to be diluted a hundredfold (the flasks were stirred strongly). This was due to the low measurement range of the TOC analyzer (0.03 µg/L to 50 mg/L). This might have distorted the results to some extent, but possibly only in terms of the absolute values, not the relative TOC reductions themselves.

5.4.5 COD analytics (Publication II)

The COD values of the O/W samples (Publication II) were determined using the Hach Lange photometric cuvette test. Different cuvettes, containing the needed reagents in correct amounts, were used for different measuring ranges up to 60,000 mg/L of COD. Thus, the approximate measurement range needed to be known beforehand. In this method for determining COD, oxidizable substances in the sample react with potassium dichromate in a strongly acidic (H_2SO_4) solution. A small amount of silver is also present in the solution as a catalyst.

After heating the cuvettes for 2 h at 148 °C using a Hach-Lange HT 200S thermostat system, Cr^{3+} ions are formed depending on the COD value of the sample. The intensity of the green color in the sample caused by the Cr^{3+} ions is then evaluated by measuring the absorbance of the sample at a wavelength of 605 nm with a Hach-Lange DR 2800 spectrophotometer. The dichromate COD procedure described above will oxidize most organic compounds almost completely; however, some aromatic compounds (such as benzene, toluene, and ethylamines) are only partially oxidized (Karhu 2015, 89).

5.4.6 BOD and biodegradation analytics (Publication II)

BOD analytics (Publication II) were carried out for both the pure oils and the O/W samples with the manometric respirometric BOD OxiTop® method, according to the OECD 301 F standard (OECD 1992). This method is based on accurate measurement of pressure difference, which arises from oxygen consumption in the gas phase, while the simultaneously formed CO_2 is absorbed into NaOH pellets. For pure oils (RSO, SFO, MCO, and MO), BOD_{28} (BOD value after 28-day measurement) and the degree of biodegradation were determined, whereas for O/W wastewater samples from two EC experiments (experiment 11: SFO 2%, Al-EC; and experiment 12: MO + MCO 2%, Al-EC), BOD_7 was determined.

The OxiTop® Control system (WTW) was used in these measurements, applying a constant temperature of 20 ± 0.2 °C. Filtered influent wastewater from the municipal WWTP of Oulu was used as a microbe source (inoculum) in standard conditions. Pure oils could be directly added to the BOD OxiTop® bottle. However, the O/W samples had to be diluted suitably before adding them to the bottle, which was finally sealed for the duration of the measurement. This was due to a similarity with the COD cuvette test—the approximate measuring range needed to be known beforehand. The degree of biodegradation [%] of pure oils was calculated based on

the relation between the measured BOD [g/g] value and theoretical oxygen demand, ThOD [g/g] (degree of biodegradation [%] = BOD/ThOD * 100). The ThOD values were evaluated based on the measured carbon and hydrogen contents of the studied oils, which were measured using Perkin-Elmer 2000 Elemental Analyzer Series II. The theoretical basis of the BOD measurements can be found in more detail, e.g., in Karhu *et al.* (2009) and Roppola (2009).

5.5 Sludge analytics

The amount of EC sludge generation was approximated in Publication II using a procedure developed during the experiments. Drogui *et al.* (2008) were later found to have used a similar procedure for sludge volume approximation in their experiments. In this method, at the end of an experimental EC run, 4–9 water samples were taken from the filling vessel (see Fig. 5) and left to settle for 24 h. After this, the height of the formed sludge layer was measured and compared with the height of the whole water-sludge column, providing a sludge percentage value. This value was multiplied by the height of the whole water-sludge column in the filling vessel, and the volume of the sludge could then be calculated using the thickness of the sludge layer and its surface area. Sludge surface area (as well as the sludge layer thickness) could be measured easily using simple tools. (Publication II)

In Publications III–IV, the total phosphate and nitrogen contents of the sludges formed during EC treatment were analyzed using ICP-OES and X-Ray diffraction (XDR). The ICP analyses were conducted at an accredited test laboratory, Ahma ympäristö Oy, Oulu, Finland. The XRD analyses were conducted at the University of Oulu by the staff of the Microelectronics and Materials Physics laboratories. The water content of the EC sludge was determined (Publications II–IV) at the University of Oulu according to the SFS-EN 12880 standard (SFS-EN 2000).

5.6 Quality control

The water samples in this work were mostly fixated to ensure better reliability and reproducibility of the results. The water samples were pretreated according to Mäkelä *et al.* (1992, 20–27) by adding suitable strong acid (HNO_3, HCl or H_2SO_4) and possibly filtering them through 0.45 µm filter paper, after which they were refrigerated.

The EC experiments conducted in Publications III and V were mostly at least duplicated or triplicated and the results showed good repeatability. In Publications II and IV, due to the preliminary nature and/or large scope of these works, the experiments were mainly conducted in single. In Publication II, a 20-min blank-run without electricity was performed before each actual experiment. This recirculation of the water in the EC apparatus was done to both further homogenize the O/W emulsion and ensure that no separation occurred without electricity.

In most of the analytics done/supervised by the author of this work, all readings of data were done at least 2–3 times, and duplicates of samples were mostly used. For example, in the TOC measurements, the analyzer was set to conduct 3–4 measurements and discard the value that varied the most from the other measured values. After this, the average of the remaining values was used as the final TOC value. Similar procedures were applied in other measurements such as turbidity and COD as well, as applicable. Reproducibility was found to be mainly good in all of the aforementioned analytics. Furthermore, the analytical/measurement instruments were calibrated regularly to ensure the reliability of the results. Since the other (i.e. the majority of) water sample analytics of this work were conducted in an accredited laboratory, their results may be considered to be reliable.

6 Results and discussion

6.1 Literary research of recent EC studies (Publication I)

Older, prestigious reviews of EC are mainly focused on the technology itself and have been published by Mollah *et al.* (2001), Chen (2004), and Holt *et al.* (2005). However, at the time that Publication I was being written, to the best of our knowledge, only a few authors, e.g. Emamjomeh & Sivakumar (2009) and Butler *et al.* (2011) (the latter was published midway during the writing process of Publication I) had scrutinized EC technology and its applications more recently. This was despite the fact that a large number of studies on EC treatment of various types of water and wastewater had been reported in the scientific literature since them. Moreover, scientific papers presenting a practical overview of optimal operating conditions of various types of feasible EC applications had been largely absent. Furthermore, and very importantly, the OC and EEC values of feasible EC processes had not been broadly scrutinized earlier.

Therefore, a need for an update on recent feasible applications of EC existed. Due to the fact that EC is currently attracting strongly renewed interest as a research subject and new research is being published continually, a line had to be drawn at where to limit the scope of this study. Thus, the scientific EC literature discussed in Publication I had originally been studied mainly during 2008–2011. More review papers on EC have been published after this, such as those by Khandegar & Saroha (2013), Kabdaşlı *et al.* (2012), and Sahu *et al.* (2014), but these papers also lack, e.g., the broad economic overview presented in this work. Furthermore, in this work, in addition to optimal process parameters for treatment time, current density, and initial pH, some of the practically important functional parameters of the EC systems used in the studies discussed were mapped out. These parameters included the volume of wastewater treated, the working mode of the EC reactor (batch/continuous), electrode gap, and also whether the wastewater used had been real or synthetic (typically modeling a given wastewater type).

6.1.1 The waters and wastewaters studied

It was shown in this study that EC is a feasible, economical, and ecological alternative in the treatment of various types of water and wastewater with promising results. The waters and wastewaters of the studies discussed in

Publication I were divided suitably into seven categories by their type, although some of them could have been included in more than one of these categories. The names of the categories were: tannery, textile and colored wastewater; pulp and paper industry wastewater; oily wastewater; food industry wastewater; other types of industrial wastewater; surface water as well as model water and wastewater containing heavy metals, nutrients, cyanide, and other elements and ions. It should be noted that some studies conducted (mostly) during 2008–2011 were left out of consideration in Publication I because wastewaters of the given type or very similar wastewaters had already been discussed. In all, 86 EC studies were thoroughly analyzed, although in all, clearly over 100 were discussed. It should be noted here that even though it was found that EC had been used to treat a variety of types of water and wastewater, and also ones containing humics, PBDW treatment by EC had not been discussed in the scientific literature earlier. This gave the author of this work the idea of experimenting on this subject, as presented later in Chapter 6.5 and its subsections.

The number of papers belonging to each category and the genuineness of the wastewater used in them is presented in Table 4. The latter was studied in order to survey the real-world applicability/feasibility of EC better.

Table 4. Number of EC studies analyzed by wastewater categories.

Water or wastewater category	Number of EC studies analyzed	Number of EC studies with real wastewater
1: Tannery, textile, and colored wastewater	14	4
2: Pulp and paper industry wastewater	5	5
3: Oily wastewater	9	6
4: Food industry wastewater	10	6
5: Other types of industrial wastewater	22	18
6: Surface water	10	5
7: Model water and wastewater containing heavy metals, nutrients, cyanide, and other elements and ions	16	1

As it can be seen from Table 4, slightly over half of the discussed EC studies were carried out using genuine water or wastewater. In a few studies both genuine and similar types of model wastewater were used. Since the removal efficiencies of

various pollutants were mostly high in these studies (see Publication I, Tables 1–7 for details) and real wastewater had been used rather extensively, especially in the different industrial wastewater categories, it can be said that the range of feasible applications is expanding. Interestingly, although EC is currently under vigorous global development, it was noted that a large number of the studies discussed here had been conducted in the Middle Eastern countries and India.

As seen from Table 4, real wastewater had been used by all authors in category 2 (pulp and paper industry wastewater). Also, nearly all the authors of EC studies in categories 3, 4, and 5 had used real industrial wastewater. Model wastewaters had been used much more extensively in the EC studies of tannery, textile, and colored wastewaters (category 1). Only a third of such studies discussed here were done using real wastewater. It should be stated that studies on EC treatment of colored wastewater using synthetic wastewater were found to be particularly plentiful—extensive research has been done in this field, with promising results. Thus, as previously stated, numerous studies were left out due to their similarities to the ones presented here. This was also true regarding category 3, and some of the EC studies of category 7 of Table 4. The EC studies presented in category 7 can be simplified to have been carried out using small-scale laboratory batch reactors and artificial water or wastewater with only one particular pollutant removed.

6.1.2 Optimum process parameters and process economy

Generally, a relatively narrow pH range could be found where the process performed the very best. Interestingly, in most cases, this pH range was found to be close to the neutral pH value. However, in most studies the EC process seemed to be feasible over a wide initial pH range.

In almost all of the studies scrutinized, the electrode materials used were made of Al, Fe, or SS in different combinations. The superiority of different electrode materials seemed to vary between the different types of aqueous solutions being treated. Therefore, this must always be determined case-specifically. Occasionally, Al and Fe perform so similarly that no preference can be made based on pollutant removal efficiency or OC/EEC values alone. In the studies by Chavalparit & Ongwandee (2009), Vandamme *et al.* (2011), Vasudevan *et al.* (2009a), Vasudevan *et al.* (2010), and Zhang *et al.* (2011), Al/graphite, (Al & Fe)/(inert net of IrO_2 & TiO_2), Mg/galvanized Fe, Mg/SS, and Fe/Ti, respectively, were tested as the anode/cathode combination in EC. All of these were found to perform well.

In the major part of the EC studies discussed, optimal treatment times were found to be in the range of 5–60 min. Moreover, over half of the authors found treatment times of 30 min or less to be sufficient. Note that these figures do not include possibly required sedimentation times.

Optimal current densities (*i*) varied greatly. However, in most studies they were observed to be in the range of 10–150 A/m^2. Thus, anything over this may be considered to be a high *i* value, although it should be noted that if shorter treatment times are desired, high values of *i* may come into question.

Fluctuation in both OC and EEC values between the different water types being treated was found to be large. Thus, in these studies, the OC and EEC values varied between 0.0047–6.74 €/m^3 and 0.002–58.0 kWh/m^3, respectively. Generally, the economical values were, however, rather low—typically about 0.1–1.0 €/m^3 and 0.4–4.0 kWh/m^3, respectively. Naturally, these observations are probably related to the high variability of pollutant levels between different waters and wastewaters. For example, oily and other industrial wastewaters are typically highly polluted, whereas surface waters and the artificial modeled waters and wastewaters were only mildly polluted in comparison, bearing relatively low concentrations of pollutants.

6.1.3 Practical parameters of the EC systems studied

The distance between the electrodes (*d*) varied between 2–70 mm. However, most of the EC systems used by the authors used an electrode gap of 5–20 mm. The effect of d on the feasibility of EC was rarely studied; e.g. in Aoudj *et al.* (2010), Ghosh *et al.* (2010), Murthy & Parmar (2011), and Terrazas *et al.* (2010). This was also true regarding the effect of solution temperature and mixing speed. All of these parameters have been shown to have a varied effect on the removal efficiencies of EC (Katal & Pahlavanzadeh 2011, Mameri *et al.* 1998, Murthy & Parmar 2011, Phalakornkule *et al.* 2010b, Uduman *et al.* 2011, Vepsäläinen *et al.* 2009, Yilmaz *et al.* 2008).

Several authors also made comparisons between the connection modes of EC. In all but one of these studies, a monopolar mode (MP) was found superior to a bipolar mode (BP), using either Al-EC or Fe-EC. However, the superiority between serial and parallel modes varied more. (Asselin *et al.* 2008a, Asselin *et al.* 2008b, Kobya *et al.* 2011, Kongjao *et al.* 2008, Solak *et al.* 2009)

Most of the authors had conducted their EC studies using a small (typically 0.25–2 L) laboratory-scale reactor, applying magnetic stirring. Furthermore, nearly

all of the EC systems presented in these studies operated in a batch mode. However, some EC systems operated in a continuous mode. Larger EC systems as well as scale-up systems have also been investigated occasionally, but this has been rare. In the studies presented in Table 5, promising results were obtained both from using a continuous mode and in the scalability of EC, also with real wastewater. Indeed, EC systems larger in size and/or working in a continuous mode should be applied more in future studies.

Table 5. Studies applying large-scale, successful scale-up, and/or continuous EC systems.

Water or wastewater type treated[1]	Scale-up	Batch/Continuous	Volume treated [L]	Removal efficiency [%]	Reference
Tissue paper wastewater (R)	Yes	Batch	4.5	COD: 50 Turbidity: 92	Terrazas *et al.* (2010)
Industrial oil emulsion (R)	Yes	Continuous	23	COD: 95 Turbidity: 99	Meas *et al.* (2010)
Contaminated groundwater (petroleum hydrocarbons) (R)	-	Continuous	0.2	TPH[6]: ~85–91[5]	Moussavi *et al.* (2011a)
Almond industry wastewater (R)	Yes	Continuous	~54[2]	COD:81 Various parameters: 65–99	Valero *et al.* (2011)
Highly complex industrial wastewater (R)	-	Batch	4[3]	COD: 69 Turbidity: 80 Fecal coliforms: >99	Linares-Hernández *et al.* (2009)
Automotive assembly plant rinse waters (R)	-	Continuous	3.5	(COD: 77 TOC: 40 Various parameters: 98–100)[5]	Kobya *et al.* (2010)
Molasses process water (R)	-	Batch	6.25	COD: 79 Color: 95	Ryan *et al.* (2008)
Coking wastewater (R)	-	Continuous	2	Color: 91	Zhang *et al.* (2011)
Underground water (R)	-	Batch	5[3]	Turbidity: 98 TSS: 99	Sadeddin *et al.*(2011)
Contaminated (As) groundwater (R)	Yes	Batch	50[4]	As: 100 Phosphate: 100	Wan *et al.* (2011)
Dye-containing waste-waters (S) x 2	-	Continuous	4.42	COD: 93/n.d. Color: 99/89	Phalakornkule *et al.* (2010a)
Dye-containing wastewater (S)	Yes	Batch	9	COD: 64 Color: 80	Parsa *et al.* (2011)
Dye-containing wastewater (S)	-	Continuous	3	Color: 95	Mollah *et al.* (2010)

Water or wastewater type treated[1]	Scale-up	Batch/Continuous	Volume treated [L]	Removal efficiency [%]	Reference
Dye solution mixture (S)	-	Continuous	n.d.[7]	COD: >80 Color: 95	Merzouk *et al.* (2009)
Water containing B (S)	Yes	Batch	8.5	B: 86	Vasudevan *et al.* (2010)
Water containing Cd (S)	Yes	Batch	2,000[3]	Cd: 98	Vasudevan *et al.* (2011)
Water containing P (S)	-	Batch	5	P: 100[5]	Lacasa *et al.* (2011)
Cyanide-laden wastewater (S)	-	Continuous	0.25	Cyanide: 100	Moussavi *et al.* (2011b)

[1] Real wastewater (R); synthetic wastewater (S), [2] Approximated from the data in the article, [3] Reactor volume (sample volume not mentioned), [4] Field test, in which aerated EC was operated by locals (17 households in a small Eastern Indian village), [5] Estimated from the data in the article (precise value was not given), [6] Total petroleum hydrocarbons,[7] n.d. = Not determined.

6.1.4 Disinfection by EC

Several studies have found EC to be effective and economical for electrochemical disinfection of water and wastewater. EC studies in which total disinfection of microbes, bacteria, and algae was achieved with EC have been published by Gao *et al.* (2010), Ghernaout *et al.* (2008), Linares-Hernández *et al.* (2009), Ricordel *et al.* (2010), and Roa-Morales *et al.* (2007). In these studies, cyanobacteria-containing wastewater, dam water, highly complex and highly polluted industrial wastewater (a mixture of wastewaters from 144 different factories, received at a WWTP), river and pond water, as well as pasta and cookie processing wastewater were treated, respectively. All of these studies except the first were conducted using real water or wastewater.

6.1.5 Repeatability of EC

Related to quality control, duplication or triplication experiments were performed in a number of papers scrutinized in Publication I. These experiments exhibited very low (a few percent) experimental error. Furthermore, genuine wastewater was used in all but one of these studies. Therefore, they confirmed that the EC process is highly repeatable, also with real wastewater. (Apaydin *et al.* 2009, Asselin *et al.* 2008a, Hanafi *et al.* 2010, Janpoor *et al.* 2011, Katal & Pahlavanzadeh 2011, Vandamme *et al.* 2011, Zaied & Bellakhal 2009, Zodi *et al.* 2011) This is in good accordance with the research of the author of this work (Publications III and V).

6.1.6 Innovations and combinations of EC systems with other methods

Most of the studies analyzed in this work followed a typical pattern of presenting the results of treating a certain type of water or wastewater using EC. However, innovations related to EC systems as well as combining EC with other methods for its more efficient use, as presented in a small number of papers, are presented in Table 6 along with the main results of these studies. Such innovations are needed to significantly develop EC technology further in the future.

Table 6. Innovations and combinations of EC systems with other methods for their more efficient use.

Studied system	Results	Reference
EC + EM	The 10-min EM pretreatment was found to slightly increase the removal efficiency of humic acids by EC from 96% to 100%.	Ghernaout *et al.* (2009)
EC (Fe) + H_2O_2 = modified E-F	The modified E-F process was 10% more efficient in removing pollutants than EC alone. Its energy consumption was 20% lower. The cost of adding H_2O_2 was not considered (all of it was consumed). Triplication tests showed an experimental error of about 3%.	Apaydin *et al.* (2009)
EC (Al) + aeration + H_2O_2 = modified E-F	The modified E-F process reduced wastewater COD by 90%, compared with 80% by EC alone.	Roa-Morales *et al.* (2007)
EC + bentonite (200 mg/L)	With bentonite addition (as a coagulant), similar near-complete pollutant removal efficiencies were achieved with a 26-min EC treatment, as opposed to 35 min without it.	Xu *et al.* (2002)
EC + ultrasound	COD reduction from simulated laundry wastewater rose from 54% to 62% when ultrasound was added to an EC system. Sonolysis alone didn't provide any COD reductions. It should be noted that the power draw of the ultrasonic cleaning bath used was 80 W, while the EC system itself functioned at about 1 W.	Wang *et al.* (2009)
EC + UV	Pesticide-contaminated (metribuzin) wastewater was treated using UV, EC, and EC + UV. In (similar) optimum conditions, removal efficiencies of 12%, 89%, and 95% were achieved, respectively.	Yahiaoui *et al.* (2011)
EC + EO	After 6 min of optimized Fe-EC, a 90-min EO step was conducted, using a boron-doped diamond (BDD) anode. After the EC step, 75% of COD was removed (EEC_{EC} = 0.14 kWh/m^3). After the additional EO step, 97% of COD was removed (EEC_{total} = 12.0 kWh/m^3). The authors noted that EO alone had achieved 100% COD removal from the same real carwash wastewater earlier, however at a huge EEC value of 375 kWh/m^3.	Panizza & Cerisola (2010)
EC + aeration	Aeration in the Fe-EC cell increased the removal efficiency of petroleum hydrocarbons by approximately 22 percentage points (up to 95%) under similar conditions.	Moussavi *et al.* (2011a)
EC + aeration	Aerating of the Fe-EC reactor raised cyanide removal efficiency from 94% to 100% (similar conditions).	Moussavi *et al.* (2011b)
EC + PACl	COD removal efficiency rose from 94.5% to 99% (in optimum conditions) by adding 0.5 mg/L of PACl.	Tezcan Ün *et al.* (2009)

Studied system	Results	Reference
EC + APC	Al-EC in APC mode was found to perform slightly better (98% in 30 min) than in DC mode (96% in 45 min) in cadmium removal from a synthetic solution. The EEC value was significantly lower using APC (0.45 kWh/m^3) than when using DC (1.00 kWh/m^3). The scale-up of the APC-EC to a 2,000-L process was successful.	Vasudevan *et al.* (2011)
EC + APC	Equal Cr(VI) removal efficiency was achieved using DC and APC. However, treatment times were 3–25% (with varying initial concentrations) shorter applying APC. Thus, APC was found more economical.	Keshmirizadeh *et al*. (2011)
EC + RSM	High levels of significance and very low percentages of experimental error (related to theoretical models) were achieved.	Aleboyeh *et al.* (2008), Chavalparit & Ongwandee (2009), Kumar *et al.* (2009), Kushwaha *et al.* (2010), Tir & Moulai-Mostefa (2008), Vepsäläinen *et al.* (2009), Zodi *et al.* 2010)
EC + partial recirculation of supernatant from EC sludge drying	Proposedly, once this (industrial-scale) process had stabilized, a basal quantity of coagulant (acting as a coagulant initiator) was introduced into the wastewater from the supernatant. Consequently, removal efficiencies were found to increase without increasing the EEC value. Sludge generation also diminished.	Meas *et al.* (2010)
EC + H_2 gas recollection	About 90% of the generated gas could be collected. Converting (assuming 50% efficiency) it to electricity for the EC process itself could have reduced its EEC value by 8.5–13%. Also, the high-quality hydrogen could have been saved for use as a reactant.	Phalakornkule *et al.* (2010a)

As stated previously in Chapter 3.4.1, EC is easily hybridizable with other methods. Thus, as presented in Table 6, a few of the EC systems studied operated in a hybrid treatment mode. These included electromagnetic (EM) treatment prior to EC, a modified electro-Fenton process (E-F), ultrasound, UV light, aeration, as well as addition of bentonite and PACl to enhance coagulation.

The use of EM is based on an attractively simple approach in which the water being treated flows through a magnetic field, in either a continuous or batch mode. Consequently, slight changes are proposed to some of the physicochemical properties of the water. (Ghernaout *et al.* 2009) In the modified E-F method (see Table 6), hydrogen peroxide was added to an Fe-based EC process to bring about oxidation reactions. In the classical E-F process (electrochemical equivalent of the older chemical Fenton process), hydrogen peroxide is continuously produced *in situ* from electrochemical reduction of oxygen at a suitable cathode. An iron catalyst is also added to the solution. (Brillas *et al.* 2009) Simplified, ultrasound waves affect the electrochemical systems through dual effects—dissolution enhancement and sonolysis. The former may occur, e.g., due to improvement of hydrodynamics to increase mass transfer or by continuously regenerating new surface due to cavitation and/or microstreaming. (Wang *et al.* 2009) In sonolysis, high-power ultrasound may destroy pollutants by producing free radicals H• and OH• (strong oxidants) from water (Adewuyi 2001). The mechanism of aeration enhancement of the (Fe-based) EC process has been proposed to be due to aeration-transferred oxygen accelerating the oxidation of electrogenerated Fe^{2+} in solution to Fe^{3+}. Greater $Fe(OH)_3$ flocs will then form, thus improving pollutant removal. (Moussavi *et al.* 2011a) Moreover, aeration improves mixing of the reactor's content. This increases the size of flocs and improves contact between precipitates and the target contaminant. Subsequently, enhancement of the adsorption of contaminants onto the flocs occurs. (Moussavi *et al.* 2011b)

Continuing on, as presented in Table 6, innovations such as collecting the hydrogen gas produced during EC using simple equipment, partial recirculation of supernatant from EC sludge drying, and applying APC instead of DC power have been studied, with promising results. Furthermore, as presented in Table 6, RSM (along with analysis of variance, ANOVA) has been successfully applied by several authors to optimize the EC process. In this study, it was found that RSM could be applied readily with EC to find case-specific optimum operating conditions. It should be noted that more than half of the RSM-EC studies discussed here were

conducted with real wastewater. This further proves the applicability of RSM with EC.

In addition to those presented in Table 6, interesting remarks were made in the studies by Kushwaha *et al.* (2010) and Xu *et al.* (2002). In the first paper, synthetic dairy wastewater had been treated by EC. The authors suggested (based on thermal gravimetric and differential thermal analyses; TGA and DTA) that EC sludge could be dried and used as fuel in boilers/incinerators or in fuel briquette production. A similar suggestion was presented by Kumar *et al.* (2009); EC sludge (heating value 5.3 MJ/kg) from the treatment of biodigester effluent from an alcohol distillery could be used in making blended fuel briquettes along with other organic fuels. In the latter study, real egg processing wastewater was treated by EC. In addition to good treatment results, valuable by-products (EC sludge) bearing high digestible protein and fat values were yielded. Also, Linares-Hernández *et al.* (2009) found that using Al and Fe anodes simultaneously outperformed (higher removal efficiencies, less sludge produced) the use of either metal alone, combining the advantages of both. Furthermore, El-Ashtoukhy & Amin (2010) used a novel batch gas-stirred (cathodic H_2) EC cell in their studies. Proposedly, this reduces the capital costs and OC value of an EC reactor by replacing mechanical stirring, provided that the reactor is designed properly.

6.1.7 Further literary updates

As previously stated, more recent EC review papers have been published after Publication I. Of these, the work of Khandegar & Saroha (2013) is of particular interest. Similarly to those in Table 6, this study presents combinations of EC with other methods (in Table 5 therein). Also, in Table 6 of the mentioned work, studies in which EC is compared with other technologies are laudably presented. Now, in this chapter, a handful of recent interesting applications of EC and innovations related to it, most of which have not been discussed in either of the aforementioned papers, are addressed briefly.

Zhang *et al.* (2013) studied the removal of phosphate (initially 16 mg/L, and 120 mg/L COD) from genuine landscape water using a recirculated batch Al-EC process powered directly by photovoltaic solar modules. The conductivity of the landscape water (initially 420 µS/cm) was raised by adding 150–600 mg/L NaCl. Consequently, the photovoltaic module output current increased rapidly (up to about 1.5 A), clearly improving the performance of EC. Meteorological conditions were found to have a significant effect on the removal of P from the water. Using

solar-powered EC to treat this kind of water was found rapid and feasible, with 96–99.9% P_{tot} removal in optimum conditions. Furthermore, García-García *et al.* (2015) studied a small-scale (V = 0.125 L) combined EC+EO process using Cu electrodes (BDD anode in EO) and powered by solar cells (1–3 A current) in treatment of highly polluted and complex industrial wastewater. Complete COD and color removal were achieved.

Kobya *et al.* (2014) investigated the application of Fe-EC for treatment of red mud dam wastewater. Red mud stands for highly toxic bauxite refinery residues from aluminum industry (Bayer's process). Optimal removal efficiencies for the V (98%), Si (83%), Al (98%), As (99%), Mo (99.7%), and Ga (99.95%) abundantly present in the wastewater were achieved by applying a modified initial pH of 8 (naturally 12.2), i of 50 A/m^2, and operating time of 45 min. The corresponding OC value was 0.813 €/m^3.

EC treatment of a Delhi-based hospital's operating theatre wastewater was studied by Mahajan *et al.* (2013). An Fe/Fe (anode/cathode) electrode combination was found superior to Al/Al and Fe/Al electrode combinations. COD (initial value 20,000 mg/L) could be removed totally in 75 min by applying i of 122 A/m^2. No NaCl additions were needed. Experimental error was determined as 3%.

Domestic wastewater may be categorized into two parts, namely blackwater (toilet flushing) and greywater, which is less polluted but is generated at a greatly higher rate. Thus, recycling and reuse of treated greywater for, e.g., gardening or toilet flushing may be of great significance in the future. About 70% of the COD (initial value 320–733 mg/L) and 99.9% of the pathogens could be removed by Al-EC from greywater derived from an Indian middle-class household, with OC and EEC values of about 0.15 €/m^3 and 0.3 kWh/m^3, respectively. (Vakil *et al.* 2014)

Ben Hariz *et al.* (2013) investigated the removal of pollutants from a petroleum refinery's sulfidic spent caustic wastewater—which is highly alkaline and black in color—by EC. Fe anodes were found clearly more efficient than Al anodes in this application. Interestingly, when a second successive EC unit was used to treat the solution optimally treated (t = 30 min, i = 212 A/m^2) by the first unit (reaching a plateau), removal percentages rose from about 85% to more than 98% for both sulfide and organics (COD). The initial values of sulfide and COD had been extremely high, 34,517 mg/L and 72,450 mg/L, respectively. Heavy metals could be removed nearly completely by the first EC unit. EC was concluded to be highly efficient and relatively fast compared with conventional existing techniques for treating such waste.

Oncel *et al.* (2013) compared EC and CC in the removal of elements (including heavy metals) such as Fe, Al, Ca, Mg, Mn, Zn, Si, Sr, B, Pb, Cr, and As (varying concentrations, mainly about 10–740 mg/L) from highly polluted coal mine drainage wastewater on a laboratory scale. It was concluded that the EC process was more effective than CC with respect to removal efficiency (>99.9% and 28–99.9%, respectively), amount of sludge generated, and operating cost (1.98 €/m^3 and 4.53 €/m^3, respectively). A very high *i* value of 500 A/m^2 and a treatment time of 40 min were found optimal. No pH modification (naturally about 2.5) or NaCl additions were needed in the EC process, whereas the initial pH value had to be raised to 8 to obtain optimal results using CC.

Highly polluted and black-colored landfill leachate from an Algerian town was treated by EC. The initial COD and N_{tot} values of the solution were 28,200–34,200 mg/L and 1,600–1,630 mg/L, respectively. Raw leachate solution was used; no adjustments were made. Pollutant removal efficiencies by Al-EC (70% COD, 24% N_{tot}, 56% color, and 60% turbidity) were slightly higher than those of Fe-EC. However, the latter was chosen as the most appropriate anode material (less toxic and more acceptable in the agricultural field). Also, the OC of Fe-EC was found to be slightly lower (0.47 \$/m^3) than that of Al-EC (0.54 \$/m^3). In both cases a high *i* of 500 A/m^2 was applied for 30 min. The EC process was found to remove microorganisms (about 99% total Coliform and 96% Clostridium) efficiently from the leachate. In this study, repeatability experiments were conducted, showing a relative standard deviation of < 3%. Superfaradaicity was also investigated, showing excess Al dissolution (compared with theoretical values) of about 16%, which is in good accordance with the results obtained by our research group on Al-EC (Publications III and V). (Bouhezila *et al.* 2011)

Amrose *et al.* (2014) presented field trial results for removal of As from real groundwater with a recirculated 600 L Fe-EC reactor with subsequent alum addition (6–15 mg/L as Al to accelerate settling; no filtration was used) in West Bengal. The system was operated over 3.5 months (for 1–2 batches on most weekdays, a total of 64,480 L). Electrode polarity was reversed with each batch. No NaCl additions were made. The product water consistently had As (initially 224–308 µg/L) levels < 5 µg/L. Fe (initially 12–16 mg/L) and Al concentrations in the product water were found to be below the WHO-recommended levels of 0.3 mg/L and 0.2 mg/L, respectively. A trained local operator reported easy operation and maintenance (occasional light brushing of electrodes), and undertook small repairs of the reactor without supervision. The reactor operated reliably, robustly, and at a low cost (0.83 \$/m^3 amortized capital and consumables, before

optimization of the process) while producing minimal waste (sludge). The total EEC value of the system (including all stages, i.e. pumping, etc.) was 2.31 kWh/m^3 without any optimization. Several design changes to reduce EEC were noted for the next generation prototype.

CC, EC, and sono-EC were compared in the treatment of a model dye-containing solution (Rhodamine 6G, 100 mg/L) by Raschitor *et al.* (2014). Removals of about 60% could be achieved by applying large doses of coagulants, using either CC or EC (electric charge). However, the use of sono-EC enhanced the efficiency of EC up to 95%, even when a lower electric charge was applied. This is a significantly larger improvement than observed by Wang *et al.* (2009), as presented in Table 6.

The performance of a continuous bipolar combined EC+EO reactor was evaluated by Mahvi *et al.* (2011). This system was comprised of two distinct units: electrochemical (10 L) and separation (15 L). In the electrochemical unit, Al (dissolving anode in EC), RuO_2/Ti (non-sacrificial EO anode), and SS (cathode) plates were used. After successful removal of both phosphate and ammonia from artificial solutions, real effluent from an anaerobic reactor was treated. Here, the reactor (HRT = 60 min) was simultaneously able to achieve removal efficiencies of 98%, 98%, and 72%, for phosphate (initially 48 mg/L), ammonia (initially 28 mg/L), and COD, respectively. The current used was low (3 A), and no NaCl was added to the wastewaters.

Nguyen *et al.* (2014) presented a novel, large pilot-scale (~53 m^3/d) hybrid treatment system which combined a rotating hanging media bioreactor, a submerged membrane bioreactor, and Al-EC as post-treatment. This system was used to treat influent at a Korean municipal WWTP for 16 months in succession; during the latter half EC was also applied in a continuous mode. The EC process study was applied as a post-treatment add-on, since it has potential for reasonably easy retrofitting to existing facilities. The results indicated that, using EC, the removal percentages of P_{tot} were maintained stably and constantly at a high level of 98.8–99.9% on average (0.03 mg/L P_{tot} in the final effluent). Without using EC, P_{tot} removal efficiency was only in the range of 65–82%. It should be noted that the P_{tot} content of the wastewater before EC was low (< 2 mg/L). However, the EEC and applied *i* and HRT values were also very low, about 0.27 kWh/m^3, 4.4–4.8 A/m^2, and 2 min, respectively.

In a very interesting and recent paper by Nasr *et al.* (2015), artificial intelligence (3-6-1 neural network and adaptive neuro-fuzzy inference system) was developed to simulate the influence of variables on the removal of turbidity from

greywater by Al-EC. High R-values of 0.99 (training), 0.84 (validation), and 0.89 (testing) were achieved. Current density was identified as the most influential output. The developed network was concluded to be usable for prediction and control of the EC system, however, a continuous mode and field-scale experiments should also be conducted in the future.

A novel EC reactor was found to be effective for treatment of real cheese whey wastewater by Tezcan Ün *et al.* (2014). The reactor consisted of a rotating horizontal Fe screw anode inside a U-shaped Fe cathode and it operated in a continuous mode (working volume of 1000 mL). In optimum conditions (i = 600 A/m^2, t = 20 min, HRT = 20 min), a high initial COD value 15,500 mg/L could be reduced by 84%. No NaCl additions and virtually no initial pH modification were needed. Using RSM was also studied, providing a good R^2 value of 0.85, thus proving its feasibility in optimizing the EC process.

Novel types of EC systems have also been presented by Ardhan *et al.* (2014) and Hamdan & El-Naas (2014). The first paper dealt with the development of a reduced-cost anode as a substitute for a traditional plate or tubular electrode. In this work, a small polyvinyl chloride (PVC) tube was packed with machine shop turnings while SS tubes were used as a cathode. The system was found to perform well and is presented in Fig. 8. In the latter paper, use of an air-mixed EC column system (see Fig. 9) applying a helical cathode and a rod-shaped anode was investigated. Both electrodes were made from iron and the system operated in a continuous mode. It was compared with a typical stirred tank continuous EC unit. The results showed that while removal efficiencies were high and similar for both systems, this system was more economical. The low EEC value was proposed to be attributed to the small distance between the rod and helical electrodes, and the use of the rod as a sacrificial electrode instead of a rectangular sheet resulted in lower operating voltages.

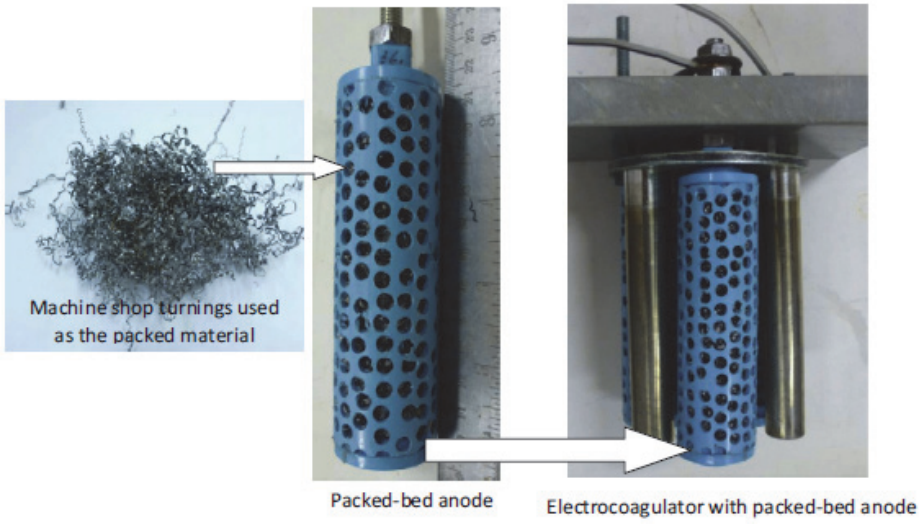

Fig. 8. Novel anode made of Fe scrap for a low-cost EC system. Adapted from Ardhan *et al.* (2014).

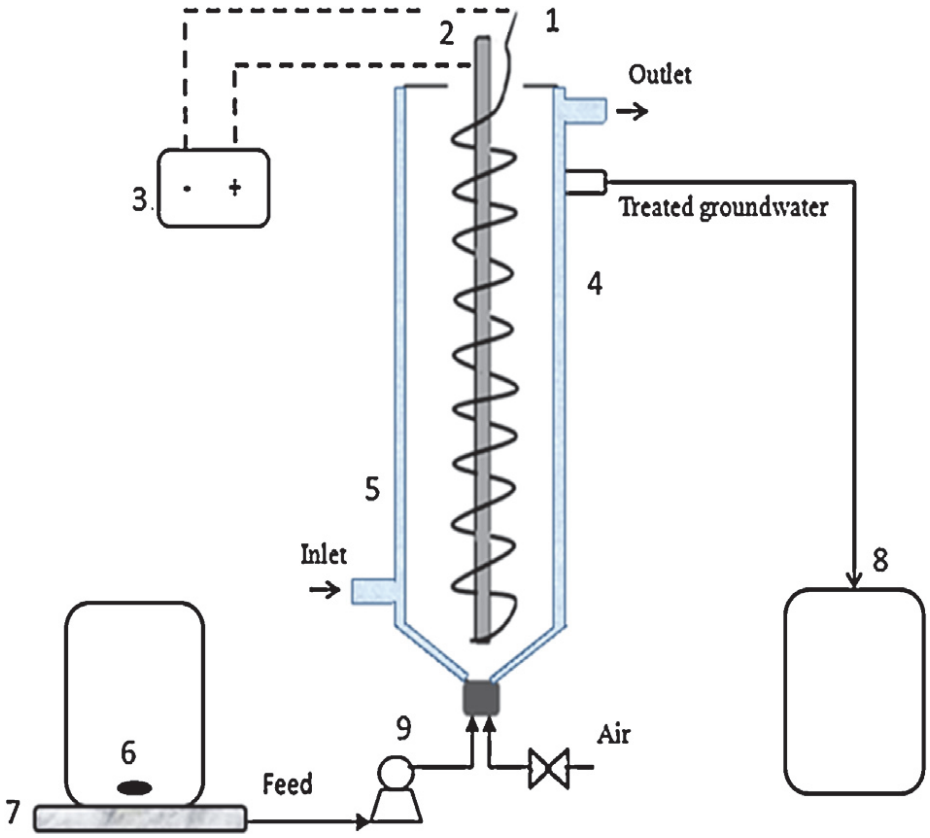

Fig. 9. A novel EC column system applying a helical cathode (1) and a rod-shaped anode (2). Adapted from Hamdan & El-Naas (2014).

6.1.8 Summary of the literary research

The range of feasible and economical EC applications is constantly expanding. EC has vast potential in purification of various types of water and wastewater. It can be combined with other methods/technologies. Innovations have been appeared, yet more are needed to increase the attractiveness of EC. Further research is needed especially using larger-scale and/or continuous systems as well as real wastewater instead of only artificial solutions. The fundamentals of the EC process should also be explored more thoroughly.

6.2 EC treatment of oily wastewater (Publication II)

The main purpose of this part of the work was to comparatively study the effectiveness of EC on a large scale for treatment of both bio and synthetic O/W emulsions when using Al or SS as the anode material. To the best of our knowledge, there were no earlier comparative studies on EC treatment of both bio oils and synthetic oils. Thus, in this study, the OC and EEC values of EC treatment of O/W emulsions were also estimated, which also added to the novelty of this paper. Additionally, treatment of, e.g., TO-containing wastewater using EC was not found in the scientific literature. This study was performed with a bench-scale EC apparatus, which may also be considered to be a novel design. In it, continuous recycling of the sample during experimental runs was performed. Its electrode configuration consisted of multiple vertical electrodes and one electrode which also served as a basin, as presented earlier in Chapter 5.2.3.

6.2.1 Details of the EC experiments

In this work, after preliminary experiments, 16 EC experiments were conducted in total. These experiments are presented in Table 7 (oil emulsions, current densities, and treatment times used) along with their OC and EEC values and the COD removal efficiencies achieved. In Publication II, the prices of SS 316 hot-rolled plate (iron content 67 w-%) and Al were estimated to be 4514 €/t and 1723 €/t, respectively. The percentages in the first column illustrate the oil content of the emulsions. As an example, chronological samples from two O/W treatment EC experiments (8 and 10) are presented in Fig. 10.

Table 7. Details of the EC experiments using O/W emulsions, their OC and EEC values, as well as the COD removal efficiencies achieved.

Experiment: emulsion type/anode	Treatment time[2] [min]	Current density [A/m^2]	EEC [kWh/m^3]	OC[3] [€/m^3]	COD removal [%]
1: RSO 0.6%/SS	60	40	2.0	2.42	35
2: SFO 0.6%/SS	60	50	2.5	2.93	25
3: SFO 2%/SS	60	35	1.6	2.22	55
4: SFO 2%/SS	60	40	1.8	2.68	95
5: MO+MCO 2%/SS	60	40	2.3	2.93	90
6: MO+MCO[1]/SS	60	40	2.8	3.91	80
7: MO+MCO 2%/SS	60	40	2.3	2.89	90
8: RSO 2%/SS	80 (80)	40	2.6	3.86 (3.86)	80
9: SFO 2%/SS	60 (40)	40	1.6	2.14 (1.43)	65
10: SFO 2%/Al	60 (20)	70	2.0	0.41 (0.13)	80
11: SFO 2%/Al	60 (20)	70	2.5	0.47 (0.14)	70
12: MO+MCO 2%/Al	60 (20)	70	2.4	0.46 (0.13)	90
13: MO+MCO 2%/Al	80 (20)	70	2.5	0.48 (0.11)	85
14: MO+MCO[1]/Al	60 (16)	70	2.5	0.54 (0.14)	25
15: TO 2%/Al	150 (120)	70	5.9	1.18 (1.01)	95
16: TO 2%/Al	175 (150)	70	7.7	1.46 (1.26)	95

[1] EC-treated effluent from the previous run was used (repeated EC treatment), [2] Optimum value in brackets, [3] OC for total treatment time (in brackets = optimal treatment time).

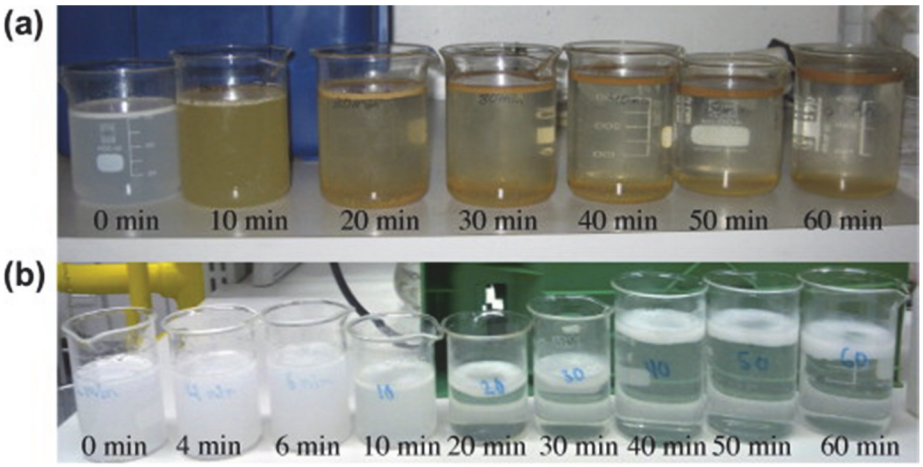

Fig. 10. Chronological samples from the O/W treatment EC experiments: (a) experiment 8: RSO 2% (SS anode) and (b) experiment 10: SFO 2% (Al anode). Adapted from Publication II.

6.2.2 Removal efficiencies and process economy

As shown in Table 7, on the whole, the efficiency of the EC apparatus with this type of electrode geometry was high. Optimal treatment times were found to be short; typically less than 20 min. However, no specific optimization of process conditions (e.g. for initial pH) was done in this study. It should be noted that the current densities used were not equal for different anode materials due to the different A_{eff} of the electrodes. However, the average current values used were similar (about 8 A) and were used in the economic calculations.

In this study, it was observed that of all the parameters measured, the turbidity of the O/W emulsions decreased the most in all experiments, 75–100%, while the TOC values decreased the least, 20–75%. COD and TSC reductions were in the range of 25–95% and 40–98%, respectively. The development of the COD, TSC, and turbidity values during the EC experiments are presented in detail in Publication II. Asymptotical decreasing of the parameters was typically visible after the first 10 minutes of EC. The decrease of the BOD_7 value (discussed in Publication II) occurred very rapidly (in 10 min) and nearly stopped after that. In total, up to 85–95% of BOD_7 could be removed. Interestingly, a strong correlation between the COD and TSC values was observed. Similar behavior with real oily wastewaters has been reported in Karhu *et al.* (2013). Consequently, since TSC measurements are easy to perform even in an online mode, TSC may be considered a good process adjustment parameter for oily wastewater treatment.

Energy consumption was low for both types of electrode configurations (Al/SS and SS/Al), as presented in Table 7. The EEC values for the treatment of the O/W emulsions were about 1.6–2.8 kWh/m^3 and 2.0–7.7 kWh/m^3, using SS and Al anodes, respectively. The corresponding OC values were in the ranges of 2.14–3.91 €/m^3 and 0.41–1.46 €/m^3 for SS-EC and Al-EC, respectively. Thus, despite the lower EEC value, here SS-EC was found to be more expensive overall than Al-EC due to the much higher metal material price and metal dissolution. As it can be seen from Table 7, EC treatment of the TO emulsion was significantly more costly than that of other O/W emulsions, at least by Al-EC. All of the abovementioned figures are in good accordance with the results of Publication I, thus supporting them. In that paper, it was observed that the economic numbers of the EC treatment studies with oily wastewater (category 3, see Table 4) were typically close to each other. On average, OC and EEC values of about 0.2–0.4 €/m^3 and 2–6 kWh/m^3 had been estimated, respectively.

6.2.3 EC sludge analyses

The volume and water content of the sludge were determined in experiments 8 (RSO 2%), 9–11 (SFO 2%), and 13 (MO+MCO 2%) of Publication II. In the first two of these experiments, SS-EC was used, while in the rest, Al-EC was used. The sludge generated during EC treatment either rose to the surface of the filling vessel or sank to its bottom. As an example, chronological samples from two O/W treatment EC experiments (8 and 10) are presented in Fig. 10. The EC sludge generated by SS-EC could be separated more easily and was stronger than the Al-EC sludge. However, it contained more bound water. Furthermore, the water content of different sludges was found to vary greatly. The volumes of EC sludge for different emulsion types were, however, similar (89–115 L/m^3).

6.2.4 Other analyses

Laser diffraction measurements were performed for samples from test runs 11 (SFO 2%/Al), 13 (MO+MCO 2%/Al), and 15 (TO 2%/Al). Average droplet sizes of 9.8 µm, 5.1 µm, and 5.9 µm were detected, respectively. Thus, the small droplet sizes proved that the emulsification of oils had been successful. Droplet sizes were found to increase during EC treatment, proving that the breaking of O/W emulsions and the forming of agglomerates had started. Laser diffraction measurements could not be performed for the end samples of each experiment because these samples did not contain enough droplets. Successful removal of oil from the wastewaters was thus proven.

Interestingly, it was found that when the once-treated MO+MCO (2%) emulsions were treated again with EC, high removal efficiencies could still be achieved. In the second treatment, reductions of COD were 80% and 25%, TSC reductions were 65% and 40%, and turbidity reductions, 90% and 80%, for SS-EC and Al-EC, respectively. Consequently, respective total removal efficiencies were raised to 98% and 89% of COD, 99.3% and 73% of TSC, as well as 99.5% and 99.6% of turbidity. The increase in removal efficiencies by the second successive EC treatment was suggested to occur because sludge removal (from the top of the water) between the experiments destabilized the chemical balance of the whole studied solution. As presented earlier in Chapter 6.1.7, applying repeated EC treatment was later also studied by Ben Hariz *et al.* (2013), who also achieved good results.

6.2.5 Summary of the oil removal studies

According to the results of Publication II, pollutant removals achieved for the O/W using either electrode combination were of similar magnitude. However, SS-EC apparently slightly outperformed Al-EC in the treatment of MO+MCO emulsions. The converse was observed for SFO. Furthermore, no such comparison was made with RSO and TO, as they were treated using only one anode metal. Of all the O/W emulsions treated, the highest removal efficiencies were achieved for TO and MO+MCO emulsions. To summarize; EC treatment of O/W emulsions of these types was shown to be feasible.

6.3 EC treatment of phosphate-containing wastewater (Publication III)

In this part of the work, optimization of the EC process in removing phosphate from synthetic wastewater (SWW, 100 mg/L) that models municipal sewage was studied first. As discussed in Publication III, using various conventional technologies to treat phosphate-containing wastewater has been studied extensively in the scientific literature. Furthermore, although phosphate-containing wastewater has also been treated by EC in the scientific literature multiple times before, these studies have lacked, e.g., scale-up studies of the EC process. On the whole, scale-up studies of EC treatment of any kind of water or wastewater have been rather scarce, as stated earlier in Chapter 6.1.3. Therefore, here we sought to scale up the optimized SWW-EC process. In addition to SWW, treatment of real industrial phosphate-containing apatite mining wastewater (MWW) and dairy wastewater (DWW) with EC was also tested. To the best of our knowledge, treatment of this kind of MWW with EC has not been reported earlier in the scientific literature. The OC and EEC values of the EC process were also evaluated in Publication III.

The phosphate content of the sludges formed during EC treatment was analyzed to investigate the possibility of utilizing the EC sludge derived from real phosphate-rich wastewaters. Particularly, such utilization could include use as an additive in granulated bio ash-based fertilizer products (so-called symbiosis pellets). This idea is novel, and can be considered to be a “hot topic” in the waste utilization sector, also as a part of the intrinsically topical themes of circular economy, and on the other hand, bioeconomy. Indeed, according to the new Finnish waste law, the status of bio ash may be changed from waste to by-product via chemical studies. After this, bio ashes can be mixed/doped with other by-products, thus raising the

levels of nutrients (e.g., P, N, and/or K) to levels required by legislation regarding fertilizer products. Such mixing/doping has been forbidden earlier. Furthermore, according to the present EU and corresponding Finnish (new waste law, effective on May 1, 2012) waste strategies, all kinds of waste (including sludge) must be utilized (reused, recycled) primarily as material. (Ashby 2016, Ma *et al.* 2015, Ministry of the Environment 2011, O'Brien *et al.* 2015, Roininen & Kuokkanen 2013, Scarlat *et al.* 2015)

6.3.1 Optimization and scale-up of synthetic wastewater treatment

The effects of multiple parameters on the efficiency of the EC process were evaluated and optimized. Namely (and in this order), these were the anode/cathode materials used (Al/Fe, Al/SS, Fe/Al, SS/Al, and Fe/SS; determined in a pre-study), initial pH (5–9), current density (25–150 A/m^2), treatment time (0–30 min), electrode gap (7–15 mm), and supporting electrolyte (NaCl/KCl/$NaNO_3$; 0.5–1.0 g/L).

Fe/Al performed similarly to Al/Fe, while SS was clearly inferior as the anode material. Both Fe and SS anodes were found to color the water. A clear trend of rising phosphate removal efficiency with lowering initial pH was observed. It was found that there was very little difference in removal efficiency with different electrode gaps (although the tested scale was small). However, the EEC values rose significantly when the gap was increased, due to the rising voltage. Of the three supporting electrolyte types tested, NaCl proved to be clearly the most suitable overall.

Finally, in optimum process conditions 96% of phosphate could be removed from the SWW in the laboratory-scale EC experiments. The optimum conditions were found to be: anode/cathode = Al/Fe, initial pH = 5, current density = 100 A/m^2, treatment time = 15 min, supporting electrolyte = 1.0 g/L NaCl, and electrode gap = 7 mm.

These optimum values were mimicked as best they could in the scale-up runs. Current density and electrode gap could not be directly replicated due to a different EC apparatus geometry and A_{eff}. Instead, the dissolved metal mass per SWW volume and a treatment time of 15 min were set as constants. Furthermore, due to practical reasons, Al/SS was used instead of Al/Fe. However, these electrode combinations had been shown to produce very similar phosphate removal results in the earlier part of the study (optimization). The composition of the SWW remained the same.

In this study, three parallel scale-up experiments were conducted (using the same process conditions). All of them progressed similarly to the laboratory-scale experiments and were highly reproducible; 87–92% of initial phosphate was removed by EC.

6.3.2 Treatment of real apatite mining wastewater and dairy wastewater

These experiments were conducted using only the laboratory-scale EC system and an Al/Fe electrode combination. Based on the data obtained, it was summarized that EC is a feasible alternative in treating real phosphate-containing apatite MWW and DWW over a wide pH range. Optimum phosphate reductions of 79% and 93% could be achieved, respectively. EC produced clear and colorless water in both applications, but some odor was still left. This was probably due to the nitrogen compounds present. Interestingly, As could also be removed efficiently from MWW.

6.3.3 Process economy

The OC and EEC values were found to be low for all the wastewaters studied here. In optimum conditions, the respective values for small-scale SWW-EC were found to be 0.17 €/m^3 or 6.91 €/$kg_{phosphate}$ and 0.75 kWh/m^3 or 25.8 kWh/$kg_{phosphate}$. The corresponding values in the scale-up experiments were evaluated to be 0.16 €/m^3 (6.07 €/$kg_{phosphate}$) and 0.62 kWh/m^3 (23.3 kWh/$kg_{phosphate}$). Thus, the scale-up was found to have succeeded well, even better than expected.

The OC and EEC values in the treatment of real MWW were estimated to be 0.28 €/m^3 (75–80 €/$kg_{phosphate}$) and 2.11 kWh/m^3 (570–620 kWh/$kg_{phosphate}$), respectively. Correspondingly, for DWW these values were 0.31 €/m^3 (2.50 €/$kg_{phosphate}$) and 1.46 kWh/m^3 (11.65 kWh/$kg_{phosphate}$).

It should be noted that the results of this study are well in line with those found in the scientific literature, where complete removal of phosphorus (SWW) has been reported by at least Lacasa *et al.* (2011) and Vasudevan *et al.* (2009b). In the EC studies of the former, an EEC value nearly identical (0.73 kWh/m^3) to that achieved in this study was reported for an initial phosphate concentration of 27 mg/L (very similar to our study), applying Al-EC and a current density of 50 A/m^2, and treatment time of 20 min. In the study by Lacasa *et al.* (2011), the treated water volume was 5 L.

6.3.4 EC sludge analyses

In each EC experiment of Publication III, EC sludge was generated on top of the EC cell. The results exhibited that the EC sludges from all the wastewater types treated in this particular work contained high amounts of phosphorus. Consequently, it may be possible to further utilize them, e.g., as additives in granulated bio ash-based symbiosis pellets for fertilization. However, further studies on this are required. The sludge itself may also need further treatment to allow this kind of utilization.

Based on ICP-OES analyses, dried SWW sludge from the laboratory-scale experiments contained 121–143 g/kg Al and 39–49 g/kg P_{tot}. In the scale up experiments, the corresponding values were 162–182 g/kg Al and 46–48 g/kg. Scaling up the EC process had therefore succeeded well also in terms of sludge composition. The resulting diffractogram from XRD analysis (SWW-EC sludge) revealed that all the tops matched aluminum oxide.

Total Al concentrations of about 2600 mg/L and 3200 mg/L were detected by ICP in the MWW and DWW sludges (both not dried), respectively. The corresponding P_{tot} concentrations were about 120 mg/L and 2800 mg/L, respectively. Since DWW had also had a twentyfold initial P_{tot} concentration over MWW, both of these sludges were proposed to be of somewhat similar structure.

EC-treated DWW and a close-up of the resulting DWW sludge are presented in Fig. 11. Before treatment, the solution was milky white and highly turbid. As it can be seen from Fig. 11, a small amount of sludge also settled to the bottom of the EC vessel. Similar behavior had been observed in some of the O/W experiments of Publication II.

Fig. 11. EC-treated DWW (on the left) and resulting DWW sludge.

6.3.5 Summary of the phosphate removal studies

Good scalability of the SWW-EC process was achieved, despite the different geometry of the EC systems used (and also the water recirculation applied in the large-scale system). The repeatability of the EC experiments in this work was found to be good. In the end, EC was shown to be a feasible technology in the treatment of real phosphate-containing wastewaters. Furthermore, the EC sludges generated by treating such wastewater contained a large amount of phosphorus. Thus, they may be eligible for further utilization, e.g., in granulated bio ash-based symbiosis pellets for fertilization.

6.4 EC treatment of DPRW (Publication IV)

In this part of the work, hygienized anaerobic digester plant reject water (DPRW) derived from Biotehdas Oy (Vampula plant) was treated. To the best of our knowledge, this kind of wastewater has not been treated with EC before. Direct utilization of the DPRW might be possible in agriculture/forestry if its excess nutrient (especially nitrogen) levels could be sufficiently reduced. Thus, the main

idea of this preliminary experiment was to investigate whether EC could be used simultaneously as a wastewater treatment method and as a means to recover valuable nutrients for further fertilization use (similarly with Publication III). An economic analysis of the process was also done.

6.4.1 Details of the EC experiments

In all, 16 preliminary experiments on EC treatment of DPRW were conducted. The experiments were started using diluted (up to 80% dilution) wastewater, and the dilution was gradually lowered. In the end, raw DPRW was used, however with modified initial pH. Al/Fe (anode/cathode) and Fe/Al electrode combinations were used.

The current densities used in this work were rather high: 200–300 A/m^2. This was due to the high pollutant concentrations of the DPRW. Due to the high conductivity of the DPRW, no NaCl additions were needed even when using diluted solutions. Correspondingly, voltages remained low.

Adjustment of initial pH was also tested. The natural pH of the DPRW was about 8.1–8.3; adjusted values were about 5.0, 6.5, and 9.5. The DPRW exhibited a strong buffering effect; a significant amount (about 20 L/m^3) of 12 M HCl had to be added to it to lower its pH value to 5.0. Also, a significant amount of foam was formed during the lowering of pH, but not when raising it. Interestingly, at studied initial pH values other than 5.0, a layer of solid matter/slime was formed on the anode surface during the experiments. This layer was suggested to have been composed of mainly organic matter. Furthermore, it may have hindered the functionality of the anode. The color of this slime was green for Fe-EC and light for Al-EC. Thus, it was proposed to have been due to anodic dissolution.

6.4.2 Results and process economy of the DPRW experiments

Due to the preliminary nature of this work as well as the progress made during the work, mainly only the results of experiments 14 (Al/Fe, 45 min) and 16 (Fe/Al, 90 min) are discussed here, since they were found “optimal”. These two experiments were the only ones in which significant DPRW clarification could be brought about, and thus the only ones to have their water samples analyzed. In both experiments an initial pH value and a current density of 5.0 and 300 A/m^2 were applied, respectively. Also, the DPRW was non-diluted.

It was found that both Al-EC and Fe-EC could remove virtually all of the phosphorus and TS from the DPRW. The respective COD and DOC removal efficiencies were about 75% and 20–30% (the higher value was for Al-EC). Almost no nitrogen could be removed from the DPRW by EC, although it must be stated that its initial concentration was extremely high. Residual Al could be totally removed by filtration. However, residual Fe levels remained very high (over 270 mg/L) after filtration. This may explain the greenish color of the treated solution in experiment 16. It should be emphasized that successful separation could have been achieved with shorter treatment times in both of the processes (especially Fe-EC). This would have resulted in lower residual metal concentrations as well as OC and EEC values.

OC values of 4.68 €/m^3 and 5.27 €/m^3 were estimated for the Al-EC and Fe-EC processes, respectively. Of this cost, as much as 4.0 €/m^3 consisted of HCl addition alone. Thus, the OC values of the actual Al-EC and Fe-EC processes were about 0.68 €/m^3 and 1.27 €/m^3, respectively. In this work, the price of commercial grade strong (12 M) HCl was estimated to be 0.20 €/kg_{HCl}. However, in practice, cheaper alternatives could be used. Furthermore, it might be possible to recirculate part of the EC-treated DPRW (pH about 6.0 after the Al-EC process) to the beginning of the EC process. Consequently, the need to add acid to raw DPRW might be significantly lower. The EEC values for experiments 14 and 16 were 2.72 kWh/m^3 and 7.56 kWh/m^3, respectively.

6.4.3 EC sludge analyses

During the "optimal" experiments 14 (Al-EC) and 16 (Fe-EC), significant amounts of EC sludge was consistently generated on the top of the EC vessel. After switching power and mixing off at the end of these experiments, the EC vessel was completely filled with turbid water. The solution contained a considerable amount of flocs and its color was dark green with Fe-EC and light brown with Al-EC. When Fe-EC was used, the green-colored floc settled to the bottom of the EC vessel (in about 60 min). The DPRW remained somewhat turbid and colored (yellowish green). However, when Al-EC was used, the light-colored floc separated to the surface of the solution (in about 15 min), and the solution turned clear and only slightly yellow.

Interestingly, it was found that the EC sludge generated by Al-EC was denser than the corresponding Fe-EC sludge (both the surface and especially the bottom sludge). Furthermore, it didn't break up as easily when collected. Fe-EC sludge is

generally thought to be stronger/denser and to settle faster than corresponding Al-EC sludge (Zodi *et al.* 2009, Zodi *et al.* 2011).

In Fig. 12, DPRW (with a modified initial of pH of 5.0) before EC treatment is presented along with EC-treated DPRW samples from experiments 14 and 16 (before and after settling/separation). It is worth mentioning that the (settled and filtered) Al-EC-treated sample presented in Fig. 12 (on the right) was visually transparent and clear "in nature". The analytical results of the EC sludge samples (experiments 14 and 16) are presented in Table 8.

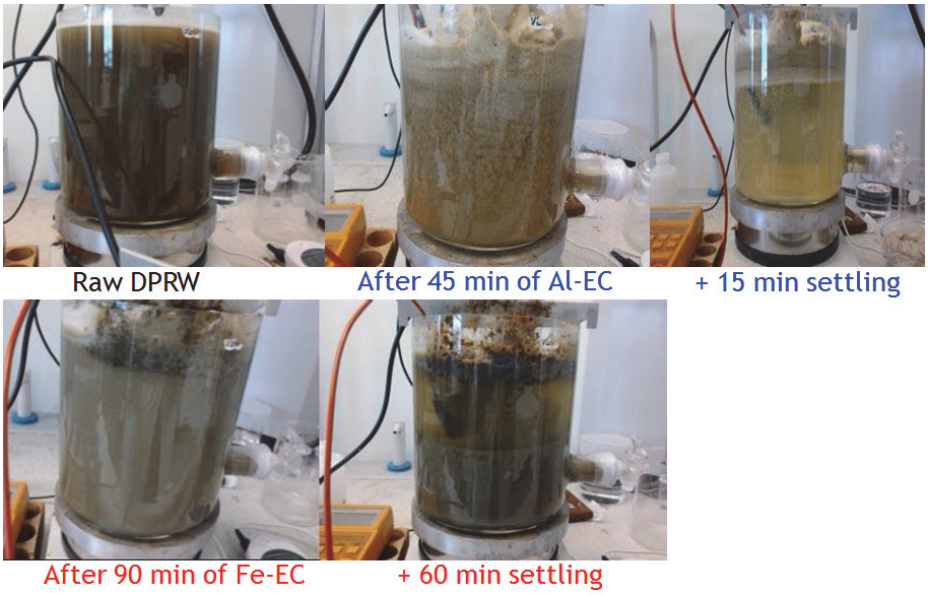

Fig. 12. DPRW samples from Publication IV.

Table 8. Analytical results of the EC sludge samples (experiments 14 and 16) of Publication IV.

Experiment: anode metal	EC sludge sample	P_{tot} [mg/L]	N_{tot} [mg/L]	Al [mg/L]	Fe [mg/L]	TS [%]
14: Al-EC	surface sludge	6,480	104,000	48,000	n.d.[1]	4.0
16: Fe-EC	surface sludge	4,500	73,700	n.d.[1]	178,000	5.4
16: Fe-EC	bottom sludge	1,230	162,000	n.d.[1]	84,600	1.8

[1] n.d. = Not determined.

As observed from Table 8, the lowest TS content was found in the Fe bottom sludge. This may explain its weakness, as mentioned above. On the whole, TS values varied between 1.8–5.4%. As shown in Table 8, the EC sludges contained very high amounts of the dissolved anode metal as well as nitrogen. This was despite the fact that nitrogen couldn't be removed effectively from the DPRW. The sludges were also found to contain some phosphorus. Therefore, utilization of this kind of EC sludge may be possible in the future, particularly as an additive in bio ash-based fertilizer products. However, before this, they would have to be dried and possibly otherwise pretreated first. The high anode metal content should also be taken into consideration.

6.4.4 Summary of the DPRW studies

In this preliminary study it was found that the EC process didn't function well unless the initial solution pH was lowered to about 5. On the whole, Al-EC outperformed Fe-EC in this application by a large margin. Such a difference in the performance of Al and Fe anodes is rare. Utilization of the DPRW EC sludge may be possible in the future due to its high nutrient content. Based on these interesting results, research on this subject will be continued.

6.5 EC treatment of peat bog drainage water (Publication V)

Annually, about 7% of Finland's energy supply and 20% of its district heat is produced from peat, making it one of the most important energy sources in Finland (Geological Survey of Finland 2015). Approximately 3% of the total global landmass is peatland. Peat energy is produced and used mainly in Finland, Belarus, Estonia, Ireland, Indonesia, Sweden, and the Russian Federation. (World Energy Council 2015) Due to their northern location, most of these countries have a long, cold winter season.

Even though domestic energy can be produced from peat and vast reserves of it exist in Finland, there is much debate over its utilization. One of the main objections to peat energy production (especially in Finland) is the generation of peat bog drainage water (PBDW). Proper treatment of PBDW may even be considered to be a key question affecting the future of the entire (at least) Finnish peat industry.

Humic substances (HS), as well as nutrients, may be removed from PBDW using physicochemical processes, biological processes, membrane processes, etc.

(Asam *et al.* 2012) The use of traditional peatland buffer zones and/or wetlands (mainly called overland flow areas, OFAs) is of particular interest and importance. However, they require large investments related to the enormous land area needed for them to function (Asam *et al.* 2012, Ihme 1994, Kadlec & Wallace 2009, Postila *et al.* 2014). The effectiveness of conventional methods of treating PBDW is also often limited. Thus, to meet the increasingly strict environmental regulations, innovations are needed.

EC has been successfully used to treat real and (mostly) synthetic waters containing humic acids (HA)/HS, e.g., in the studies by Bazrafshan *et al.* (2012), Ghernaout *et al.* (2009), Vik *et al.* (1984), Vepsäläinen *et al.* (2009), and Yıldız *et al.* (2008). In these studies, optimized removal efficiencies of 80–100% were achieved. However, as previously stated in Chapter 6.1.1, to the best of our knowledge no earlier scientific research on EC treatment of PBDW has been conducted and published. Furthermore, extensive economic analysis of the EC process was not provided in any of the aforementioned papers. Thus, the primary aim of Publication V was to prove the feasibility of EC in treating PBDW.

In Publication V, after first optimizing HA removal from an artificial solution, real PBDWs from three northern Finnish peat bogs were also treated using EC. A scale-up study (from a laboratory-scale to a 1-m^3 EC system) to treat cold PBDW was also conducted. Economic values of the EC process were also evaluated and discussed.

6.5.1 Optimization of synthetic wastewater treatment

In the first part of this work, treatment of SWW containing 100 mg/L HA and 0.5 g/L NaCl was optimized. Similarly to the experimental part of Publication III, the effect of multiple individual parameters on the efficiency of the SWW-EC process was investigated. In order, these were: the anode/cathode materials used (Al/Fe and Fe/Al), initial pH (4–9), current density (25–100 A/m^2), treatment time (0–15 min), and solution temperature (10–30 °C).

Both electrode combinations were found to perform well and the results were similar. However, using Al as the anode material was chosen as optimal, mainly due to the possible coloration of water by Fe. Similarly to the results of Publication III, lowering the initial pH value enhanced pollutant removal. However, the differences were clearly more significant here. It should be noted that this kind of behavior is usual in common chemical aluminum coagulation practice, where initial solution pH is typically adjusted to 5–6. Furthermore, these results are in

good accordance with those presented in the works of, e.g., Bazrafshan *et al.* (2012) and Yıldız *et al.* (2008). In those studies, HA-containing SWWs were treated by Fe-EC and Al-EC, respectively. In the SWW experiments of Publication V, it was found that solution temperature did not affect HA removal efficiencies practically at all. Therefore, it was suggested, and this is very important for practical usage, that it could be possible to treat real PBDW also in the cold northern climate (in rural areas).

In the end, 90% COD_{Mn} and 80% DOC removal efficiencies were achieved. Optimum process conditions for the SWW treatment were found to be: anode/cathode = Al/Fe, initial pH = 4, i = 100 A/m^2, and t = 10 min.

6.5.2 Treatment of real peat bog drainage water

In all of these experiments, 0.5 g/L NaCl was added to the real PBDWs due to their low conductivities. At first, PBDW1 was treated using the laboratory-scale EC system. A current density of 70 A/m^2 was applied. Two electrode combinations, Al/Fe and Fe/Al, were tested. This experiment was also scaled up from a volume of 1800 mL to 4500 mL, also testing both Al/Fe and Fe/Al. In all four experiments, the turbid water turned colorless and transparent, and brown floc rose to the top of the EC vessel, as illustrated in Fig. 13. Treatment times of 60–90 min (electrical charges of 400–600 C/L) were found to be optimal at this scale.

Fig. 13. Real PBDW before and after laboratory-scale Al-EC treatment. Adapted from Publication V.

Large-scale (1 m^3) experiments using cold (T = 10–11 °C) PBDW2 and PBDW3 were conducted next. Current densities of about 60 A/m^2 and 75 A/m^2 were applied, respectively. Treatment times of 60–120 min (75–150 C/L and 90–180 C/L, respectively) were found to be adequate. Clear water could be produced by EC.

On the whole, the scaling up of EC was found promising and high pollutant removal efficiencies from real PBDW could be achieved. Total removal of P_{tot}, TS, and color was observed, while N_{tot}, COD_{Mn}, and DOC/TOC removal efficiencies were about 33–41%, 75–90%, and 62–75%, respectively. Furthermore, the EC-treated PBDWs had near-neutral pH values (initially slightly acidic). Residual amounts of the dissolved anode metal material were found to be low in all of the experiments on real PBDW. In fact, their amounts in the EC-treated water were lower than their initial values, and Fe was removed completely.

6.5.3 Process economy

The OC and EEC values (in optimum conditions) in EC treatment of both SWW and real PBDW were evaluated in Publication V and are presented in Table 9.

Table 9. Optimum OC and EEC values for the water types treated in Publication V.

Water type	Volume treated [L]	Anode/cathode	EEC [kWh/m^3]	OC [€/m^3]
SWW	1.8	Al/Fe	0.94	0.15
PBDW1	1.8	Al/Fe	0.97–1.46	0.17–0.24
PBDW1	1.8	Fe/Al	1.00–1.51	0.16–0.23
PBDW1	4.5	Al/Fe	1.21–1.82	0.20–0.29
PBDW1	4.5	Fe/Al	1.23–1.85	0.19–0.27
PBDW2	950	Al/Fe	0.23–0.44	0.06–0.09
PBDW3	975	Al/Fe	0.35–0.69	0.08–0.12

As it can be seen from Table 9, the OC and EEC values for the SWW were found to be similar to those obtained for the real PBDWs. Al-EC and Fe-EC performed rather similarly, thus both were proposed to be viable options for this application. Additionally, due to the low EEC values, it may be possible to utilize solar energy, for example, as the power source, especially in rural areas. It should be noted that the large-scale EC experiments seemed to produce clearly the lowest economic values, which was rather surprising, yet positive.

In a study by Vepsäläinen *et al.* (2009), removal of natural organic matter (NOM) from inlet river water of a Finnish paper mill by EC was studied. With maximum NOM removal (about 80% of DOC), an EEC value of 0.4 kWh/m^3 was observed. This is in good accordance with the results of this study.

6.5.4 Summary of the humic substance removal studies

To conclude, EC was found to be a cost-efficient alternative in treating real PBDW containing HS. Solution temperature didn't affect the EC process. Due to the low power consumption, it may be possible to utilize solar power in this application of EC. However, practical problems of PBDW treatment by EC in field conditions remain. Therefore, experiments in field conditions as well as using a continuous mode should be conducted.

6.6 Other analytics

6.6.1 Superfaradaicity

The superfaradaic effect, described in Chapter 3.2.4, was studied in Publications III and V. However, in both cases, superfaradaic dissolution of only Al was discussed, mainly due to practical reasons. In Publication III, superfaradaicity was studied in each test run and for all the wastewater types studied, excluding the pre-study. In Publication V, this part of the research was limited to the SWW experiments only.

The results of these studies were clear and in good accordance with each other, as well as with existing scientific literature: in Publication III, 17–33% (22–25% on average) superfaradaic Al dissolution was observed. This was the case regardless of the wastewater type studied and the operating parameters of EC. Furthermore, in Publication V, regardless of the operational parameters, virtually all of the results exhibited an 18–32% excess in Al dissolution over the theoretical value given by Eq. (6).

6.6.2 Development of solution temperature

The Joule heating effect of the EC cell was studied in Publications II–V. According to Joule's first law, also known as the Joule effect/heating or ohmic heating, the amount of thermal energy Q [J] released is directly proportional to the square of the current, as presented in Eq. (11):

$$Q = I^2 R t \tag{11}$$

where R is the resistance [Ω]. Thus, the warming effect of EC is due to the ohmic drop and electrode overpotentials, which generate heat in the EC cell and liquid. It should be noted that when notably too high currents are used (and mixing is not sufficient), energy may be (even dramatically) wasted in heating the solution. (Calvo *et al.* 2003, Rodriquez *et al.* 2007)

In every experiment conducted in this work, solution temperature was found to increase. These increases are presented in Table 10.

Table 10. Temperature increases in the wastewater samples treated in this work.

Publication	Wastewater type	Temperature increase
II	All	0.02–0.03 °C/min
III	SWW (laboratory-scale)	0.07–0.09 °C/min
III	SWW (scale-up)	0.02–0.03 °C/min
III	DWW	0.02–0.03 °C/min
III	MWW	0.05–0.06 °C/min
IV	DPRW	0.08/0.06[1] °C
V	SWW	1.2 °C
V	PBDW	0.9 °C

[1] Experiments 14/16 (found "optimal", see Chapter 6.4.3).

As it can be seen from Table 10, the temperature increase was highest with the laboratory-scale SWW (0.07–0.09 °C/min) in Publication III. The lowest (0.02–0.03 °C/min) temperature increase was observed with the DWW. This was suggested to have been due to its high content of suspended solids (visual observation, not measured). In the laboratory-scale EC experiments, it was observed that as the value of current density was raised, the amount of heat generated consequently increasingly deviated above the linear projection. This is in line with Eq. (11)—applying a higher current increasingly results in energy wasted in heating the solution. The temperature increment value (0.02–0.03 °C/min) obtained in the SWW scale-up experiments differed from the laboratory-scale experiments. This might have been due to the difference in the EC apparatus structures and current densities. In Publication III, all of these values were found to be repeatable, particularly for real wastewater.

In the experiments of Publication IV, the solution temperature increase was significantly higher (mostly to values between 25–50 °C) than in the other papers. This was most probably (at least partly) due to the high current densities (and longer treatment times) used. When raw DPRW was treated with Fe-EC, the solution temperature rose tremendously from room temperature to 74 °C in 150 min and no separation was achieved. In Publication V, the solution temperature increases were found to be consistently repeatable and insignificant.

To conclude, in this work, the increases in solution temperatures were found to be repeatable, somewhat similar over the line, and of a small order of magnitude (about 0.02–0.09 °C/min) in optimum process conditions. Thus, the efficiencies of the EC processes had been high and only a small portion of the energy had been wasted in heating the solution. Furthermore, this phenomenon was concluded to have had no effect on the EC processes themselves.

6.6.3 Development of solution pH

In every experiment of this work, the pH of the EC-treated solution had changed from its initial value (mostly upwards). Furthermore, this change was always notably fastest during the beginning of a given experiment and stabilized toward its end. Using a higher current density resulted in higher final pH values. All of these observations were to be expected. Also, highly reproducible results were obtained. In this work, Fe-based EC was found to cause a larger increase in pH than Al-EC with similar solutions. Similar results have been reported by, e.g., Asselin *et al.* (2008a), Asselin *et al.* (2008b), and Zongo *et al.* (2009). One explanation for this could be that aluminum complexes more hydroxide ions than iron, thus resulting in a lower final pH value. However, differing results have also been reported, e.g., in the works of Katal & Pahlavanzadeh (2011) and Kobya & Delipinar (2008).

In Publication II, solution pH values increased in every experiment. At the end of all the experiments, final pH values was found to be alkaline (about 8.8–10.9). It should be noted that the increases in the pH value would have been smaller using optimum treatment times. The increases in pH values were found to be greater for bio O/W emulsions than for synthetic O/W emulsions, regardless of the anode material used. The final pH values of similar types of EC-treated O/W emulsions were higher when SS-EC was used instead of Al-EC.

In the laboratory-scale SWW experiments of Publication III, the final pH value was in the range of 8.2–9.2. Lower values were observed when lower initial pH values were applied (and vice versa). This was regardless of the operating parameters. In the scale-up experiments, the increase in the pH value was found to be highly reproducible and scalable; final pH was about 9.1. The increases in pH values observed in all of the MWW and DWW experiments (using Al-EC) were also consistently reproducible. As an exception to this, in a short (15 min) preliminary MWW experiment done with an unmodified pH value of 11.8, a final pH value of 11.6 was observed. Thus, a slight neutralization effect of MWW was noted; however, removal efficiencies of pollutants were low.

In experiments 14 (Al-EC, 45 min, $pH_{initial}$ = 5.0) and 16 (Fe-EC, 90 min, $pH_{initial}$ = 5) of Publication IV, final pH values of 6.0 and 7.8 (about 8.0 at 45 min) were observed, respectively. Thus, again, Fe-EC raised the solution pH more than Al-Fe.

EC brought the solution's pH toward neutral in all of the SWW experiments of Publication V. Final pH values of about 5.2–7.4 (depending on the value of *i*) and

8.7 were observed for initial pH values of 4 and 9, respectively. These results were highly reproducible. In all of the PBDW experiments, the pH value was found to rise. This can be seen as a positive phenomenon, since EC could also be used to simultaneously neutralize typically slightly acidic PBDW.

6.6.4 Behavior of current and voltage

Applied current and voltage didn't remain fully constant for the whole EC run in any of the experiments conducted in this work. However, the degree and direction of the evolution of these parameters varied, and in some of the experiments only negligible changes were observed. Furthermore, EC is easily automated. This kind of behavior of the EC system was proposed to be of somewhat low significance and attributable to, e.g., changes in solution conductivity and resistance, which are, in turn, due to changes in temperature and pollutant concentrations. If needed, voltage was altered to keep the current at a constant value. As stated before, average current (and voltage) values were used for all of the economic calculations.

Erratic behavior of current was observed during the experiments of Publication II—similar results have not been reported elsewhere. This phenomenon proposedly occurred due to the unconventional structure of the EC cell. When SS-EC was used, the current typically increased during EC; therefore voltage had to be decreased by 0.5 V (initial values of 4.5–7.5V) to maintain stable current (and to prevent shorting). Conversely for Al-EC, the current usually decreased during EC, leading to a need to increase voltage. The changes in current tended to stabilize toward the end of the experiments with both electrode combinations. However, typically the voltage had to be altered multiple times during an EC experiment, leading to a significant difference between initial and final values.

It should be noted that the same bench-scale EC apparatus was used in the scale-up experiments of Publication III, where repeatable current/voltage results were obtained with only a small decline (2–7%) from the initial voltage in each experiment. However, as presented in Chapter 5.2.1, the (anode) Al metal was fully submerged in these experiments, while in the experiments of Publication II, it was only partly submerged. This may explain the difference in current/voltage behavior between these papers, at least partly.

Like in the scale-up experiments of Publication III, in the laboratory-scale experiments of Publications III, IV (experiments 14 and 16), and V, a small (gradual) deviation from the initial voltage had to be made to keep the current constant. In Publication III, average voltage changes were 3–4% (decrease) for SWW and

DWW and 1% (increase) for MWW. In experiments 14 and 16 of Publication IV, applied voltages had to be gradually decreased from 3.3 V to 2.9 V (12%) and from 4.5 V to 4.1 V (9%), respectively. In Publication V, voltage decreases were in the range of 3–13% in every experiment with real PBDW; a clear tendency of Fe anodes to cause a larger decrease was also noted.

7 Summary

In this work, the current state of scientific literature was first broadly reviewed and discussed. After this, the applicability of EC in treating oil-in-water emulsions containing bio oils and synthetic oils, real wastewater containing abundant i.a. phosphorus and nitrogen, and peat bog drainage water (PBDW) was investigated. It should be noted there are no earlier scientific publications on EC treatment of PBDW, which is currently interesting and topical, at least in the Nordic countries.

Lastly, the possibility of simultaneously using EC as a wastewater treatment method and as a means to obtain valuable nutrients from eligible wastewater for further use in fertilization was studied preliminarily. Currently, this is also a "hot topic" in the environmental sector as well as from the viewpoints of circular and bioeconomy.

The main results of this study are:

- The range of feasible EC applications is constantly expanding and EC has vast potential in the purification of various types of water and wastewater. Combinations of EC with other methods as well as new designs and innovations have also been investigated with promising results.
- In the experimental part of this work, EC was found to be a feasible treatment method for all the water and wastewater types studied.
- EC could also neutralize the industrial wastewater samples and the PBDW treated in this work.
- Good scalability and repeatability of the EC process were observed.
- The OC and EEC values of the water and wastewater types treated by EC in this work (in optimum conditions) and in the prior literary studies varied between 0.0047–6.74 €/m^3 and 0.002–58.0 kWh/m^3, respectively. Naturally, these observations are probably related to the high variability of pollutant levels in different waters and wastewaters. Generally, however, the economic values were very low (typically about 0.1–1.0 €/m^3 and 0.4–4.0 kWh/m^3, respectively).
- In most of the literary EC studies, optimal treatment times and current densities were found to be in the range of 5–60 min and 10–150 A/m^2, respectively. This also applies to every wastewater type treated in the experiments of this work, excluding the digester plant reject water (DPRW, although those results were only preliminary).

- Based on the results of this work and the literature review, generally a relatively narrow pH range, usually very close to neutral pH, can be found where the process performs the very best. However, interestingly, the EC process seems to be feasible over a wide initial pH range.
- The superiority of different electrode materials seems to vary between different types of aqueous solutions being treated. Therefore, this must always be determined case-specifically. Occasionally, Al and Fe performed very similarly.
- In this work, the EC sludges generated by treating wastewater with high nutrient concentrations contained high amounts of P and N. Thus, after possible pretreatment, they may be eligible for further utilization in the future, e.g., in granulated bio ash-based symbiosis pellets for fertilization.

8 Future work

As stated before, the range of feasible EC applications is expanding. This kind of work should be continued. However, larger-scale systems and systems applying a continuous mode should be used in such studies. Real wastewater should also be applied more often instead of artificial model solutions. These are general guidelines for future EC studies. Also, the OC and EEC values of the EC process should always be estimated in such studies.

Innovations related to EC should be sought to increase its attractiveness as a water and wastewater treatment method. Hybridizing EC with other treatment methods, e.g., as a pretreatment method for membrane technologies such as reverse osmosis (RO), should be also explored. This kind of research is currently being planned in our research group. Since EC is a feasible technology in treating oily wastewater—and also cold water—experiments in which EC is utilized to treat oil spills occurring in oil production in arctic conditions (which will be started in the future) are also being planned.

In this study, a baseline and idea for utilizing EC sludges derived from treating nutrient-containing wastewater was given. However, this subject greatly requires further, more in-depth research. This research should include sludge analytics, testing of drying of sludge, bio ash co-granulation experiments (with EC sludge additives), etc. It should be noted that such studies are going to be conducted in the near future, since this subject has already attracted scientific and industrial attention.

Since the PBDW-EC results obtained in this study have attracted significant scientific and industrial interest, these studies will be continued, also in practical experiments. As a matter of fact, this work has already been started. In these studies, using EC in real rural environments will be investigated, also in a continuous mode later on. Also, applying, e.g., solar energy in this (and other) EC application requires further studies.

The ecological effects of EC are rather obscure and should be addressed in more detail. Thus, more comparison studies with CC, for example, should be done, taking into account the OC values and removal efficiencies as well as the ecological and carbon footprints of these processes. Also, deeper research on the core basis/theory of EC is needed to develop a better understanding of the technology as a whole.

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